Platinum catalysed aqueous alcohol oxidation: experimental studies and reaction model discrimination

A.P. Markusse [*], B.F.M. Kuster, J.C. Schouten

Laboratory of Chemical Reactor Engineering, Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, Netherlands

Abstract

The platinum catalysed aqueous oxidation of alcohols and carboxylic acids is studied using electrochemical methods under circumstances typical for catalytic oxidation reactions, being 40°C and pH 8. The investigated reactants are cyclohexanol (CL), methyl α-D-glucopyranoside (MGP), sodium oxalate (OA), and sodium formate (FA). Two catalytic oxidation regimes are distinguished: the intrinsic kinetic regime, and the oxygen transport limitation regime. Save OA, all reactants react on adsorbate-free, reduced platinum. On adsorbate-free, reduced platinum carbonaceous adsorbates are formed, inhibiting catalytic reactions. This situation is found when operating in the oxygen transport limitation regime. Under intrinsic kinetic conditions, platinum catalyst deactivation is caused by platinum oxide formation. Platinum oxide reduction is inhibited by the presence of adsorbed oxygen. A kinetic model for MGP oxidation, platinum deactivation, and reactivation is evaluated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Alcohol oxidation; Catalysis; Deactivation; Electrochemistry

1. Introduction

Platinum catalysed selective oxidation of organic compounds such as alcohols and carbohydrates provides useful products and intermediates for various applications in fine chemistry. In general, the oxidant used is oxygen and the solvent is water. The platinum catalyst is generally supported on activated carbon or graphite. This process is attractive due to low environ-mental impact, high selectivity, and mild reaction conditions (20–80°C, ambient pressure).

In general, two different reaction operation regimes can be distinguished: the oxygen transport limitation regime and the intrinsic kinetic regime. The regime is determined by the oxygen transport rate. The amount of oxygen present at the catalyst surface has a large influence on the behaviour of the platinum catalyst, especially on catalyst deactivation. Catalyst deactivation is a major issue in platinum catalysis, preventing large-scale use of these oxidation processes in fine chemistry [1].

When the oxygen transport to the catalyst is limited and the catalyst surface is largely unoc-

* Corresponding author. Fax: +31-40-244-6653.
E-mail address: a.p.markusse@tue.nl (A.P. Markusse).

cupied, catalyst poisoning is likely to occur. Carbonaceous reactant degradation products are strongly adsorbed to the catalyst surface, thus blocking the active sites. These degradation products have been studied by various authors, using electrochemical methods [2–4].

In the intrinsic kinetic regime, where oxygen is present in excess, platinum catalyst over-oxidation occurs, as shown by in situ extended X-ray absorption fine structure (EXAFS) spectroscopy [5]. Platinum oxides are formed on the catalyst surface, dramatically decreasing the catalyst activity. Under extreme or long-term oxidative circumstances or in the presence of strong chelating agents, platinum dissolution has been observed [6].

Within our laboratory, the oxidation of several alcohols and carbohydrates has been studied through kinetic analyses and various catalyst characterisation methods, including EXAFS and electrochemistry. The catalysts used were promoted, and unpromoted platinum and palladium catalysts supported on activated carbon, carbon fibrils, and graphite [5–9]. Several models have been proposed to explain oxidation and deactivation kinetics, including a complete model for oxidation of methyl α-D-glucopyranoside (MGP) and platinum catalyst deactivation and reactivation [8]. In this model, the active oxygen species is assumed to be adsorbed O. The proposed mechanism for platinum catalyst deactivation is the formation of platinum oxide, which can be reduced by the reactant in the absence of oxygen.

The aim of this paper is to provide electrochemical evidence for the proposed kinetic model. Electrochemistry offers the opportunity to study catalytic oxidation of organic reactants in the absence of gaseous or dissolved oxygen. Most publications on electrochemical oxidation of organic reactants report data from strong acid or alkaline solutions [2–4,10]. Selective catalytic alcohol oxidations are preferably carried out in neutral or slightly alkaline solutions, due to the sensitivity of the reactants (especially carbohydrates) and products [1]. The present

contribution aims to elucidate reaction and deactivation mechanisms using cyclic voltammetry at pH 8, and compare these with the oxidation reaction mechanism proposed in Ref. [8].

