On the adsorbates formed during the platinum catalyzed (electro) oxidation of ethanol, 1,2-ethanediol and methyl-α-D-glucopyranoside at high pH

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Abstract

The irreversible adsorbates of ethanol, 1,2-ethanediol and methyl-α-D-glucopyranoside (MGP) have been studied with FTIRS and cyclic voltammetry. Both ethanol and 1,2-ethanediol display full C–C(OH) dissociative adsorption and dehydrogenation. In the case of ethanol adsorbed CO and C are formed of which the latter partially oxidizes further to adsorbed CO. In the case of 1,2-ethanediol CO is formed as the only adsorbate. The adsorption of MGP occurs similarly to the small alcohols; it decarbonylates to form adsorbed CO and a small fraction of C adatoms. It is shown that the catalytic alcohol oxidation can be regarded as an electrochemical process that consists of two independently acting half-reactions that determine the open circuit potential (o.c.p.). The roughness of the surface greatly affects the o.c.p. measured during catalytic alcohol oxidation; smooth platinum leads to high o.c.p. values and platinized platinum leads to low o.c.p. values. These low and high open circuit potentials correspond respectively to a diffusion limited regime where diffusion of oxygen is rate limiting and a kinetic regime. The reaction rate is considerably lower in the kinetic regime than in the diffusion limited regime. The surface is highly covered with adsorbed oxygen or hydroxyl during oxidation of ethanol and MGP in the kinetic regime, whereas the surface is devoid of adsorbed oxygen in the diffusion limited regime and is instead covered with a high steady state amount of CO and C species. The deactivation of the catalyst is found to occur both in the diffusion limited and in the kinetic regime of the MGP oxidation. Whereas in the diffusion limited regime, the deactivation is caused by a slow accumulation of carbonaceous residue, and in the kinetic regime, changes in the properties of adsorbed oxygen cause deactivation. © 1997 Elsevier Science B.V.

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1. Introduction

The platinum catalyzed oxidation of alcohols, especially polyols, in aqueous phase is attractive because of the mild reaction conditions and the high selectivities that can be obtained. In this way, various valuable intermediates for the food and pharmaceutical industry can be prepared. Catalytic oxidation also offers environmental advantages with respect to classical oxidation methods, since oxygen itself is reduced to water and thus waste production is low. A major problem in the catalytic oxidation of alcohols is the deactivation of the catalyst, that has been

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found for various catalytic oxidation reactions [1–9]. Four possible causes have been proposed to explain the deactivation phenomena; (i) chemical poisoning, (ii) overoxidation of the catalyst surface, (iii) corrosion and (iv) particle growth. Overoxidation is widely accepted as the probable cause of the loss of activity in catalytic literature, although some have found the adsorption of byproducts to be responsible for deactivation [2].

Electrochemical studies can provide valuable information on the catalytic oxidation of alcohols with oxygen in the liquid phase on supported platinum catalysts, since catalytic oxidation can be regarded as an electrochemical process. The electrocatalytic oxidation of small alcohols has received considerable interest in the context of possible applications in fuel cells [10]. As a result, most electrochemical studies have been carried out at low pH, so that carbon dioxide produced at the fuel cell anode is removed easily from the electrolyte, whereas at high pH carbonate is formed which accumulates in the electrolyte. This difference in reaction conditions complicates the translation of knowledge obtained with electrochemical studies to the catalytic alcohol oxidation.

These electrochemical studies have been combined with IR and mass spectrometry techniques that have been developed during the last two decades; reflection Fourier transform IR spectroscopy (FTIRS) and differential electrochemical mass spectrometry (DEMS). These techniques have shown for primary alcohols at low pH that in addition to the formation of the acid and aldehyde, dehydrogenation and dissociation of the C–C(OH) bond occurs, leading to formation of adsorbed CO [11–18], according to:

$$R-CH_2OH \rightarrow R_{ads} + CO_{ads} + 3H^+ + 3e$$
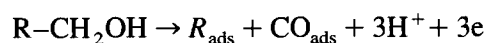
Little is known of the composition of the coadsorbates R_{ads} that are formed along with CO and in previous papers we have paid attention to this subject [14,16]. The adsorbates R display no further C–C bond breaking and are largely de-

hydrogenated. Part of the hydrocarbon adlayer can be hydrogenated at low potentials to the corresponding gaseous hydrocarbon whereas the other part is insensitive toward hydrogenation, probably due to graphite formation. The oxidation of C_1 can occur in the same potential region as for CO and at potentials where platinum is covered with oxides. Hydrocarbon adspecies containing two or more carbon atoms can only be oxidized to CO_2 in the oxide region.

It has been argued that, in addition to CO and R, irreversible adspecies are formed at low pH with the carbon backbone intact and several adsorbate structures have been proposed [12,17,18]. The few FTIRS experiments that have been carried out in basic electrolyte for ethanol and 1,2-ethanediol have established the formation of CO [11,19,20], but no claims have been made up to now that adspecies are formed with the carbon backbone intact. For secondary alcohols it is generally found that no CO is formed during adsorption [13,21,22]. The energy required to break two C–C bonds is apparently too high to enable CO formation. In the electrochemical literature CO has been generally indicated as the species that is responsible for poisoning of the alcohol electrooxidation [10,13]. Therefore, the electrooxidation of alcohols only starts at potentials where CO is being oxidized to CO_2, generating free platinum sites. In a previous report we suggested that not only CO is responsible for poisoning, but that the coadsorbates R_{ads} that are formed along with CO in the dissociative adsorption will also contribute to poisoning [16].

As yet it is unclear how to translate the observations made in electrochemical systems to the catalytic oxidation. Whereas CO formation is usually observed in electrochemical studies, the possibility of CO poisoning is not considered in papers concerning catalytic oxidations. For several reasons a comparison between electrochemical and catalytic oxidation is tentative. Electrocatalytic studies have generally involved simple alcohols and smooth platinum

electrodes, whereas catalytic studies have been performed with complex cyclic polyols and carbon supported platinum catalysts. In addition, electrochemical studies use cyclic voltammetry, implying non-stationary conditions, whereas catalytic studies use stationary conditions. Up till now, open circuit potential measurements of catalytic reactions have provided the important insight that deactivation of the catalyst is accompanied by an increase of the catalyst potential [1,2,4,7–9]. There is no consensus, however, on the interpretation of this result. It has been attributed as an increase of the oxygen coverage as well as a result of site coverage by reactants, intermediates, or products.

The main theme of this report concerns the state of the catalytic surface during selective oxidation of alcohol compounds at high pH. The reaction conditions were varied such that the reaction rate was either limited by diffusion of oxygen or kinetically limited. We have chosen to study the oxidation of ethanol, which has been used as model compound in electrochemical and catalytic studies, and methyl-α-D-glucopyranoside (MGP), a cyclic polyol that can be selectively oxidized to methyl-α-D-glucosiduronate, an intermediate in the synthesis of vitamin C. The irreversible adsorbates present during reaction were isolated and studied thereafter with cyclic voltammetry and FTIRS. The catalyst is known to deactivate during oxidation of MGP and special interest will be given to this reaction to establish the causes of deactivation. In order to obtain insight in the fundamental adsorption behaviour of alcohols, the composition of the adsorbates formed from ethanol, 1,2-ethanediol and MGP were studied with cyclic voltammetry and FTIRS. The results will be compared to those for acid electrolytes.

2. Experimental

Fourier transform infrared measurements were performed with a Biorad FTS 45A spec-

trometer, equipped with a liquid nitrogen cooled MCT detector. All IR spectra were recorded with 4 cm^{-1} resolution. The bottom of the electrochemical cell consists of a CaF$_2$ prism with 65° beveled edges. The platinum electrode has a diameter of 9 mm and is embedded in a PTFE holder. P-polarized light has been used in all IR measurements. Electrochemical measurements were performed with an Autolab PG-STAT 20 computer controlled potentiostat and an EG and G Parc model 175 universal programmer connected to a Wenking POS 73 potentioscan. A Hg/HgO electrode was used as a reference-electrode. All potentials will be referred to RHE. All measurements were performed with platinised platinum, that was obtained via electrodeposition from a 0.05 M H$_2$PtCl$_6$ + 0.01 M HCl solution on smooth platinum. A deposition current of 10 mA/cm^2 was used for the DEMS gauze-electrode, while 0.5 mA/cm^2 was used for the IR electrode. The electrode areas, determined from the hydrogen desorption region in the cyclic voltammogram, were 53 cm^2 and 10 cm^2 respectively. Platinized platinum was chosen in order to minimize the influence of impurities on the adsorption process as well as to increase the mass signals in the DEMS technique. Potential cycling between 0 and 1.5 V was carried out until a stable voltammogram was obtained. Electrolytes were prepared using ultrapure water (18.2 MΩ) obtained with an Elga water purification system. In the infrared experiments and cyclic voltammetry experiments 0.1 M KOH was used. Oxygen was removed from the electrolyte with argon 4.6.

