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de Bruijn, F.A.; Kuster, B.F.M.; Marin, G.B.M.M.

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On-line characterization of platinum/graphite catalysts during liquid phase oxidations using cyclic voltammetry

F.A. de Bruijn, B.F.M. Kuster, G.B. Marin *

Laboratorium voor Chemische Technologie, Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract

Platinum/graphite and tin/platinum/graphite catalysts have been characterized by cyclic voltammetry during liquid phase oxidations. A newly developed electrochemical cell allows the characterization of catalysts without transfer from the liquid phase to the gas phase. The platinum particle diameter, the degree of platinum coverage by carbonaceous species and the degree of platinum coverage by promoter metal were determined quantitatively during the oxidation of methyl-α-D-glucopyranoside and ethanol. Reductive conditions can lead to the growth of the platinum particle diameter and to coverage by carbonaceous species. Hydrogen treatment at a pH of 13 leads to an increase of the platinum particle diameter from 2.7 nm to 7.4 nm and to complete coverage by carbonaceous species. After preparation of platinum/tin catalysts only twenty percent of the tin content of the catalyst is situated on the platinum surface. The degree of platinum coverage by tin can change during reaction. During the oxidation of methyl-α-D-glucopyranoside, deposition of tin from the graphite support on the platinum leads to an increase of the degree of platinum coverage by tin from 0.40 to 0.72.

Keywords: In-situ characterization; Platinum; Oxidation; Cyclic voltammetry; Liquid phase

1. Introduction

There is an increasing trend toward the replacement of the stoichiometric liquid phase oxidations practised up to now by catalytic alternatives. Especially the production of fine chemicals and pharmaceuticals generates large quantities of inorganic salts that can accumulate up to 100 kg per kg of the desired product

* Corresponding author.
Noble metal catalyzed oxidations with molecular oxygen are an attractive alternative, as the oxidant is converted to water and the oxidations are in general more selective [2]. Carbon is the usual support [1,3], although in some cases alumina and silica are better alternatives.

The major drawback of the catalytic oxidations with oxygen is the limited lifetime of the catalyst [3]. Possible causes of deactivation during liquid phase oxidations are: oxidation of the active metal [4], loss of active surface area due to site coverage by either reaction components or poisons [5], particle growth [6] and corrosion of the metal [5,6]. The actual cause of activity loss depends on the type of reaction and the conditions applied. It seems that when the oxidation rate is controlled by the gas/liquid transfer of oxygen, the catalysts are more likely to be the subject of coverage by carbonaceous products than when the catalysts are applied in the kinetic regime [7–10]. This phenomenon is reported to be more pronounced when the catalyst is preduced by the organic reactant [5,7]. When the oxidation is performed in the kinetic regime, strong chemisorption of oxygen can take place on the active metal leading to what is referred to as over-oxidation [6,8,11]. It was found recently [12] that during the oxidation of ethanol up to three steady-states can occur at the same reaction conditions, depending on the start-up procedure. A low steady-state activity was established with an oxidative start-up and a high steady-state activity with a reductive start-up. This behaviour could only be described when the formation of sub-surface oxygen was taken into account [13]. Under oxygen transfer limited conditions, it is less likely that this sub-surface oxygen will be formed. As the reactivity of the alcohol has a strong influence on the oxygen coverage during oxidation [14,15], it will also determine the extent to which sub-surface oxygen is formed. This explains why over-oxidation is observed in the oxidation of methyl-α-D-glucopyranoside ((2R)-2r, hydroxy-methyl-6t-methoxy-tetrahydropyran-3t,4c,5t-triol), leading to a low steady-state, and not in the oxidation for ethanol, while in both cases a reductive start-up is used [11]. Additionally, the oxidized platinum can be subject to dissolution and redeposition so that the already low activity becomes even lower and a steady-state is never reached [6].