2. Experimental

Cyclic voltammetric measurements were performed in a thermostated three-compartment 120 ml electrochemical cell. Potentials and currents were controlled by means of an Autolab PGSTAT20 potentiostat/galvanostat. An aged platinised platinum electrode with a geometric surface area of 3.52 cm^2 and a hydrogen adsorption capacity of 38.4 mC (3.98×10^{-7} mol e^- or H_{ad}, real surface area, 183 cm^2) was used as the working electrode. Another platinised platinum electrode served as the counter electrode. A $Hg/Hg_2SO_4/sat.$ K_2SO_4 reference electrode was used. All potentials are referred to the reversible hydrogen electrode (RHE).

All solutions used were prepared with Millipore superQ water (18 $M\Omega/cm$) and analytical grade reagents. All solutions were buffered at pH 8 using 46.5 mol/m^3 sodium dihydrogen phosphate and 26.8 mol/m^3 sodium tetraborate. The conductivity of the solutions was improved by adding 500 mol/m^3 sodium perchlorate. For comparison with catalytic reaction circumstances, all measurements were performed at 313 K, while argon was bubbled through the solution. The organic reagents used were cyclohexanol (CL), MGP, sodium oxalate (OA), and sodium formate (FA).

Prior to adsorbate measurements, the platinum electrode was stripped by a reductive (-0.03 V during 20 s) and an oxidative (1.27 V during 20 s) treatment. The electrode was exposed to a 100 mol/m^3 pH 8 solution of the organic reactant (CL, MGP, OA or FA) for 30 min, during which the electrode potential was kept at 0.67 V. The electrode was rinsed with distilled water and placed in a blank pH 8 electrolyte. Starting from 0.67 V in negative direction, cyclic voltammograms were recorded

in the range 0.03–1.46 V at scan rate 5 mV/s. This procedure is referred to as 'indirect oxidation' by Gootzen et al. [2]. From the first scan, the differences in the hydrogen region (0.03–0.37 V) and the oxygen region (0.75–1.46 V) were examined. The second and later scans were identical with cyclic voltammograms recorded with a clean platinum electrode in fresh, blank electrolyte.

3. Results and discussion

The presence of adsorbed oxygen or hydrogen on the platinum surface has a large influence on the oxidation of organic reactants. In order to investigate the reactivity of platinum towards CL, MGP, OA, and FA, cyclic voltammograms were recorded using 100 mol/m^3 solutions of these reagents. The platinum electrode potential was cycled between 0.03 and 1.46 V vs. RHE.

First of all, the buffering capacity of the electrolyte needs to be examined. Local pH changes can distort the voltammograms dramatically, as shown by Pletcher and Sotiropoulos [11] using unbuffered neutral solutions. From the hydrogen adsorption and desorption peaks in blank electrolyte (Fig. 2), a peak shift of +50

mV is observed. This corresponds to a 0.85 pH decrease, which is acceptable.

The features to be found in a typical voltammogram are indicated in Fig. 2. As shown in Fig. 1, the two alcohols (CL and MGP) show two significant peaks: a broad peak around 1.15 V due to the oxidation of carbonaceous residue, and a distorted peak around 0.6 V due to direct alcohol oxidation and (to a minor extent) carbonaceous residue formation. This behaviour has been observed for various alcohols, including ethylene glycol [12] and 1-butanol [3,10]. The deformation of the alcohol oxidation peak in the negative-going scans stems from platinum oxide reduction, which also takes place in this region. Clearly, a reduced platinum surface is necessary for this type of alcohol oxidation.

OA shows a large current in the oxidic region, above 1.1 V vs. RHE. As stated by Chollier et al. [13], OA oxidation strongly depends on pH. In 0.5 M sulfuric acid, OA oxidation starts at 0.8 V vs. RHE. The cyclic voltammogram of FA is diffusion and conductivity controlled, due to the extremely high reactivity of this reactant. Its oxidation commences around 0.4 V just above the hydrogen adsorption region.