Adsorption experiments were performed at 0.3 V for 10 min with 1 mM or 5 mM concentrations of the various alcohol compounds in 0.1 M KOH. CO (Hoek Loos, purity 4.6) was adsorbed at 0.15 V by leading CO through the solution for 10 min. All other chemicals, p.a. quality, were obtained from Merck. After adsorption the electrolyte was replaced by fresh 0.1 M KOH solution, while keeping the electrode at the adsorption potential.

3. Results

3.1. Adsorbate study

Ethanol was adsorbed from a 1 mM containing electrolyte solution at 0.35 V for 10 min. An anodic current was observed during adsorption, that amounts to a total charge of 323 $\mu C/cm^2$. The ethanol solution is replaced by fresh electrolyte after adsorption and a cyclic voltammogram (c.v.) is subsequently recorded. If the scan is started at the adsorption potential in the positive direction, referred to as 'direct' oxidation, a broad peak is present at 0.65 V, as shown by the full line in Fig. 1. The dashed curve represents the voltammogram recorded in blank electrolyte. A broad oxidation wave is present in the oxide region, that is not completely terminated at the reversal potential of 1.35 V. However, the amount of charge associated with oxidation of adsorbate in a second cycle is only very small. If the oxidation is preceded by cycling 4 times through the hydrogen region, referred to as 'indirect oxidation', then a reduction wave is observed at potentials below 0.25 V as shown in Fig. 2. The subsequent oxidation at 0.65 V has narrowed and shifted to 0.60 V. The broad oxidation wave at higher potential has nearly
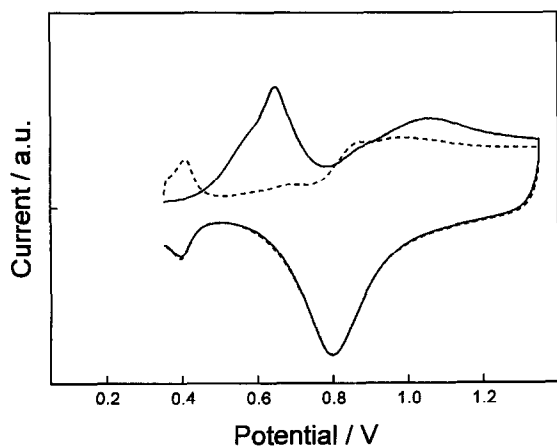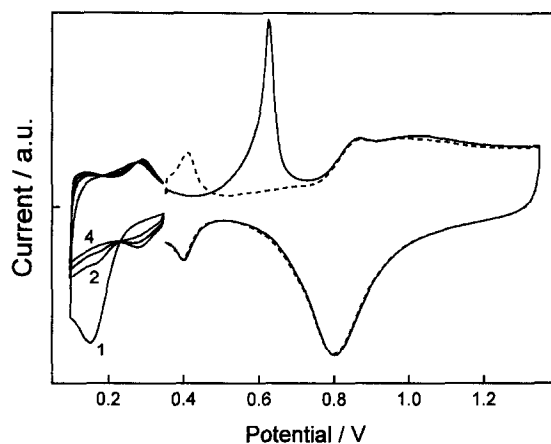

Fig. 2. C.V. of the oxidation of irreversible ethanol adsorbate on platinized platinum: 'indirect' oxidation (————) and blank (---). $E_{ads} = 0.35$ V in 1 mM ethanol in 0.1 M KOH, followed by electrolyte exchange. Scan rate 5 mV/s.

completely vanished. The total oxidation charge, including the peak at low potential as well as the broad wave at higher potential, has decreased from 263 $\mu C/cm^2$ for the 'direct' oxidation to 130 $\mu C/cm^2$ for 'indirect' oxidation. The charge involved in the reduction, Q_{red}, can be determined by subtracting the charge involved in the anodic part of each cycle below 0.35 V from the charge involved in the cathodic part of the scan below 0.35 V, adding up the charges of the 4 reduction cycles. The cathodic part of the scan consists of both reduction of adsorbate and formation of adsorbed hydrogen from solution protons on uncovered platinum sites. The anodic part of the scan only consists of oxidation of adsorbed hydrogen. Subtracting both values gives the charge involved in reduction; $Q_{red} = 122$ $\mu C/cm^2$. Note that hydrogen which is liberated during adsorption by C–H bond breaking is immediately oxidized to H^+ during the adsorption and is thus not involved in the reactions described here.

The cyclic voltammogram of 1,2-ethanediol adsorbates formed at 0.35 V from 1 mM 1,2-ethanediol shows no significant reduction in the potential region below 0.35 V, in contrast with ethanol. This means that the 1,2-ethanediol adsorbates are insensitive toward hydrogenation.
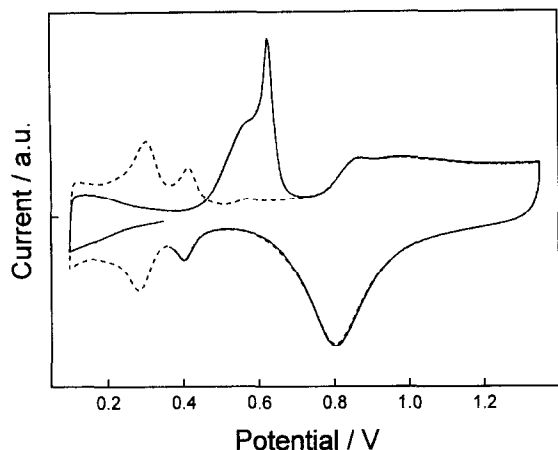

Fig. 1. C.V. of the oxidation of irreversible ethanol adsorbate on platinized platinum: ' direct' oxidation (————) and blank (---). $E_{ads} = 0.35$ V in 1 mM ethanol in 0.1 M KOH, followed by electrolyte exchange. Scan rate 5 mV/s.

Fig. 3. C.V. of the oxidation of irreversible 1,2-ethanediol adsorbates: 'indirect' oxidation (————) and blank (- - -). $E_{ads} =$ 0.35 V in 1 mM 1,2-ethanediol in 0.1 M KOH, followed by electrolyte exchange. Scan rate 5 mV/s.

Fig. 4. C.V. of the oxidation of MGP adsorbates: 'direct' oxidation (————) and blank (- - -). $E_{ads} = 0.35$ V in 1 mM MGP in 0.1 M KOH, followed by electrolyte exchange. Scan rate 5 mV/s.

Only an oxidation wave is present at 0.60 V with a shoulder at 0.57 V, as shown in Fig. 3. No oxidation wave is observed at potentials in the oxide region. The total oxidation charge in the cyclic voltammogram is 198 $\mu C/cm^2$ and the charge transferred during adsorption was 269 $\mu C/cm^2$, which leads to a Q_{ads}/Q_{ox} ratio of 1.36.

The cyclic voltammogram recorded after adsorption of 5 mM methyl-α-D-glucopyranoside at 0.35 V is depicted in Fig. 4. In the direct oxidation, represented by the solid line, a peak is present at 0.65 V in the double layer region and a small broad oxidation wave is present in the potential region between 1.05 and 1.35 V in the oxide region. The amount of charge involved at high potential is considerably lower than for ethanol, making the voltammogram similar to that of 1,2-ethanediol. The total oxidation charge, including the peak at low potential as well as the broad wave at higher potential is 250 $\mu C/cm^2$ for the 'direct' oxidation.

For comparison, we measured the cyclic voltammogram of CO, that was adsorbed at 0.15 V for 10 min, followed by electrolyte exchange. As shown in Fig. 5, the oxidation of adsorbed CO starts at 0.25 V and displays three peaks at 0.38, 0.57 and 0.63 V. The oxidation peaks at 0.63 and 0.57 V are in agreement with
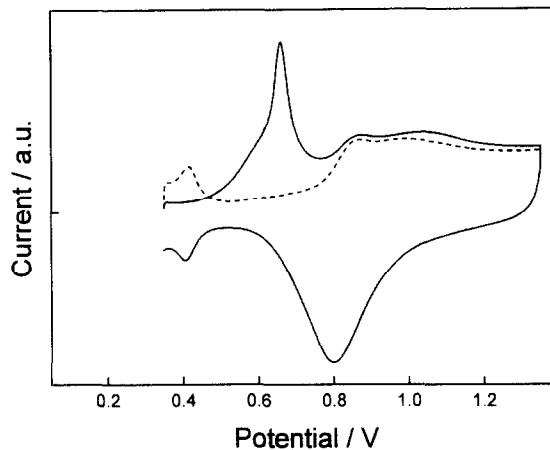
the previous study of adsorbed CO on polycrystalline platinum in KOH electrolyte [23]. This study further showed the peak positions to depend strongly on the scan rate used and a third oxidation peak at 0.44 V was observed only at a sufficient low scan rate of 4 mV/s. In our experiments this peak is observed even at much lower potential, probably as a result of a lower adsorption potential. It is remarkable that adsorbed CO can be susceptible toward oxidation at such a low potential, where platinum is usually covered with hydrogen, thus expecting reducing conditions instead of oxidizing condi-
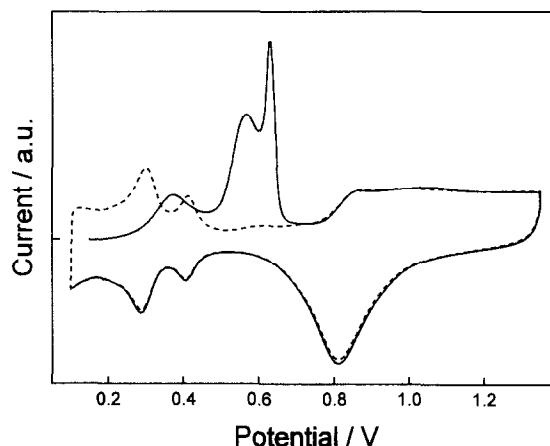