The performance of platinum catalysts is often enhanced by the deposition of a promoter metal on the platinum surface. Good results have been achieved with bismuth [7,9,10,16], lead [10,17] and tin [10]. Promoter metals can, however, also be the subject of corrosion [5], and optimal performance depends on the degree of coverage by the promoter metal [7,18]. Beyond this optimal degree of coverage, the promoter metal acts as a poison, decreasing the availability of active sites necessary for reactant adsorption.

Prevention of deactivation during reaction demands a characterization technique capable to discriminate between the above mentioned causes for activity losses. Transfer of the catalyst from the liquid phase to the gas phase or vacuum can create changes in adsorbate coverage or surface states leading to misinterpretations, hence the characterization can best be performed in the liquid phase.
Electrochemical techniques such as open-circuit potential measurements and cyclic voltammetry are well suited to provide information on the surface state and adsorbate coverage of platinum surfaces during reactions [19]. The measurement of the open-circuit potential can be performed in-situ, i.e. during reaction. From this potential, the coverage of hydrogen and oxygen atoms can be evaluated [10,20].

Cyclic voltammetry is a technique that can be considered as the liquid phase equivalent of the gas/solid temperature programmed techniques TPD, TPO and TPR [21,22]. The main parameter in cyclic voltammetry is the electric potential of the catalyst, which is changed linearly in time, just as the temperature is increased linearly in the temperature programmed techniques. As a function of the catalyst potential an electric current is measured. Cyclic voltammetry has been mainly used for the characterization of fuel cell electrodes, consisting of carbon supported platinum catalysts [23–27], to study the influence of the preparation method on the electrocatalytic performance. It has also been applied as an ex-situ technique for the characterization of graphite supported catalysts before and after the oxidation of alcohols and carbohydrates [11,28]. The prereduction of platinized platinum by the organic reactant as followed in-situ by cyclic voltammetry showed that a dramatic decrease of the available platinum surface area was caused by the formation of by-products [5,7,29].

In this paper an electrochemical cell is described which offers the possibility of quasi in-situ characterization of graphite-supported platinum catalysts, both unpromoted and promoted, during reaction. Tin was used as a model to study the possibility of characterizing catalysts promoted with metals such as tin, lead and bismuth. Emphasis is put on the quantitative determination of the platinum particle size and the degree of coverage of platinum by carbonaceous species for the unpromoted catalysts, and on the determination of the degree of platinum coverage by tin.

2. Experimental

2.1. Catalyst

A 4.4 wt.-% platinum on graphite catalyst was used. The preparation method has been described by Richard and Gallezot [30]. It consists of the deposition of platinum tetramine hydroxide by means of ion-exchange on a preoxidized graphite support. The graphite was supplied by Johnsson Matthey (CH10213). After ion-exchange, the platinum complex is decomposed and reduced with molecular hydrogen at 573 K during 3 h. After this reduction, the catalyst is stored in air until use for liquid phase reactions.

The fraction of exposed platinum atoms, as determined by CO pulse
chemisorption, amounted to 0.52. The BET surface area of the catalyst after preparation amounted to 100 m$^2$/g. Graphite is used as a catalyst support instead of the more frequently used activated carbon because of its better electric conductivity [31], the smaller BET surface area [32], and the lower level of impurities [33] compared to activated carbon. A high BET surface area causes a large capacitive current, as the catalyst/liquid interphase acts as a capacitor, which must be charged continuously due to the changing potential of the catalyst during cyclic voltammetry.

Tin promoted catalysts were prepared in the reactor set-up by the addition of a solution of 0.1 N HClO$_4$ containing SnSO$_4$ at 298 K to a platinum on graphite catalyst that was treated with molecular hydrogen at 363 K during half an hour. Although not a prerequisite for Sn-adsorption, hydrogen pretreatment was preferred in order to obtain probably a single Sn-valency, avoiding possible dismutation reactions. A tin/graphite catalyst was prepared in the same way by using the preoxidized graphite support instead of the platinum/graphite catalyst.