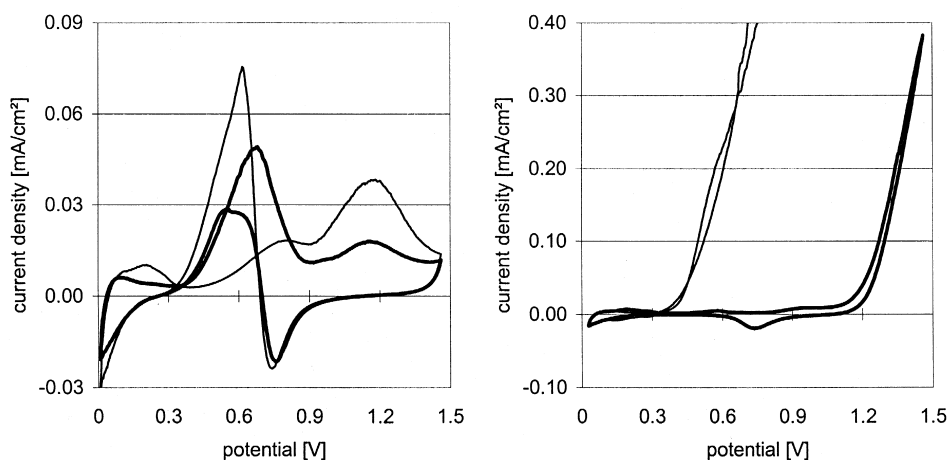The results of our adsorbate studies are presented in Table 1. The first scan after electrode

Fig. 1. Cyclic voltammograms in the range 0.03–1.46 V, scan rate 5 mV/s, 40°C. Electrode potential [V] on horizontal axis, current density [mA/cm^2] on vertical axis. In the left figure thin line for 100 mol/m^3 CL, thick line for 100 mol/m^3 MGP; in the right figure thin line for 100 mol/m^3 FA, thick line 100 mol/m^3 OA.
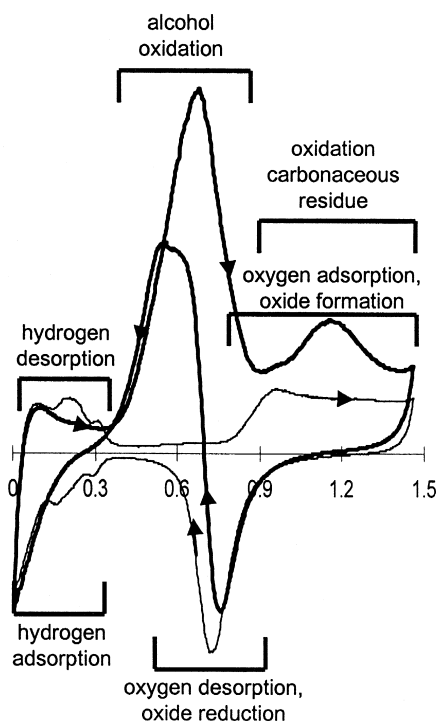
Fig. 2. Cyclic voltammograms in the range 0.03–1.46 V, scan rate 5 mV/s, 40°C. Electrode potential [V] on horizontal axis, current density [mA/cm^2] on vertical axis. The thin line represents blank electrolyte, the thick line for 100 mol/m^3 MGP.

transfer to a blank solution gives information about the adsorbates formed. The decrease in hydrogen peak charge (0.03–0.37 V) is a measure for the amount of platinum surface sites blocked by the reactant or its degradation products. In the oxygen region (0.75–1.46 V), all reactants showed an increase of the peak charge in the first scan. This appears as a broad peak with its maximum at 1.12–1.20 V, superimposed on the broad platinum oxidation peak. As Gootzen et al. [2,14] showed for several alco-

hols, including MGP, this peak can be attributed to complete oxidation of carbonaceous residues towards carbon dioxide. Their residue oxidation charge after adsorption of a 5 mol/m^3 MGP solution at pH 13 was 250 μC/cm^2 [2], which is much more than the charge we found for a 100 mol/m^3 MGP solution at pH 8. As mentioned by Mallat and Baiker [1], carbohydrate oxidations should be performed at pH between 7 and 9, due to side reactions at higher and lower pH. These side reactions, forming carbonaceous residue, are the cause of platinum deactivation in the oxygen transport limitation regime.

In order to investigate the reactivity of oxidised, deactivated platinum towards the alcohols, the platinum electrode potential was cycled between 0.77 and 1.46 V vs. RHE. We assume that after 10 consecutive scans, a full oxide layer has formed. The results are shown in Fig. 3. The small currents in the voltammograms are largely due to double-layer charging. The net charge consumption in one scan in blank electrolyte was 14 μC/cm^2; in MGP, 47 μC/cm^2; and in CL 69, μC/cm^2. For MGP, assuming selective oxidation (4 e$^-$ per MGP), this amounts to an average turnover frequency of 1.0×10^{-4} s^{-1}. The maximum oxidation current in the double-layer region (at 0.68 V, Fig. 1) was 49.2 μA/cm^2, which is equivalent to a turnover frequency of 5.9×10^{-2} s^{-1}. The catalytic turnover frequency at equivalent circumstances is 1.58×10^{-2} s^{-1} [7]. Clearly, free Pt^0 sites are much more active for alcohol oxidation, but the reaction pathway via platinum oxide is significant for the relation between reactant concentration and oxide coverage in