Fig. 5. C.V. of the oxidation of adsorbed CO on platinized platinum in 0.1 M KOH. $E_{ads} = 0.15$ V. Scan rate 5 mV/s.

tions. It is for the first time that adsorbed CO is found to oxidize at such a low potential. Comparison of the cyclic voltammogram obtained for CO with those of 1,2-ethanediol, ethanol and MGP shows that it is very similar to that of 1,2-ethanediol, but differs somewhat from that of ethanol and MGP.

We have also performed adsorption experiments of CO, ethanol and 1,2-ethanediol at 0.45 V, which will not be extensively discussed here. We confine ourselves to the remark that all charges involved in the oxidation of adsorbates formed at 0.45 V are approximately 30% lower than after adsorption at 0.35 V, due to considerable further oxidation of the initially formed adsorbate. This was confirmed by the observation that the current did not converge to zero during adsorption.

IR spectra were obtained by subtracting single-beam spectra before (R_0) and after (R_1) oxidation of the adsorbate. The first single beam was obtained at the adsorption potential of 0.35 V whereas the second was obtained at 0.35 after a potential excursion to 1.35 V. Fig. 6 compares the spectra, given as $\Delta R/R_0$ ($\Delta R = R_0 - R_1$), in the wavenumber region between 2100 en 1600 cm^{-1} as obtained for ethanol, 1,2-ethanediol, MGP and CO. This wavenumber
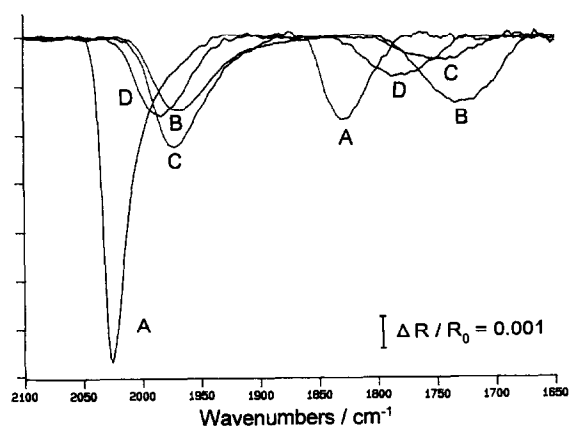
region is typical for linear and bridge bonded CO. It is clear from the vibrations around 2050 and 1800 cm^{-1} that both linear and bridge bonded CO are present on the surface. The relative amount of bridge bonded CO is larger than was observed in acid electrolyte [14]. The CO vibrations for the various alcohol compounds are smaller than after adsorption of CO and as a result they have shifted to lower wavenumbers as expected for decreasing CO coverage. Although the CO coverage is not exactly proportional to the integrated absorbance, it can nevertheless give a fair indication. Whereas the IR peaks in Fig. 6 for the various alcohol compounds appear much smaller than for pure CO, the integrated CO absorbances, and thus the CO coverages, are nevertheless considerable due to the broadness of the IR peaks.

3.2. Measurement of open circuit potentials: implications of surface roughness

We have determined the effect of surface roughness on the open circuit potentials measured during catalytic ethanol oxidation. Before measurement of the o.c.p., the solution was saturated with oxygen for 15 min, while keeping the electrode in a reduced state at 0.1 V. During the actual o.c.p. measurement oxygen was led over the solution. Fig. 7 shows the o.c.p. for smooth and platinized platinum in a solution of 0.1 M ethanol in 0.1 M KOH. For smooth platinum the o.c.p. quickly rises to 1 V whereas for platinized platinum the o.c.p. stabilizes at 0.35 V. When oxygen was passed through the solution, the o.c.p. increased for platinized platinum, the final value depending on the flow rate. It is well known that the reduction of oxygen at 0.35 V is diffusion limited, whereas the oxidation of ethanol is kinetically limited. This shows that the increase of the o.c.p. upon convection is a result of the improved oxygen transport to the electrode. The potential of 0.35 V indicates that no adsorbed oxygen is present on the surface during reac-

Fig. 6. FTIRS spectrum, given as $R_0 - R_1 / R_0$, in the wavenumber region for CO_{lin} and CO_{bridge} after adsorption of (A) CO, (B) 1,2-ethanediol, (C) ethanol and (D) MGP. $E_{ads} = 0.15$ V for CO and 0.35 V for the alcohols. Resolution 4 cm^{-1}, $E_0 = E_1 = 0.35$ V.
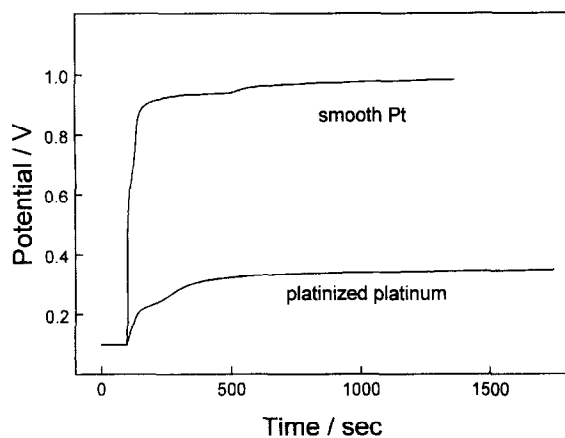
Fig. 7. Open circuit potential during catalytic oxidation of 0.1 M ethanol in 0.1 M KOH with O_2 on smooth and platinized platinum. The catalyst was reduced at 0.1 V before measurement.

tion. For smooth platinum the o.c.p. did not change when oxygen was led through the solution, indicating that the reaction rate is kinetically limited. The o.c.p. of 1 V indicates that a high coverage of adsorbed oxygen or hydroxyl species is present. The large difference between smooth and platinized platinum originates from the difference in roughness, which will be discussed in the next section.

According to the additivity principle of Wagner and Traud [24] the open circuit potential can be envisaged as the potential where the two half reactions each proceeds with the same current, although of opposite sign. However, this only holds when the redox couples act independently. We performed some simple experiments on platinized platinum to check whether this was the case for the catalytic ethanol oxidation by measuring separately the oxygen reduction current and the oxidation current in 0.1 M ethanol at 0.35 V, which corresponds to the o.c.p. measured for the catalytic ethanol oxidation on platinized platinum, as shown in Fig. 7. In accordance with the Wagner and Traud principle, we found the current values for oxygen reduction and ethanol oxidation to be exactly the same but of opposite sign, which confirms that the catalytic oxidation of ethanol with oxygen can be envisaged as an electrochemical

process consisting of two independently acting half reactions. In agreement with this conclusion we found that the presence of 0.1 M ethanol had absolutely no effect on the size of reduction current of oxygen at 0.1 V, where ethanol oxidation does not yet occur.