Immediately after the addition of the SnSO$_4$ solution, the gas flow was switched from nitrogen to hydrogen. The concentration of the SnSO$_4$ used for promotion was varied between $1.5 \cdot 10^{-1}$ and 1 mol m$^{-3}$. The pH of the final solution during promotion amounted to 2. After half an hour the gas flow was switched to nitrogen and the catalyst was washed with 4 l of Millipore superQ water (18 M$\Omega$ cm). Reactions with promoted catalysts were performed immediately after promotion, i.e. without exposure to ambient conditions. The tin content of the catalyst was analyzed after preparation and after reaction using a spectrophotometric method. After preparation the amount of tin deposited was equal to the amount of tin added to the promoting solution.

2.2. Reactions

All reactions were carried out in a continuous flow stirred three phase reactor with a liquid volume amounting to $0.6 \cdot 10^{-3}$ m$^3$. The reactor was operated at a constant molar feed flow rate of the organic reactant and atmospheric pressure. The pH was measured and kept constant by adding a 0.1 N NaOH solution with a titration unit. Oxygen and nitrogen were fed by mass flow controllers in such way that the oxygen concentration in the liquid phase was constant.

A catalyst concentration of 3.33 kg m$^{-3}$ was used in all experiments. Platinum/graphite or tin promoted platinum/graphite catalysts were used for the oxidation of methyl-\(\alpha\)-d-glucopyranoside, ethanol or ethylene glycol at various reaction conditions. In addition the platinum graphite catalyst was subjected to a hydrogen treatment and the tin promoted catalyst to an oxygen treatment.

Before reaction all platinum on graphite catalysts were prereduced in the liquid phase by molecular hydrogen at 363 K for half an hour. The pH was not kept constant during this reduction but was generally between 4 and 5. One
experiment consisted of a hydrogen treatment in the liquid phase at a pH of 13
during a prolonged period. The tin promoted catalysts were used as such.

The oxidation of methyl-α-D-glucopyranoside was started by introducing
oxygen gas in the reactor after the methyl-α-D-glucopyranoside had been in
contact with the catalyst for 15 to 40 min. In the case of ethanol oxidation,
oxygen and ethanol were introduced in the reactor simultaneously. For both
reactions the start-up procedure applied was found to give the highest reaction
rate and the best reproducible results. All reported reaction rates are free of any
mass or heat transfer limitation, i.e. the reactions are performed in the kinetic
regime.

2.3. CO-pulse chemisorption

The surface area of the platinum metal was determined on a modified Carlo
Erba gas chromatograph equipped with a thermal conductivity detector. Helium
was used as carrier gas. Catalysts were dried overnight at 333 K at 5 kPa.
Before the chemisorption measurement, the platinum was reduced by hydrogen
at 373 K for half an hour. CO-pulse chemisorption measurements were per-
formed on the fresh catalyst and on catalysts used for reaction. An amount of
100 mg was used for surface area determination in duplicate. The fraction of
exposed platinum atoms was calculated assuming a 1:1 stoichiometry [34],
leading to:

\[ FE^{CO} = \frac{d V_{CO} M_{Pt}}{R T W_{cat} w_{Pt}} \]  

(1)

It is implicitly assumed that the number of exposed platinum atoms is equal to
the number of surface atoms, which is determined by the platinum particle size.
For spherical and hemispherical particles, the relation between the platinum
particle diameter and the fraction of exposed platinum atoms is given by [34]:

\[ d_{Pt} = \frac{1.25 \text{ nm}}{FE} \]  

(2)

assuming a platinum atom density of 1.31 \( \cdot 10^{19} \text{ m}^{-2} \) [35]. All measured
fractions of exposed platinum atoms are reported in terms of the platinum
particle size as calculated from Eq. (2).

In promoted catalysts, the degree of coverage of platinum by tin-atoms can be
calculated by the ratio of the fraction of exposed platinum atoms before and
after tin deposition:

\[ \theta_{Sn}^{CO} = 1 - \frac{FE_{Sn}^{CO}}{FE_{0}^{CO}} \]  

(3)

as CO does not adsorb on tin [36].
2.4. Cyclic voltammetry

A novel electrochemical cell has been designed which enables the direct characterization of a catalyst suspended in water without the need of drying the catalyst sample. A schematic representation of this electrochemical cell is given in Fig. 1.