Table 1
Results of adsorbate studies of various organic reactants on platinised platinum at 0.67 V vs. RHE. Peak charge increase (μC/cm^2 and percentage of blank hydrogen peak) in the hydrogen region (0.03–0.37 V) and the oxygen region (0.75–1.46 V)

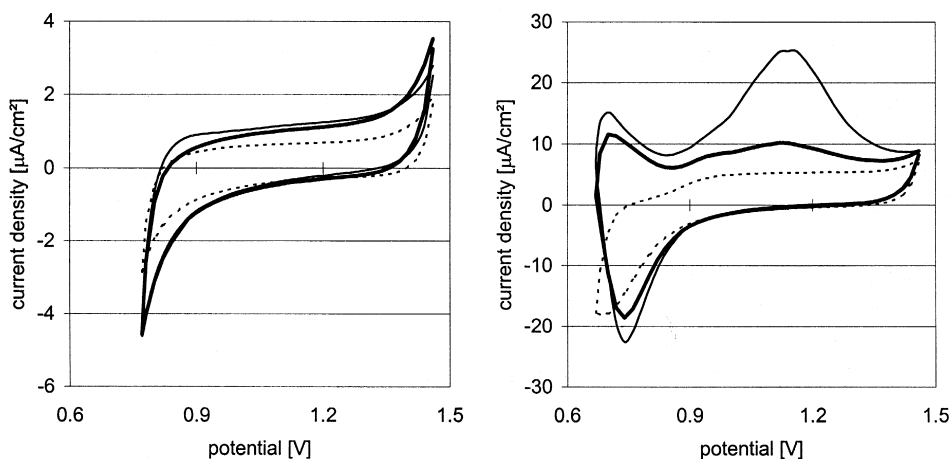| Reactant	H-region [μC/cm^2]	H-region [%]	O-region [μC/cm^2]	O-region [%]
CL	−68	−32	454	216
MGP	−30	−14	86	41
OA	−115	−55	244	116
FA	−46	−22	123	58

Fig. 3. Cyclic voltammograms in the ranges 0.77–1.46 V (left figure) and 0.67–1.46 V (right figure), scan rate 5 mV/s, 40°C. Electrode potential [V] on horizontal axis, current density [mA/cm^2] on vertical axis. Dotted lines represent blank electrolyte, thin lines for 100 mol/m^3 CL, thick lines for 100 mol/m^3 MGP.

deactivated catalysts. For methanol, formaldehyde and formic acid, this pathway has been observed by Oxley et al. [15] using open-circuit potential decay measurements.

The formation of carbonaceous residues was incited by expanding the potential range towards the double-layer region. The platinum electrode potential was cycled between 0.67 and 1.46 V vs. RHE. In the section between 0.67 and 0.77 V, the platinum surface is partially reduced. The results are shown in Fig. 3. The net charge consumed in one scan in blank electrolyte was 0.07 mC/cm^2; in MGP, 0.86 mC/cm^2; and in CL, 1.74 mC/cm^2. This indicates that carbonaceous residue is only formed in the double-layer region, corresponding to the oxygen transport limitation regime. The charge involved in oxidation of carbonaceous residue is larger for CL than for MGP. Two explanations are possible: CL is less stable on clean platinum surface and forms more residue or CL residue requires more electrons for complete oxidation.

When discussing the implications of these findings for platinum catalyst performance, one should consider some important differences between platinised platinum electrodes and commercial supported platinum catalysts. The platinum particle size in commercial catalysts is approximately 2 nm. The formation of carbonaceous residues probably requires several adjacent platinum surface sites. On small particles, and in the presence of adsorbed oxygen, these clusters may not be available (ensemble effect). Still, poison formation is likely to occur under oxygen transport limited circumstances. Also, mass transfer restrictions within the catalyst may cause oxygen and reactant concentration gradients.