3.3. Isolation of adsorbates present during diffusion limited oxidation

We devised an experiment to isolate the adsorbates that are present on the surface during the diffusion limited oxidation of the alcohol on platinized platinum. This consists of interruption of the oxidation by applying a potential of 0.15 V, where the oxidation reaction stops and intermediates can be hydrogenated off the surface. Among the irreversible C–C(OH) dissociative adsorbates that are possibly present during reaction, CO will remain on the surface at 0.15 V, whereas CH_x species can be hydrogenated off the surface. The catalytic oxidation was carried out in a quiescent solution of 1.7 mM ethanol in 0.1 M KOH, saturated with oxygen. The o.c.p. stabilized at 0.41 V and was only weakly dependent on the ethanol concentration; for 17 mM ethanol the open circuit potential shifted to 0.38 V. After 5 min of reaction at this potential, the reaction was interrupted by the potential step to 0.15 V and the oxygen supply was stopped and replaced by argon. Subsequently, the reactant solution was replaced by fresh 0.1 M KOH electrolyte, followed by cyclic voltammetric analysis of the adsorbate layer. The resulting voltammogram is shown as the full line in Fig. 8. The dashed line represents the second cycle, being equal to a cyclic voltammogram recorded in blank KOH. The ethanol oxidation was also carried out electrochemically at 0.41 V, in the absence of oxygen. The cyclic voltammogram recorded afterward is shown as the dashed-dotted line in Fig. 8. Comparing the cyclic voltammograms in Fig. 8 shows that both the chemical and the catalytic oxidation procedure result in the same voltammogram, indicating that the same adsorbates are
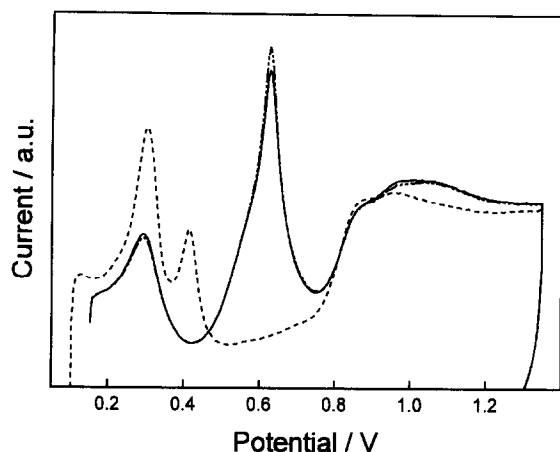
Fig. 8. C.V. after catalytic and electrochemical ethanol oxidation at 0.41 V on platinized platinum, followed by a potential step to −0.8 V and electrolyte replacement. Scan rate 5 mV/s.

Fig. 9. FTIRS spectra, given as $R_0 - R_1 / R_0$ after catalytic and electrochemical oxidation at 0.46 V on platinized platinum, followed by a potential step to −0.8 V and electrolyte replacement. Resolution 4 cm^{-1}. $E_0 = E_1 = 0.46$ V.

present. The charge involved in the oxidation of the adsorbates is 113 μC/cm^2 and it follows that the surface is considerably covered with adsorbates. Note that during the potential step to 0.15 V loss of C adspecies occurs, implying that the actual coverage is even higher.

The irreversible adsorbates formed during ethanol oxidation on platinized platinum were also studied with FTIRS, although under slightly different conditions; the electrode had a smaller roughness and the ethanol concentration was increased to 10 mM. The open circuit voltage was established at 0.46 V under these conditions. After 5 min the potential was stepped to 0.15 V and the electrolyte was exchanged for fresh base electrolyte, followed by the IR measurement. The IR spectra obtained after electrochemical and catalytic oxidation are shown in Fig. 9 in the wavenumber region between 2200 and 1100 cm^{-1}. The negative bands at 1980 and 1725 cm^{-1} originate from linear and bridge bonded CO, respectively. The positive band at 1400 cm^{-1} originates from carbonate species that are formed in the oxidation of the adsorbate. The IR experiments confirm the voltammetry experiment, showing that electrochemical and catalytic oxidation result in the same adsorbates during reaction.
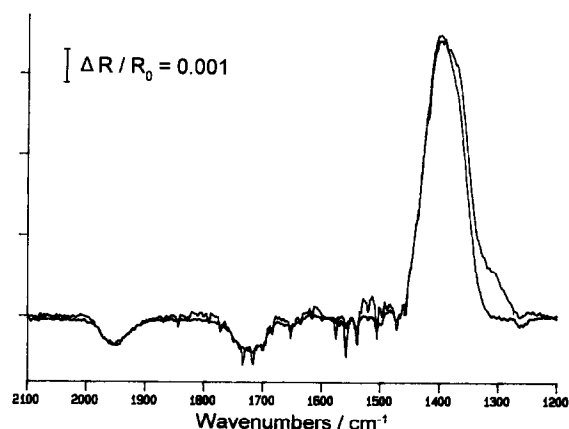
When the electrochemical oxidation of 1.7

mM ethanol on platinized platinum was performed at 0.55 V instead of 0.41 V as described above, the voltammogram shown in Fig. 10 is obtained after a potential step to 0.15 V, followed by electrolyte exchange. The coverage of irreversible adsorbates is now very low, in contrast with the results for 0.41 V. However, when the experiment was repeated a 0.55 V with a tenfold higher ethanol concentration, the adsorbate coverage increases considerably. These observations show that for 1.7 mM ethanol the reaction rate was determined by diffusion of ethanol to the surface, whereas for 17 mM the
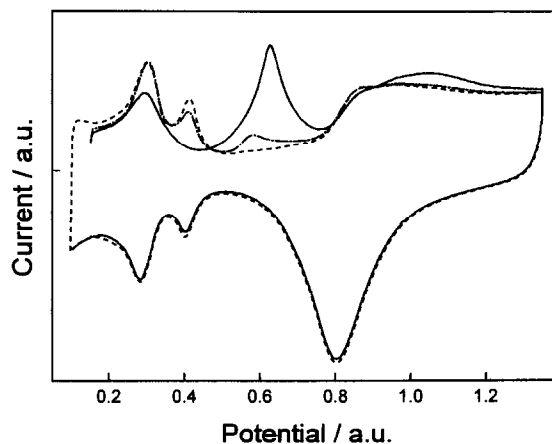

Fig. 10. C.V. obtained after ethanol oxidation at 0.55 V for 1.7 mM (- - -) and 17 mM (———), followed by potential step to 0.15 V and electrolyte replacement.

rate was kinetically limited. FTIRS experiments give further information on the products formed during the diffusion limited and kinetically rate limited ethanol oxidation. An experiment was performed in which a potential scan was made from 0.25 V, where a reference IR spectrum was recorded, to 0.55 V in the presence of 17 mM ethanol. The first spectrum recorded at 0.55 V contained two clear peaks at 1405 cm^{-1} and 1550 cm^{-1} of approximately equal size. These vibrations can be assigned to the presence of acetate in the thin layer. However, the ratio of the peak heights for the two vibrations differs from the ratio expected for acetate. This indicates that also carbonate is formed, which displays a single vibration at 1402 cm^{-1}. A second IR spectrum that was recorded at 0.55 V immediately after the first, displays a growth of the band at 1402 cm^{-1}, whereas the band at 1550 cm^{-1} remains equal. This indicates that now the acetate formation has stopped and carbonate is formed as the only product. When the electrode is pulled up from the CaF$_2$ window into the bulk of the solution, the current increases suddenly, indicating that the reaction had become diffusion limited during the FTIRS measurement. This demonstrates that carbonate is formed as the only product when the electrochemical ethanol oxidation becomes diffusion limited. A control experiment was carried out with an ethanol concentration of 0.1 M, which is high enough to prevent the diffusion of ethanol to be rate limiting. Indeed, only bands at 1405 and 1550 cm^{-1} were observed, indicating that acetate was the major product in this situation.

The same trends were obtained when the experiments were performed with MGP, apart from the fact that the open circuit potential does not reach a constant value, as described in the next section.

3.4. Catalyst deactivation during MGP oxidation

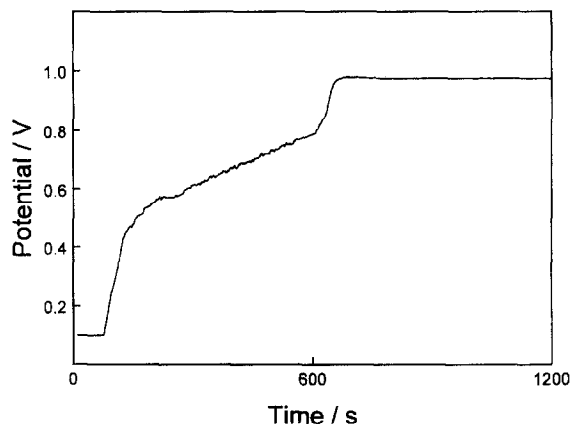Some experiments were performed to study the deactivation of the catalytic oxidation of

Fig. 11. Open circuit potential during the catalytic oxidation of 50 mM MGP in 0.1 M KOH on platinized platinum.

methyl − α-D-glucopyranoside. Fig. 11 shows the o.c.p. as a function of time for the catalytic oxidation of 50 mM MGP on a platinized platinum catalyst in 0.1 M KOH saturated with oxygen. Before the start of the measurement the potential was held at 0.1 V in order to reduce the surface. Fig. 11 shows that in contrast with ethanol the o.c.p. steadily increases in time, until it reaches a value of 0.8 V whereafter it increases to 0.99 V, where it remains stable as long as 16 h. This steady increase is in agreement with previous experiments for MGP oxidation on platinized platinum [1]. When oxygen is passed through the solution during the experiment the o.c.p. increased in the low potential region, whereas no effect was observed when the o.c.p. was 0.99 V. This shows that the reaction is diffusion limited in oxygen for low potentials and is kinetically limited at 0.99 V. The o.c.p. also increases faster when oxygen is led through the solution.