A volume of 1.6 ml catalyst slurry with a catalyst concentration equal to 3.33 kg m\(^{-3}\) is sampled from the reactor and introduced in the compartment of the working electrode. The sampling is performed with a glass pipette. The working electrode compartment consists of a Millipore GVWP09050 membrane filter with 0.22 \(\mu\)m pore size, mounted on a perspex sieve, on top of which a platinum sieve is mounted. After the introduction of the catalyst slurry, argon purged 1 N sulphuric acid is pumped via the inlet of the working electrode compartment and the counter electrode outlet through the electrochemical cell. This electrolyte flow causes the reaction liquid to be pumped off leaving the catalyst as a fixed catalyst bed on the membrane filter with the platinum sieve on top of the bed. During characterization the electrolyte flow rate is zero. Via the platinum sieve electric contact is made between the catalyst particles and the Autolab PGSTAT 20 potentiostat. If the catalyst suspension is sufficiently mixed in the reactor, the catalyst slurry is homogeneous and the sampling of catalyst is reproducible. It was tested that the reproducibility of the sampled mass of catalyst is within 5%. The counter electrode consists of a platinum coil, Hg/Hg\(_2\)SO\(_4\) is used as reference electrode. All reported potentials are referred to the reversible hydrogen electrode (RHE).

Catalyst characterization is performed by cycling the working electrode potential between 0 and 1.3 V vs. RHE at a scan rate of 2 mV/s. Fig. 2 shows the resulting voltammogram. The part of the cyclic voltammogram ranging from 0 to 0.4 V corresponding to the reductive adsorption of protons in the cathodic scan and the subsequent oxidation of the hydrogen adatoms in the anodic scan is called the hydrogen region. The degree of hydrogen coverage ranges from zero at 0.4 V to monolayer coverage at 0 V. The surface area of the platinum metal can be determined from the charge associated with the anodic oxidation of the monolayer of hydrogen adatoms taking place between 0 and 0.4 V. Assuming a Pt:H stoichiometry of 1:1 and a platinum number surface density of \(1.31 \cdot 10^{19}\) m\(^{-2}\), 2.1 C m\(^{-2}\) is transferred during the oxidation of a monolayer of hydrogen adatoms [35]. The dashed line represents the non-faradaic current, which is not caused by the oxidation of adsorbed hydrogen. This background current is mainly the result of the capacitive current caused by the charging of the graphite support and to a much lesser extent of the platinum surface.

It is common use in cyclic voltammetry to characterize the metallic surface by recording several consecutive cycles. Starting the voltammogram at 0.3 V in negative direction, the platinum surface area can be measured without oxidizing the carbonaceous adsorbed species. Hence, the first cyclic voltammogram allows
Fig. 1. (a) Schematic representation of the experimental set up for catalyst characterization by cyclic voltammetry. WE = working electrode, RE = reference electrode, CE = counter electrode. (b) Detailed scheme of working electrode.
Fig. 2. Voltammogram of 4.4 wt-% platinum/graphite after potential cycling in 1 N H₂SO₄, room temperature. Scan rate = 2 mV/s. Dashed line gives capacitive current.

to obtain the fraction of the platinum surface area which is devoid of adsorbed organic species. By the potential cycling, these carbonaceous adsorbates can be oxidatively removed, until no further change is recorded, in particular between 0 and 0.4 V during the anodic scan. The difference between the first and the last cycle gives the degree of coverage of the platinum particles by carbonaceous species:

\[ \theta_c = 1 - \frac{Q_{H}^{1}}{Q_{H}^{0}} \]  

The fraction of exposed platinum atoms is calculated by:

\[ FE^{CV} = \frac{Q_H^{0} M_{Pt}}{FW_{cat} W_{Pt}} \]  

and the platinum particle diameter by Eq. (2).