Experimental results from kinetic studies on selective platinum catalysed MGP oxidation [7] have been used for the construction and validation of a reaction model for platinum catalysed aqueous alcohol oxidations [8]. The experiments used for model validation were all in the intrinsic kinetic regime, as verified by mass transport calculations. The model equations are presented in Table 2. The reaction, deactivation and reactivation kinetics are adequately described using two oxygen species: active adsorbed atomic oxygen and inactive surface platinum oxide. The latter may be identical with the strongly adsorbed oxygen species Gootzen et al. [2] used to explain continuing deactivation at constant platinum potential 0.99 V vs. RHE.

The proposed reaction mechanism involves an adsorbed oxygen assisted alcohol dehydrogenation as the rate determining step (Eq. (4)). The consecutive step 4a, oxidation of the inter-

Table 2
Kinetic model for selective methyl α-D-glucopyranoside oxidation on graphite supported platinum

$O_2 + 2\,^* \xrightarrow{k_1} 2O\,^*$	$R_1 = k_1 c_{O_2} \theta^{*\,2}$	(1)
$MGP + {}^*p \xrightarrow{k_2} MGP\,^*p$	$\theta_{MGP} = K_2 c_{MGP} \theta_p^*$	(2)
$MG + {}^*p \xrightarrow{k_3} MG\,^*p$	$\theta_{MG} = K_3 c_{MG} \theta_p^*$	(3)
$MGP\,^*p + O\,^* + {}^* \xrightarrow{k_4} MAGP\,^*p + H_2O + 2\,^*$	$R_4 = k_4 \theta_{MGP} \theta_O \theta^*$	(4)
$MAGP\,^*p + O\,^* + {}^* \xrightarrow{k_{4a}} MG\,^*p + 2\,^*$	$\theta_{MAGP} \approx 0$	(4a)
$O\,^* \xrightarrow{k_5} ox\,^*$	$R_5 = k_5 \theta_O$	(5)
$ox\,^* \xrightarrow{k_6} O\,^*$	$R_6 = k_6 \theta_{ox} \exp(-g_{SO} \theta_O)$	(6)
$MGP\,^*p + ox\,^* \xrightarrow{k_7} MAGP\,^*p + H_2O + {}^*$	$R_7 = k_7 \theta_{MGP} \theta_{ox}$	(7)
$MAGP\,^*p + ox\,^* \xrightarrow{k_7} MG\,^*p + {}^*$	$\theta_{MAGP} \approx 0$	(7a)

mediate methyl α-D-6-aldehydoglucopyranoside (MAGP) towards the product 1-O-methyl α-D-glucuronic acid (MG), which is completely proton dissociated at pH 8, is more than 100 times faster [9]. The same is assumed for reaction steps 7 and 7a. Reaction step 4 is assumed to depend on adsorbed oxygen coverage in a linear way. A third order elementary reaction step is very unusual. As shown in Fig. 1, electrochemical MGP oxidation starts outside the oxygen adsorption region. Adsorbed oxygen is not necessary for the electrochemical reaction, but it increases the platinum open circuit potential, thus activating the active platinum sites. The linear dependence, as found in our kinetic study [8], may be a coincidence. Naturally, non-electrochemical MGP oxidation requires oxygen as the electron acceptor.

Catalyst deactivation is described with the formation of surface platinum oxide. The fast reactivation of the catalyst in an oxygen-free environment, in contrast with the slow deactivation, is described with feed-back mechanism. In this proposed mechanism the presence of adsorbed oxygen prevents the reduction of surface platinum oxide. This is comparable with the extreme hysteresis in electrochemical platinum oxidation and reduction. The model does not

include deactivation by carbonaceous poison formation, which is negligible under the reaction circumstances [7]. Direct reduction of platinum oxide, as assumed in Eq. (7), only plays a minor role in the kinetic model [8].

4. Conclusions

The platinum catalysed aqueous oxidation reactions of CL, MGP, OA, and FA have been studied using cyclic voltammetry. The experimental conditions, 40°C and pH 8, are unusual in electrochemistry, but have been chosen for comparison with heterogeneous catalysis. The alcohols CL and MGP have been found to react on clean, metallic platinum. They show very low activity towards platinum oxide. OA is only oxidised at very high potential (over 1.1 V vs. RHE). FA oxidation, like alcohol oxidation, is catalysed by metallic platinum.