We used the same experimental procedure as described for ethanol to study the irreversible adsorbates that are present on the surface during reaction. In this way we can obtain information concerning the steady increase of the open circuit potential in Fig. 11. After a certain reaction time a potential of 0.35 V is applied, followed by exchange of the solution for fresh 0.1 M KOH. The potential of 0.35 V was chosen to
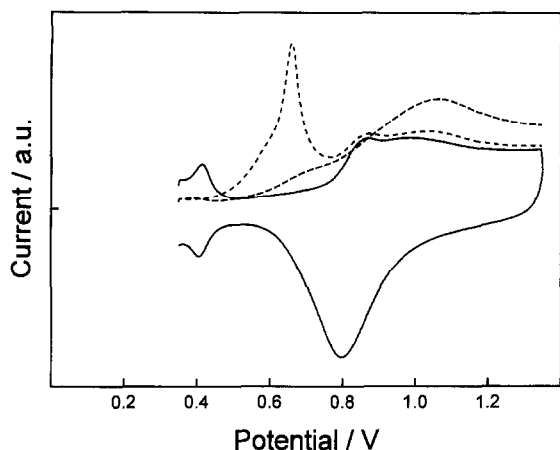
Fig. 12. C.V. recorded after catalytic MGP oxidation for 1 min (————) and 10 min (– – –), followed by potentiapotential step to 0.35 V. Blank (—). Scan rate 5 mV/s.

Fig. 13. Charge Q_{ox} involved in the oxidation waves at low (●) and high (△) potentials after catalytic MGP oxidation for various times, followed by a potential step to 0.35 V and electrolyte replacement.

prevent eventually present carbon species to be reduced off the surface, in contrast with the value of 0.15 V used for ethanol. Note however, that at 0.35 V further C–C(OH) dissociative adsorption of MGP can occur. After electrolyte exchange, a cyclic voltammogram is recorded to analyze the adsorbates that are formed during reaction, shown in Fig. 12. We found profound changes in the cyclic voltammogram that were recorded after various reaction times, corresponding to catalytic oxidation at different open circuit potentials. After 1 min reaction time the oxidation peak in the double layer region is large, whereas the broad oxidation wave in the oxide region was small. For increasing reaction time and increasing open circuit potential, the CO-like peak at low potential decreased whereas the broad wave at high potentials increased. We plotted in Fig. 13 the charge involved in the peaks at low and high potentials as a function of reaction time. It is clearly shown that the increase of the reaction potential is correlated with changes in the adsorbates that are present on the surface during reaction.

We performed some further experiments to see whether reduction treatments during reaction can reactivate the catalyst. The experiment was started with clean platinized platinum, that is exposed to a solution of 10 mM MGP satu-
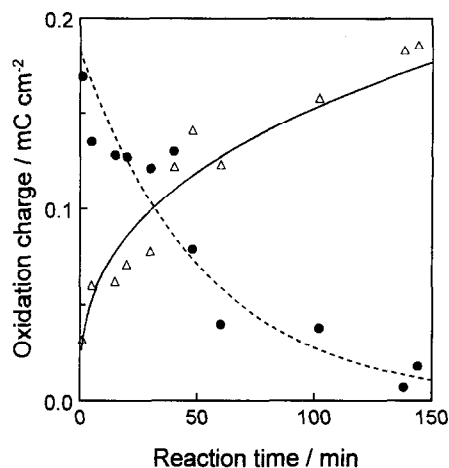
rated with oxygen. The increase of the open circuit potential with time is shown in Fig. 14. After 10 min, a potential of 0.45 V is applied, at which platinum oxides are reduced immediately off the surface to water, whereas reducible hydrocarbon fragments remain on the surface. Fig. 14 shows that indeed some reactivation occurs as indicated by the lowered open circuit potential. However, the potential increases fast and seems to continue the initial curve. When the potential is stepped to 0.1 V, the open circuit potential decreases more and equals the curve
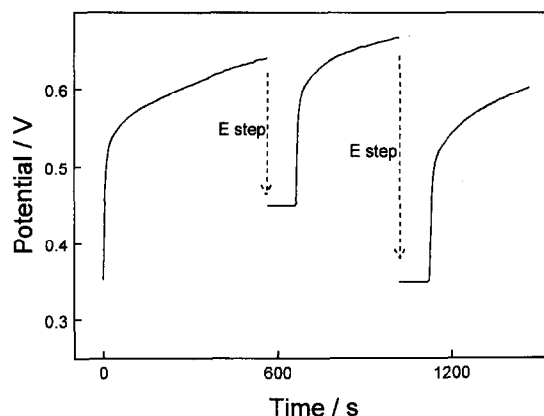

Fig. 14. Open circuit potential during catalytic MGP oxidation and the effect of potential during reductive treatment.
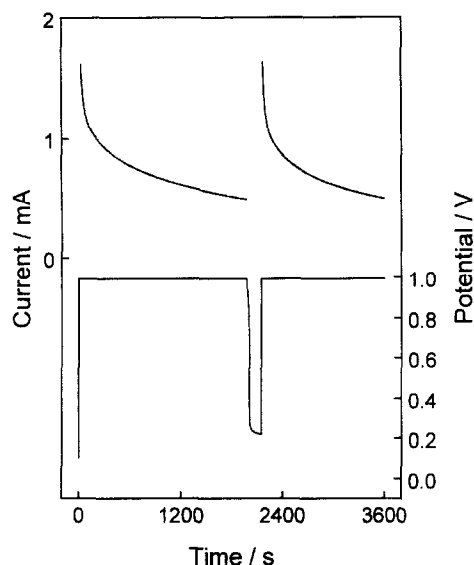
Fig. 15. Deactivation of MGP oxidation in time at 1.0 V and reactivation at open circuit potential. MGP concentration = 50 mM.

measured for clean platinum. The slope of the line is somewhat higher than for clean platinum. This might be caused by an imcomplete removal of the adsorbates during the reductive treatment.

It is remarkable that once the the potential has reached 0.99 V it remains constant for long times at 0.99 V, whereas it has been reported that the catalyst deactivates during operation in the kinetic regime [1,4,25]. Therefore, we performed some experiments to study the characteristics of the MGP oxidation at high potentials. We performed some experiments in which the MGP oxidation was carried out electrochemically at 0.99 V. Before the start of the reaction the potential was held at 0.1 V to reduce the surface. Fig. 15 shows that the current decreases in time. After 30 min the imposed potential was removed, whereafter the equilibrium potential established. As shown in Fig. 15 this results in a quick decrease of the potential to 0.25 V. After 2 min the imposed potential of 0.99 V was restored again and the current recovered its original value, indicating that the catalyst was reactivated. These results are similar to those obtained for the catalytic MGP oxidation on

carbon supported platinum catalysts in a slurry phase reactor [1]. This experiment was repeated except that the reaction was now interrupted by a potential step to either 0.45 or 0.1 V. At 0.45 V oxides are reduced and carbon species remain unaffected whereas both oxides and carbon species are reduced at 0.1 V. We found that after a potential step to both 0.45 V and 0.1 V the activity is restored to the same value when the potential was stepped subsequently to 0.99 V.

These results suggest that the state of adsorbed oxygen plays a role in the deactivation of the MGP oxidation. We further investigated the role of adsorbed oxygen by preoxidizing the electrode surface at 0.99 V for a fixed time in base electrolyte before admitting an MGP containing solution to the cell. With this experiment we can establish whether deactivation is strictly related to MGP oxidation or relates solely to the properties of the adsorbed oxygen species. Three current–time curves after 0, 15 and 60 min preoxidation are given in Fig. 16, which show that the MGP oxidation current has decreased considerably after preoxidation of the platinum electrocatalyst. However, it is remarkable that the initial rate after 15 min of preoxidation, curve B, does not correspond to the oxidation after 15 min MGP oxidation in curve A in Fig. 16. Apparently the rate of deactivation is higher in the presence of MGP. Nevertheless, it has
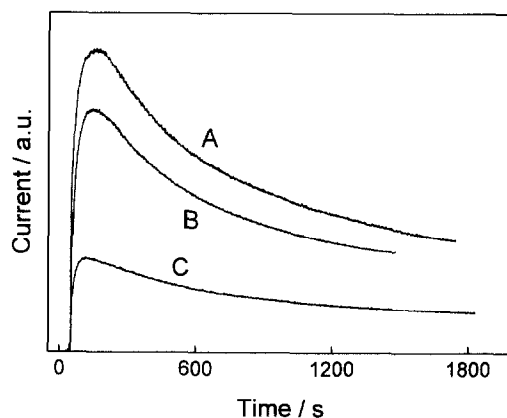

Fig. 16. The oxidation of 50 mM MGP in time at 0.99 V on electrodes preoxidized at 0.99 V for (A) 0, (B) 15 and (C) 60 min.
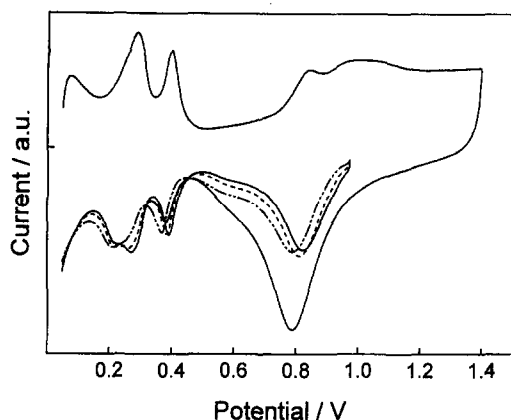
Fig. 17. The reduction of platinum oxide after polarization of the platinized platinum electrode for 0 (—), 15 (—) and 60 min (– · –) at 0.99 V.

been demonstrated that time dependent changes in the oxide covered platinum surface are involved in the deactivation of MGP oxidation. We also recorded cyclic voltammograms to study the electrochemical reduction of the formed oxygen adsorbates during preoxidation. The results are given in Fig. 17 and it is shown that the oxide reduction peak slightly shifts to negative potentials for increasing preoxidation times. It is not possible from these voltammograms to determine whether the oxygen coverage has increased because the broad oxygen reduction peak is difficult to integrate.