The experimental error of the determination of the platinum particle diameter and the degree of coverage by carbonaceous species for the catalyst exposed to ambient conditions amounts to 7% respectively 9%, based on 11 determinations.

Information on surface oxides can be obtained by starting at 0.9 V in the negative direction. Platinum oxides are reduced below this potential, while the electrochemical oxidation of the platinum surface, starts only above 0.9 V. This means that a cathodic current measured during the first scan in negative direction is caused by a platinum oxide already present on the catalytic surface.
The degree of oxygen coverage can be calculated according to:

$$\theta_O = \frac{Q_{O}^1}{2Q_{H}^1}$$  \hspace{1cm} (6)$$

The factor 2 originates from the fact that the reduction of PtO is accompanied by the transfer of 2 electrons, while the oxidation of PtH is accompanied by the transfer of 1 electron. An oxygen coverage of 1 corresponds thus to a monolayer of PtO, whereas an oxygen coverage of 0.5 can be assigned to a monolayer of PtOH, as the reduction of PtOH is accompanied by the transfer of one electron. An oxygen coverage of 2 corresponds to a monolayer of PtO$_2$. It must be kept in mind, however, that the degree of oxygen coverage as measured by cyclic voltammetry after a catalytic reaction is not representative for the steady state degree of oxygen coverage on the platinum surface during the reaction. Due to the low oxygen solubility of oxygen in water, circa 1 mol m$^{-3}$, compared to the concentration of organic reactants which are usually in the order of 100 mol m$^{-3}$ or higher, the oxygen containing species such as O and OH on the platinum surface can be removed by the organic reactant as soon as the stirring in the reactor is stopped, generally resulting in a zero-valent platinum surface. The only way to obtain insight in the oxidation state during the catalytic reaction is by measuring the open-circuit potential of the catalyst [9,10,28].

For fresh promoted catalysts, the degree of platinum coverage by tin-atoms can be calculated from the amount of hydrogen adatoms oxidized between 0 and 0.4 V vs. RHE before and after tin deposition:

$$\theta_{Sn} = 1 - \frac{Q_{Sn}^{ox}}{Q_{H}^0}$$  \hspace{1cm} (7)$$

Eq. (7) is based on the fact that no reductive adsorption of protons on tin takes place [37–39]. As dihydrogen does not adsorb on tin [36], the spillover of hydrogen from platinum to tin is unlikely. In the bimetallic catalysts, platinum atoms can thus selectively be titrated with hydrogen.

The anodic charge accompanying the electrooxidation of adsorbed tin between 0.5 and 0.9 V vs. RHE can be used as an additional diagnostic tool, the number of moles of tin-atoms being given by:

$$n_{Sn} = \frac{Q_{Sn}^{ox}}{2F}$$  \hspace{1cm} (8)$$

assuming that the electrooxidation of tin is a 2-electron process in this potential region [39]. Whether this is the oxidation of Sn(0) to Sn(II) or of Sn(II) to Sn(IV) is still a matter of debate.
3. Results and discussion