In the platinum double-layer region, i.e. without adsorbed hydrogen or oxygen, the formation of carbonaceous residues has been established for all investigated reactants. These residues are oxidised in the oxygen adsorption region at platinum potential approximately 1.15 V vs. RHE. Under oxygen transport limitation circumstances, the platinum catalyst potential will be in the double-layer region. Therefore, carbonaceous poison formation is the main cause of platinum catalyst deactivation in the oxygen transport limitation regime.

On exposure to a large excess of oxygen, the open circuit potential of a graphite supported platinum catalyst reaches about 1.0 V vs. RHE [7]. CL, MGP and FA are oxidised in this region, but OA is not. Oxalates are often found as unreactive end products of platinum-catalysed carbohydrate oxidation [16], which is supported by this observation. Catalyst deactivation by platinum oxide formation is obvious in the intrinsic kinetic regime. Platinum oxide shows very low activity towards alcohol oxidation. Deactivation by carbonaceous poison formation is unlikely in the intrinsic kinetic regime.

The kinetic model for platinum catalysed MGP oxidation, as derived in Ref. [8], is supported by the presented electrochemical data. The rate determining reaction step involves weakly adsorbed MGP and a free reduced platinum site that is activated by adsorbed oxygen. Catalyst deactivation in the intrinsic kinetic regime is due to platinum oxide formation. Platinum oxide reduction is inhibited by the presence of adsorbed oxygen.

List of symbol

c_{MG}	concentration of 1-O-methyl α-D-glucuronic acid	mol/m^3
c_{MGP}	concentration of methyl α-D-glucopyranoside	mol/m^3
c_{O_2}	concentration of dissolved oxygen	mol/m^3
g_{SO}	adsorbed oxygen feedback parameter	–
k_i	reaction constant, relative to equation i	
K_i	equilibrium constant, relative to equation i	m^3/mol
R_i	surface reaction rate, relative to equation i	$mol/mol\ Pt_s\ s$
θ_{MAGP}	fractional MAGP coverage	–
θ_{MG}	fractional MG coverage	–
θ_{MGP}	fractional MGP coverage	–
θ_O	fractional oxygen coverage	–
θ_{ox}	fractional oxide coverage	–
θ^*	fraction free chemisorption sites	–
θ_P^*	fraction free physisorption sites	–

References

[1] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.
[2] J.F.E. Gootzen, A.H. Wonders, A.P. Cox, W. Visscher, J.A.R. van Veen, J. Mol. Catal. A 127 (1997) 113.
[3] N.-H. Li, S.-G. Sun, J. Electroanal. Chem. 436 (1997) 65.
[4] N.-H. Li, S.-G. Sun, S.-P. Chen, J. Electroanal. Chem. 430 (1997) 57.
[5] A.P. Markusse, B.F.M. Kuster, D.C. Koningsberger, G.B. Marin, Catal. Lett. 55 (1998) 141.
[6] J.H. Vleeming, B.F.M. Kuster, G.B. Marin, F. Oudet, P. Courtine, J. Catal. 166 (1997) 148.
[7] J.H. Vleeming, B.F.M. Kuster, G.B. Marin, Ind. Eng. Chem. Res. 36 (1997) 3541.
[8] A.P. Markusse, B.F.M. Kuster, J.C. Schouten, Proceedings of the 8th International Symposium Catalyst Deactivation, Brugge 1999, Stud. Surf. Sci. Catal. 126 (1999) 273.
[9] Y. Schuurman, B.F.M. Kuster, K. van der Wiele, G.B. Marin, Stud. Surf. Sci. Catal. 72 (1992) 43.
[10] J.O'M. Bockris, K.T. Jeng, J. Electroanal. Chem. 330 (1992) 541.
[11] D. Pletcher, S. Sotiropoulos, J. Chem. Soc., Faraday Trans. 90 (1994) 3663.
[12] N.P. Lebedeva, G.N. Kryukova, S.V. Tsybulya, A.N. Salanov, E.R. Savinova, Electrochim. Acta 44 (1998) 1431.
[13] M.J. Chollier, F. Epron, E. Lamy-Pitara, J. Barbier, Catal. Today 48 (1999) 291.
[14] J.F.E. Gootzen, A.H. Wonders, W. Visscher, J.A.R. van Veen, Langmuir 13 (1997) 1659.
[15] J.E. Oxley, G.K. Johnson, B.T. Buzalski, Electrochim. Acta 9 (1964) 897.
[16] J.M.H. Dirkx, H.S. van der Baan, J.M.A.J.J. van den Broek, Carbohydr. Res. 59 (1977) 63.