The current for MGP oxidation in Fig. 15 can be translated to turnover frequencies per Pt atom, when it is assumed that the oxidation of MGP to MGP-ox is 100% selective and thus 4e are consumed; this yields 0.0016 MGP/(Pt s). This value is in good agreement with the reaction rates found for carbon supported platinum catalysts in a slurry phase reactor at pH = 8 operated in the kinetic regime [1,4].

4. Discussion

4.1. Adsorbate study

The observation of considerable amounts of both linear and bridge bonded CO on platinized platinum with FTIRS for 1,2-ethanediol and ethanol demonstrates that these molecules decarbonylate during adsorption, at least to a certain extent. The formation of adsorbed CO at high pH has also been observed with EMIRS in the presence of 1,2-ethanediol [26], whereas no CO vibrations were observed with FTIRS [11]. A FTIRS study of ethanol adsorbates on platinum single crystals in NaOH electrolyte has shown that only linearly bound CO is formed on Pt(110), solely bridge bonded CO is formed on Pt(100) and no CO vibration was observed on Pt(111) [19]. On the basis of these results we can ascribe the linear and bridge bonded CO vibrations in our spectra to CO species adsorbed on Pt(110) and Pt(100) related sites on the electrode surface. These two surface geometries correspond to a pair of hydrogen adsorption/desorption peaks in the cyclic voltammogram in Fig. 1. This assignment of the hydrogen peaks in the cyclic voltammogram can also be made for platinum in acid electolyte and is in accordance with an extensive electrochemical study of hydrogen desorption on single crystals [27]. The strongly bonded hydrogen peak at 0.41 V can be assigned to a stepped (100) surface, e.g. (210), (310) and (410), whereas the weakly bonded hydrogen peak originates from a Pt(110) surface geometry.

The Q_{ads}/Q_{ox} values of 1.23 and 1.36 for ethanol and 1,2-ethanediol, respectively, give additional quantitative information on the composition of the irreversible adsorbates. In the case of 1,2-ethanediol the value of 1.36 suggests that in the total oxidation of this molecule to CO_2, 5.8 electrons are transferred during adsorption and 4.2 electrons are transferred during oxidation of the adsorbate. Since 2 CO_2 molecules are formed in the oxidation of a single 1,2-ethanediol molecule, it follows that $4.2/2 = 2.1$ electrons are transferred per CO_2 molecule in the oxidation of the adsorbate. This value is within the margin of error equal to the value of 2 for CO according to:

$$CO_{ads} + 2OH^- \rightarrow CO_2 + H_2O + 2e$$
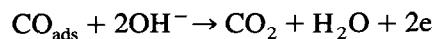
In addition, the absence of a reduction at potentials below 0.35 V and the absence of an oxidation at high potentials in the oxide region confirm that CO is the only adsorbate formed in the adsorption of 1,2-ethanediol. We found in a previous study [14] in acid electrolyte likewise that the adsorption of 1,2-ethanediol is completely dissociative. This implies that the adsorption of 1,2-ethanediol is independent of the pH and the type of electrolyte used. In accordance with this conclusion, the oxidation profile of the 1,2-ethanediol adsorbate shows a close resemblance with the oxidation profile of CO, apart from the lower coverage for 1,2-ethanediol with respect to CO. However, the adsorption of CO was performed at 0.15 V, whereas 1,2-ethanediol was adsorbed at 0.35 V. When the curve in Fig. 3 is compared with a voltammogram of CO that is also adsorbed at 0.35 V, only a small difference remains. The lower coverage for 1,2-ethanediol is probably due to spatial requirements of the C–C dissociative reaction.

The three peak structure for CO oxidation has been observed earlier for polycrystalline platinum [23], in contrast with single crystal studies, that generally report a single oxidation peak for the various crystal planes. Only at high coverages a prewave is observed for Pt(100) in carbonate electrolyte [28]. We can assign the main oxidation peaks at 0.63 and 0.57 V in the cyclic voltammogram to the different crystal planes that are predominant at the electrode surface. Comparing the voltammograms in Figs. 2 and 3 for ethanol and 1.2-ethanediol provides further evidence for the assignment of the CO oxidation peaks. The shoulder at 0.57 V is much more pronounced in Fig. 3 for 1.2-ethanediol than for ethanol in Fig. 2. Moreover more weakly bonded hydrogen is present after adsorption of ethanol with respect to 1,2-ethanediol. This shows that there is a close correlation between the weakly bonded hydrogen sites and the CO oxidation wave at 0.57 V. In combination with the FTIRS results we can assign the oxidation peak at 0.57 V to linear adsorbed CO

on Pt(110) related sites whereas the oxidation peak at 0.63 V can be assigned to bridge bonded CO on Pt(100) related sites. The third CO oxidation at 0.38 V originates from adsorbed CO molecules that are very weakly bonded and therefore we can correlate this oxidation wave with the presence of a densely packed CO adlayer, on one or both crystal planes.

In the case of ethanol, the Q_{ads}/Q_{ox} value of 1.23 indicates that of the 12 electrons transferred in the total oxidation of an ethanol molecule to CO_2, 6.6 electrons are involved in the adsorption and 5.4 electrons are transferred in the oxidation. Since two CO_2 molecules are formed in the total oxidation of a single ethanol molecule, this implies that 2.7 electrons per CO_2 molecule are involved. This value is close to the characteristic value for CO, indicating that the molecule is largely dehydrogenated. The integrated CO absorbances for 1,2-ethanediol and ethanol are approximately of the same size and since full decarbonylation was concluded for 1,2-ethanediol this leads to the conclusion that ethanol adsorbs also fully dissociative, according to:

$$C_2H_5OH + (6 - x)OH^-$$

$$\rightarrow CO_{ads} + CH_{x,ads} + (6 - x)H_2O + (6 - x)e$$
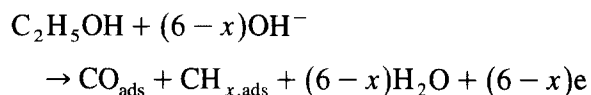
Quantitative analysis of the n_{ox} value then shows that a follow-up oxidation of CH_x to CO occurs after the initial C–C(OH) dissociative reaction. Formation of equal amounts of CO and CH_x would result in n_{ox} values between 3 ($x = 0$) and 4.5 ($x = 3$). An n_{ox} value lower than 3 can only be obtained when one of the adsorbates has oxidized further than C and therefore we conclude that the value of 2.7 originates from a follow-up oxidation of CH_x to CO according to:

$$CH_x + (2 + x)OH^-$$

$$\rightarrow CO + (1 + x)H_2O + (2 + x)e$$
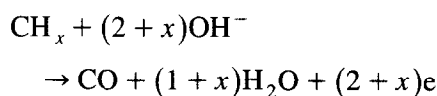
We have concluded in a previous study [14] that the same follow up reaction of CH_x also occurs in acid electrolyte, where $n_{ox} = 2.5$ was found. A recent FTIRS study [29] using labeled ethanol

provided direct spectroscopic proof for this reaction, as shown by the formation of $^{13}CO_{ads}$ from $^{13}CH_3CH_2OH$ at potentials equal to the adsorption potential used by us in acid electrolyte.