3.1. Characterization of unpromoted catalysts

3.1.1. Comparison between the determination of the platinum particle diameter by CO chemisorption and cyclic voltammetry

Table 1 gives the platinum particle diameter before and after some pretreatments or reactions performed with unpromoted catalysts, as measured by cyclic voltammetry and CO chemisorption. CO chemisorption and cyclic voltammetry give comparable values for the platinum particle diameter. The agreement is satisfactory, especially taking into account that a gas phase technique is compared with a liquid phase technique. Only in the case of the experiments performed at a pH of 13, is the platinum particle diameter as determined by CO chemisorption much larger than that determined by cyclic voltammetry. As pointed out by Scholten et al. [34], poisoning of the platinum surface leads to a too large estimate of the platinum particle diameter. The fact that by cyclic voltammetry a smaller particle diameter is measured means that the adsorbed species cannot desorb in a gas-phase environment, but can be desorbed oxidatively or reductively from the platinum surface in 1 N H₂SO₄, used as electrolyte for cyclic voltammetry. Adsorbed ionic species will in general be desorbed more easily in the liquid phase than in the gas phase. If the CO chemisorption is preceded by oxidative and reductive pretreatments, the poisoning species may be desorbed, but the platinum particle diameter may be altered at the same time. It was verified that the potential cycling during cyclic voltammetry did not lead to a change of the platinum particle diameter for the catalyst used in this work, which was prepared by means of ion-exchange. Hence, cyclic voltammetry provides a more accurate platinum particle diameter than CO pulse chemisorption.

Moreover, as the amount of catalyst needed for the characterization by CO chemisorption is approximately 10 times larger than for the characterization by

<table>
<thead>
<tr>
<th>Reaction/treatment</th>
<th>pH</th>
<th>(d_{Pt}^{CO}) (nm)</th>
<th>(d_{Pt}^{CV}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>2.4</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Oxidation of methyl-(\alpha-)glucopyranoside (a)</td>
<td>8</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Oxidation of ethanol (b)</td>
<td>1</td>
<td>2.7</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Hydrogen treatment (c)</td>
<td>13</td>
<td>9.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

\(a\) 323 K, 100 mol m\(^{-3}\) methyl-\(\alpha-\)glucopyranoside, \(P_{O_2} = 100\) kPa, 25 ks.

\(b\) 298 K, 100 mol m\(^{-3}\) ethanol, \(P_{O_2} = 100\) kPa, 15 ks.

\(c\) 363 K, \(P_{H_2} = 100\) kPa, 54 ks.
cyclic voltammetry, it is only convenient to perform catalyst characterization by CO chemisorption before the start-up and after the shut-down of a reactor. In the following sections, results from the characterization of unpromoted catalysts by cyclic voltammetry at the various stages of the investigated reactions or treatments are given.

3.1.2. Hydrogen treatment in the liquid phase

After the gas phase reduction of the platinum/graphite catalyst with molecular hydrogen at 573 K, the catalyst is stored at ambient conditions until it is used for the liquid phase reaction. It was shown previously that exposure of carbon-supported catalysts to ambient conditions leads to the oxidation of the platinum surface [28,40]. As the alcohol oxidation takes place on zero-valent platinum sites [3], the catalyst is pretreated reductively in the liquid phase before the oxidation reaction is started, as described in the experimental section.

With cyclic voltammetry, the efficiency of the reductive liquid phase pretreatment can be verified. Fig. 3 shows the first cathodic scan of the graphite supported catalyst before and after the standard liquid phase pretreatment. As can be seen from the large cathodic reduction peak at 0.6 V for the catalyst exposed to ambient conditions, the platinum surface is covered by an oxide layer. The charge transferred during the reduction of the platinum oxide is approximately twice the charge transferred during the oxidation of a monolayer of adsorbed hydrogen. According to Eq. (6), this corresponds to a platinum surface covered with a monolayer of oxygen adatoms. The sharp oxidation peak at 0.45 V during the cathodic scan of the catalyst exposed to ambient conditions can be attributed to the oxidation of carbonaceous species on the electrochemi-

![Fig. 3. Cyclic voltammogram of 4.4 wt.-% platinum/graphite exposed to ambient conditions, first scan. Full line: exposed to ambient conditions. Dashed line: after exposure to molecular hydrogen dissolved in water at 363 K during 30 min. Scan rate = 2 mV/s.](image-url)
ally reduced platinum surface. It is thus shown that some poisoning species, e.g. CO, formed during exposure to ambient conditions or during the gas phase reduction at 573 K of the platinum/graphite catalyst, can only be oxidized electrochemically when the platinum is partly reduced.