An important difference between ethanol and 1,2-ethanediol is the presence of a reduction below 0.35 V for ethanol. This reduction was also reported for Pt(110) [19] and polycrystalline Pt [10] in contrast with Pt(100) and Pt(111) [19]. No interpretation of this reduction peak has been given up to now, but we assign this peak to the reduction of CH_x to CH_4 according to:

$$CH_{x,ads} + (4 - x)H_2O + (4 - x)e$$

$$\rightarrow CH_4 + (4 - x)OH^-$$
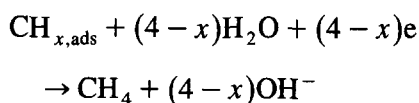
Due to the removal of CH_x species in the reduction, the amount of charge involved in the subsequent oxidation in Fig. 2 is lower than in the 'direct' oxidation in Fig. 1. The ratio of the reduction charge and the decrease in the oxidation charge $Q_{red}/\Delta Q_{ox}$ gives information on the oxidation state of the CH_x species that have been reduced to CH_4. The ratio $Q_{red}/\Delta Q_{ox} = 0.9$ found here in KOH electrolyte demonstrates that the CH_x species are fully dehydrogenated to C, since both in the reduction of C to CH_4 and the oxidation of C to CO_2, 4 electrons are involved, giving $Q_{red}/\Delta Q_{ox} = 1$. In the case of CH or CH_2, $Q_{red}/\Delta Q_{ox}$ values of 0.6 and 0.33 would have been expected.

Combining the n_{ox} values found for ethanol and 1,2-ethanediol with the oxidation charges determined with cyclic voltammetry gives the adsorbate coverage according to:

$$\theta = \frac{Q_{ox}}{n_{ox}Q_H^0}$$

where Q_H^0 is the charge involved in the desorption of a monolayer of hydrogen, determined in blank electrolyte. This procedure results in adsorbate coverages of 0.45 for ethanol and 0.46 for 1,2-ethanediol. In the case of 1,2-ethanediol

the adlayer consists completely of CO, whereas for ethanol the adlayer consists of CO and C. It can be calculated from the n_{ox} value of 2.7 that the adlayer consist of 65% CO and 35% C, corresponding to coverages of 0.29 for CO and 0.16 for C. The CO coverage is in quite good agreement with the CO coverage calculated from the charge involved in the 'indirect' oxidation: 0.30, assuming that C_{ads} has been completely reduced to methane. Comparing the charges involved in the 'direct' and 'indirect' oxidation of ethanol adsorbates shows that the C species are oxidized in the double layer region as well as in the oxide region. The charge involved in the oxide region in Fig. 1, corresponds to $\theta_C = 0.09$ monolayers when we assume that 4 electrons are involved in the oxidation of C to CO_2, whereas the oxidation charge for C_{ads} in the double layer region corresponds to $\theta_C = 0.07$. We want to stress that the FTIRS results are in agreement with the conclusions given above, that were obtained only from the charges involved in cyclic voltammetry. The normalized integrated CO absorbance of 0.45 ± 0.05 for ethanol and 1,2-ethanediol are in accordance with the respective ratios of the CO coverages that were calculated from cyclic voltammetry; $\theta_{CO,eth}/\theta_{CO,CO} = 0.38$ and $\theta_{CO,1,2\text{-ethdiol}}/\theta_{CO,CO} = 0.39$.

The results for MGP show that the C–C(OH) dissociative adsorption does not only occur for simple alcohol compounds but also occurs for more complex cyclic polyols. However, we cannot conclude from our measurements that the C–C dissociative adsorption of MGP is complete. Some experiments with glucose have shown that a small reduction is visible at low potentials and a small contribution is present in the oxide region. This implies that the decarbonylative adsorption is not complete, although it is the major adsorption pathway according to:

$$C_6H_{12}O_6 \rightarrow 6CO + 12H^+ + 12e$$

In the case of MGP then is seems reasonable to conclude that decarbonylative adsorption is not

the sole adsorption route, although it is the dominant one, according to:

$$C_7H_{14}O_6 \rightarrow 6CO + CH_x$$
$$+ (14 - x)H^+ + (14 - x)e$$
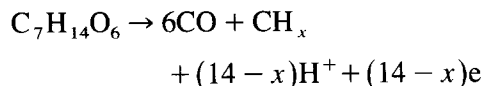
Adsorbate studies have shown that dissociation of the reactant alcohol into CO and C can occur at potentials where the oxidation to acetaldehyde and acetic acid does not occur. This demonstrates that the decarbonylative reaction is thermodynamically favored over the oxidation of ethanol to ethanal and acetic acid. However, if the surface is completely covered with dissociative adsorbates, oxidation is the only possible reaction pathway.

4.2. Open circuit potential measurements: implications of surface roughness

In this section we will discuss the difference in open circuit potential (o.c.p.) values for the catalytic ethanol oxidation on smooth and platinized platinum. We have demonstrated with simple experiments that the catalytic alcohol oxidation can be regarded as an electrochemical process and the different o.c.p. values for smooth and platinized platinum originate from a difference in kinetics of the two half reactions involved;

$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$
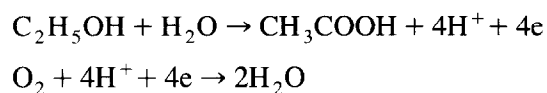
Such a local cell mechanism has already been proposed by others [24,30–33]. The oxygen reduction is diffusion limited below 0.8 V, and as a result it does not increase after roughening of the electrode surface. However, the ethanol oxidation is kinetically limited over the complete potential region and thus increases proportionally with the electrode area upon roughening of the electrode surface. As schematically shown in Fig. 18 there is for smooth platinum no potential below 0.8 V where the current of the half reactions are equal, leading to a further increase of the o.c.p. to 1 V, where the surface
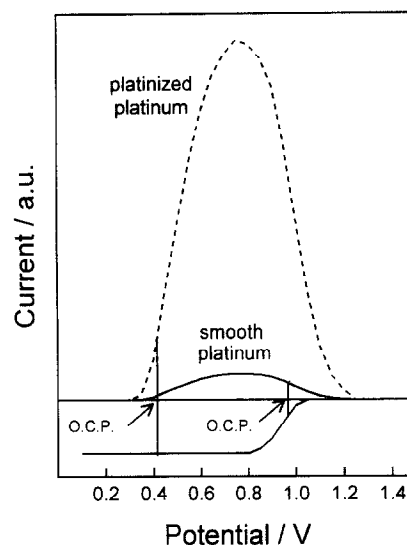

Fig. 18. Current–potential curves for ethanol oxidation and oxygen reduction on smooth and platinized platinum.

is highly covered with adsorbed oxygen or hydroxyl and where the oxygen reduction has almost, but not completely, ceased. The reaction rate of the catalytic ethanol oxidation is not limited by diffusion of oxygen to the surface but is kinetically limited. In a previous report it has been concluded that the rate of the catalytic ethanol oxidation in the kinetic regime corresponds to a surface of which only 9% of the surface atoms are available for the oxidation reaction and 91% is covered. This conclusion was reached by comparing the oxidation rate on carbon supported platinum catalysts in a slurry phase reactor with kinetic data of electrochemical adsorption studies on platinum foil [25].

For platinized platinum the o.c.p. stabilizes at 0.35 V after reductive startup of the reaction as a result of the increased ethanol oxidation with respect to smooth platinum, as schematically shown in Fig. 18. In contrast with smooth platinum the reaction rate is now diffusion limited and can be further increased by improving the mass transport of oxygen to the surface. Such a low open circuit potential has also been found for the catalytic oxidation of 2-propanol [30] and ethanol [1] on platinized platinum. On the

basis of our experiments we conclude that it is not allowed to compare the results of o.c.p. measurements on platinized platinum with measurement on carbon supported platinum in the kinetic regime as was done by Vleeming et al. [1] and Schuurman et al. [4].

The different kinetic regimes for smooth and platinized platinum affect the reaction rate considerably. The reduction rate of oxygen at 1 V is shown in Fig. 18 to be much lower than in the diffusion limited regime below 0.8 V, which indicates that the catalytic oxidation of alcohols in the kinetic regime proceeds at much lower rate than in the diffusion limited situation. Note that the occurrence of the local cell mechanism implies that adsorbed oxygen is not involved in a direct reaction with the alcohol as has been proposed [1,4–6,34–36]. Adsorbed oxygen or hydroxyl causes both the electrochemical oxygen reduction and the electrochemical ethanol oxidation to be inhibited. When adsorbed oxygen or hydroxyl were involved in the oxidation of alcohols a positive correlation would be expected between the oxygen coverage and the activity, at least for low coverages. However, this correlation has never been demonstrated with electrochemical techniques.

Summarizing, the catalytic alcohol oxidation performed in the kinetic regime corresponds to a high open circuit potential and thus a surface highly covered with oxygen or hydroxyl. In our view the situation for the alcohol oxidation in the kinetic regime can readily be referred to as overoxidation, since the high oxygen coverage causes the reaction rate to be much lower than in the diffusion limited regime. On the contrary, studies in the diffusion limited regime correspond to a low open circuit potential and thus a surface that is completely free of adsorbed oxygen or hydroxyl.