After the standard liquid phase hydrogen pretreatment, no cathodic reduction peak is observed around 0.6 V, confirming that the platinum oxide is indeed completely reduced as a result of this pretreatment [40]. The absence of the sharp oxidation peak after the standard hydrogen treatment can have two causes. Either the adsorbed species can be desorbed at the reductive conditions, or the adsorbed species cannot be oxidized electrochemically on the completely reduced platinum surface.

In both catalysts samples, the surface area as measured in the first scan is up to 20% lower than in the final scan after electrochemical cycling, indicating that a significant part of the platinum surface is covered by carbonaceous species. These species can be formed upon exposure to ambient conditions, or formed by interaction with the graphite support during the gas phase hydrogen treatment at 573 K.

The absence of oxidized platinum after the liquid phase hydrogen treatment demonstrates that the rather unsophisticated sampling of catalyst slurry by a glass pipette is sufficient to exclude the interference of air, as no reoxidation of the platinum has taken place during the transfer of the reduced sample.

The reductive liquid phase pretreatment was also performed at lower temperatures. The catalyst exposed to ambient conditions is already reduced at 303 K, the reduction being complete after 1 h.

As was reported in an earlier paper [11], a hydrogen treatment at a pH of 13 and 363 K leads to a dramatic decrease of the platinum surface area. This process was now followed in time. Fig. 4 shows the voltammogram, after potential cycling of the platinum catalyst, before and after the hydrogen treatment for 1800 s. As can be seen clearly from the hydrogen area, the surface area of platinum is decreased, combined with a positive shift of the reduction potential of the platinum oxide electrochemically formed at 1.3 V during the anodic scan. The potential at which the platinum oxide is reduced is a function of the particle diameter. The larger the particle diameter, the easier the oxides of the particles are reduced, corresponding to a more positive reduction potential [41,42].

After 54 ks this effect of hydrogen treatment is even more pronounced. Fig. 5 shows the cyclic voltammogram of the platinum catalyst after 54 ks hydrogen treatment. In the first scan, no platinum surface area is measured at all. After the hydrogen treatment for 54 ks, the catalyst activity was tested for the oxidation of methyl-α-D-glucopyranoside at 323 K and a pH of 8. No oxidation activity was measured during 1 h, meaning that the platinum surface is covered by species that cannot be removed by molecular oxygen at 323 K. It is clear that in this case the platinum surface area as measured in the first scan is the most
representative for the activity of the catalyst, whereas the voltammogram after potential cycling gives information on the platinum particle diameter $d_{pt}$. The platinum particle diameter and the degree of coverage of the platinum by carbonaceous species is given as a function of time in Fig. 6. In the first 1800 s, both the platinum particle size and the degree of coverage by carbonaceous species increase with 50%, which is an indication that the two processes are coupled. This coupling of particle growth and site coverage can be explained by the platinum particle mobility which was reported by Vleeming et al. [43]. It can
be imagined that carbon from the graphite support accumulates on the platinum surface while the platinum particle is moving across the graphite surface.

Note that sintering of platinum i.e. migration of platinum particles occurs at a much lower temperature in liquid phase than in gas phase. Therefore, migration in liquid phase certainly will be solvent and solute assisted.

CO chemisorption gives a $F_{E}^{CO}$ of 0.04 after the hydrogen treatment during 54 ks, which according to Eq. (2) corresponds to a platinum particle diameter amounting to 31 nm. The combination of site coverage with particle growth, as revealed by cyclic voltammetry, is thus masked by the measurement of exposed platinum atoms by a gas phase chemisorption technique. Combination of CO chemisorption with TEM [11] is required to conclude that the small fraction of exposed platinum atoms as measured by CO chemisorption is caused by both particle growth and formation of carbonaceous deposits.