The experiments on platinized platinum nicely illustrate that catalytic oxidation reactions proceed through a local cell mechanism. This has important consequences for the transport of reactants and products on porous electrodes. Since its reduction is diffusion limited, oxygen will

not diffuse deeply into the pores of the electrode but react in the surface region. Ethanol, however, reacts at the entire surface including deeply in the pores. The electrons that are transferred from ethanol to the metal during oxidation are transported through the metal to the surface of the electrode where they are used to reduce oxygen. The question is what the implications of these results are for carbon supported catalysts in a slurry phase reactor. The transport of oxygen to the surface of the catalyst particles is much better in a slurry phase reactor than in our experiments, which suppresses the likeliness of diffusion limitation. However, our experiments have shown that the roughness factor of the electrode is a very important parameter. For a carbon catalyst particle the roughness factor can be defined as the ratio of the true platinum surface in a particle and the outer surface of the carbon particle. This ratio can be influenced by several factors as the platinum content of the catalyst and the size of the carbon particles. This roughness factor can be quite high for carbon supported platinum catalysts and in this respect it can resemble platinized platinum. Depending on the type of alcohol, the catalyst properties and reaction conditions, the oxidation in a slurry reactor can proceed in the kinetic regime or in the diffusion limited regime. In the case that the reaction rate is limited by diffusion of oxygen, the high conductivity of the carbon support enables the local cell mechanism to occur by conduction of electrons through the carbon support, which leads to a situation where the outer shell of the catalyst particle reduces oxygen and both the outer and inner part of the particle oxidizes the alcohol. The electrons migrate through the carbon support from the inner part to the outer shell of the particle.
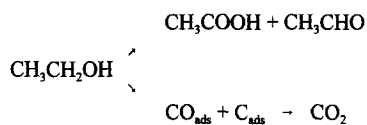
4.3. Adsorbates present during diffusion limited oxidation

Catalytic studies on alcohol oxidations are often carried out in the diffusion limited regime [2] and in some cases this has been confirmed

with potential measurements [2,9,35,37]. We found that the electrode surface is highly covered with CO and C adsorbates during the diffusion limited ethanol oxidation on platinized platinum. We cannot establish the exact coverage during the reduction since after the potential step to 0.15 V reduction of C species occurs. The adsorbate coverage during reaction depends on the o.c.p., which itself depends on several factors like the electrode roughness, ethanol concentration and the mass transport of oxygen. We suggest that in all cases where alcohol oxidation has been carried out in the diffusion limited regime [2,9,35,37], the surface is also highly covered with irreversible adsorbates that are formed from the reactant alcohol. The reported open circuit potentials can be so low that they correspond to values in the so-called hydrogen region and on that basis it was concluded by some [2] that the catalyst surface is actually covered with hydrogen during reaction. However, it should be kept in mind that in such a situation the surface is highly covered with irreversible adsorbates and not many platinum sites are left for hydrogen to adsorb. As a result only a low hydrogen coverage is necessary to reach fairly negative potentials, which means that the hydrogen coverage is much lower than suggested by some as they refer to a reduced surface [2]. In fact, the open circuit potential of 0.41 V found in our ethanol oxidation experiments does not correspond to a situation that the surface contains any adsorbed hydrogen.

Our experiments have demonstrated that the electrochemical and catalytic oxidation of ethanol result in the same coverage of irreversible adsorbates on the catalyst surface as long as the electrochemical potentials are equal. This supports the view that the catalytic oxidation can be regarded as an electrochemical process and therefore information obtained with electrochemical tools can be directly transferred to the catalytic oxidation. The key parameter is the potential.

We have clarified that the CO + C coverage is a steady state coverage and that CO and C

$$CH_3COOH + CH_3CHO$$
$$CH_3CH_2OH \nearrow$$
$$\searrow$$
$$CO_{ads} + C_{ads} \rightarrow CO_2$$

Scheme 1.

adsorbates are not only present during the initial phase of the reaction. No adspecies remained on the surface when the rate of electrochemical ethanol oxidation was made limited by diffusion of ethanol, which proves that the rate of C–C(OH) dissociative adsorption and subsequent oxidation to CO_2 is then higher than the diffusion rate of ethanol and thus the CO_2 selectivity is 100%. A subsequent increase of the ethanol concentration at this potential made the reaction rate kinetically limited again, leading to a high coverage of CO and C adspecies, which demonstrates that continuously new CO and C adspecies are being formed by C–C(OH) dissociative adsorption during oxidation of ethanol to acetaldehyde and acetic acid. This demonstrates that the presence of CO is not an initial effect; being formed during startup of the reaction and disappearing after admission of oxygen. The possible reactions are given in Scheme 1.

Our experiments on the diffusion limited oxidation of MGP have shown clearly that the increase of the open circuit potential with time is correlated with an increase of adsorbates that are oxidized at high potentials in the oxide region, whereas the amount of adsorbates that oxidize at low potentials diminish. The oxidation at high potential in the oxide region is typical for adsorbed hydrocarbon species C_xH_y, whereby CO_2 is formed. The increase of the o.c.p. can easily be understood in terms of the two electrochemical half reactions. As the surface becomes covered with these site blockers, less platinum is available for the oxidation of MGP. Because the electrochemical oxidation rate of MGP is kinetically limited, a build-up of carbonaceous residue will result in an inhibition of the MGP oxidation as less Pt surface is available for reaction. However, the electrochemical reduction of oxygen is diffusion lim-

ited and this reaction is not affected by an increasing coverage of irreversible adspecies. We infer this from the experiments with ethanol and oxygen, where the presence of 0.1 M ethanol had no effect on the oxygen reduction rate at 0.1 V. As a result the open circuit potential increases in order to maintain a net zero current. Our conclusion contrasts with those in the literature, where the slow increase of the open circuit potential was referred to as overoxidation [1].

We found that when the o.c.p. reaches 0.8 V, which corresponds to the peak potential for MGP oxidation, it quickly rises to 0.98 V, and thus the reaction transfers from diffusion limited regime to the kinetic regime. As in the case of ethanol, the platinum surface is highly covered with adsorbed oxygen or hydroxyl at 0.98 V and the majority of the carbon species formed during deactivation probably oxidizes to CO_2 at this potential. The o.c.p. remained constant within 20 mV for 16 h, which implies that the coverage of adsorbed oxygen or hydroxyl remains equal. Nevertheless, we found the catalyst both to deactivate when electrochemical MGP oxidation was carried out at 0.98 V and to reactivate after reduction of the adsorbed oxygen species at o.c.p., which is in perfect agreement with the study on carbon supported platinum in a slurry phase in the kinetic regime [1]. This means that the deactivation does not originate from a slow increase of the oxygen coverage, since this would require an increase of the open circuit potential.

Our experiments have demonstrated that the adsorbed oxygen species slowly change in time when the electrode is preoxidized in the absence of alcohol. The shift of the oxygen reduction peak in the cyclic voltammogram after different preoxidation times implies an increase of the adsorption energy of the oxygen species. In this way we can understand that while the open circuit potential during catalytic MGP oxidation in the kinetic regime remains constant the catalyst nevertheless deactivates due to changes in the oxygen adspecies. However, it should be reminded that the adsorbed oxygen atoms themselves are not involved in the catalytic oxidation but act only as site blockers. Apparently the slow change in the properties of adsorbed oxygen results in a decreased ability of the catalyst to reduce molecular oxygen and to oxidize MGP, probably by a decreased accessibility of the platinum surface for either molecular oxygen or MGP.

5. Conclusions

The irreversible adspecies formed after adsorption of ethanol and 1,2-ethanediol have completely undergone C–C(OH) dissocation accompanied by full dehydrogenation to form CO and C species in the case of ethanol and only CO in the case of 1,2-ethanediol. The C species are partially oxidized further to CO. These results show that the adsorption behaviour of these compounds at high pH is completely analogous with that at low pH [14,16]. The adsorption behaviour of the cyclic polyol MGP is similar to that of the small alcohols as the molecule completely decarbonylates to form adsorbed CO and a small fraction of C.

All our experiments show that the catalytic alcohol oxidation can be regarded as an electrochemical process, consisting of two independently acting half reactions that determine the open circuit potential. The roughness of the electrode surface greatly affects the o.c.p. during catalytic alcohol oxidation; smooth platinum leads to high o.c.p. values and platinized platinum leads to low o.c.p. values. These low and high open circuit potentials correspond to a diffusion limited regime where diffusion of oxygen is rate limiting and a kinetic regime, respectively. The reaction rate in the kinetic regime is considerably lower than in the diffusion limited regime.

During oxidation of ethanol and MGP in the kinetic regime, the surface is highly covered with adsorbed oxygen or hydroxyl. In contrast with this the surface is devoid of adsorbed oxygen in the diffusion limited regime and is

instead covered with a high steady state amount of CO and C species, which are continuously being formed by C–C(OH) dissociative adsorption. The catalyst is found to deactivate both in the diffusion limited as in the kinetic regime for MGP oxidation. Whereas in the diffusion limited regime, the deactivation is caused by accumulation of carbonaceous residue, while in the kinetic regime, changes in the adsorbate properties cause deactivation and not a plain increase of the oxygen coverage.

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