3.1.3. Active platinum surface area during the oxidation of methyl-α-D-glucopyranoside

The oxidation rate of methyl-α-D-glucopyranoside at a pH of 10.5 versus time is shown in the upper part of Fig. 7. As can be seen, the reaction rate rapidly decreases during reaction. This was shown previously to be the result of over-oxidation [6]. The reactivity of methyl-α-D-glucopyranoside is too low to keep the catalyst in the reduced state in an oxygen saturated solution. Only upon switching the gas feed from oxygen to nitrogen can the catalyst be reduced by the carbohydrate. Between run 1 and run 2 the catalyst was exposed to the reaction medium without oxygen for 16 h. The regeneration of the catalyst was only partial, the initial reaction rate of the second run being circa 30% lower than the initial reaction rate of the first run. The fact that the catalyst can be
regenerated partially by switching off the oxygen feed indicates that the decrease of the reaction rate during reaction is mainly the consequence of over-oxidation and not the cause of the latter [3]. If over-oxidation would be caused by catalyst deactivation by site coverage, switching off the oxygen feed would only enhance the coverage by organic species, and would thus lead to an even lower reaction rate.

The lower part of Fig. 7 shows the platinum particle diameter and the degree of coverage by carbonaceous species at different stages, i.e. before and after the reductive pretreatment, during reaction and after the regeneration in N₂.

The degree of coverage by carbonaceous species increases at each reductive treatment, i.e. during the reductive pretreatment with molecular hydrogen and during the overnight exposure to the nitrogen saturated reaction mixture. The overnight exposure results in an increase of the coverage by carbonaceous species by 30% compared to the coverage at the beginning of run 1. As the initial reaction rate in run 2 is 30% lower than the reaction rate of run 1, coverage of surface platinum atoms by carbonaceous species apparently makes them unavailable for the oxidation of methyl-\(\alpha\)-D-glucopyranoside. During the
oxidative conditions in run 2, part of the carbonaceous deposits are oxidized resulting in a lower degree of coverage by carbonaceous species at the end of run 2.

The platinum particle diameter can be regarded as being constant within the experimental error during the standard pretreatment and the oxidation of methyl-\(\alpha\)-D-glucopyranoside. Only the overnight exposure to the nitrogen saturated reaction mixture results in a significant increase of the platinum particle diameter amounting to 15% compared to that at the beginning of run I.

Similar experiments were performed at a pH of 8. The same phenomena were observed, but to a so low extent that the initial reaction rate could be restored within the experimental error by overnight exposure to the nitrogen saturated reaction mixture and subsequent feed of oxygen gas.

It can thus be stated that the catalyst deactivation during the oxidation of methyl-\(\alpha\)-D-glucopyranoside is not caused by either growth of the platinum particles nor an increase of the degree of coverage by carbonaceous species. Only the exposure to the reaction medium without oxygen leads to an increase of the platinum particle diameter and an increase of the degree of coverage by carbonaceous species. It must be concluded that reductive rather than oxidative conditions lead to a loss of the active platinum surface area of the catalyst. This is in agreement with gas phase literature.

The increase of the platinum particle diameter in a gaseous hydrogen atmosphere has been reported for Pt/Al\(_2\)O\(_3\) [44,45] and Pt/C [46]. The growth rate of the platinum particle diameter in vacuum was found to be larger for Pt/C than for Pt/SiO\(_2\) and Pt/Al\(_2\)O\(_3\) [47]. In liquid phase environments, the mobility of the platinum particles in Pt/C catalysts was found to be much larger than in gas phase environment, the liquid phase facilitating the transfer of platinum atoms from the platinum surface to the carbon support [48].

3.2. Characterization of tin-promoted catalysts

3.2.1. Interaction of tin with non-supported platinum

Fig. 8 shows a cyclic voltammogram of a platinized platinum electrode on which SnSO\(_4\) is deposited in the same way as the graphite supported platinum catalysts are promoted. The absence of the support makes the interpretation of the cyclic voltammogram easier.

The degree of coverage of platinum by tin, as calculated from Eq. (7), amounted to 0.74. The tin-atoms adsorbed are oxidized in two stages, one between 0.5 and 0.9 V, and the other above 1 V, where the platinum surface itself is also oxidized. The oxidation of Sn at potentials above 1 V is not displayed as a peak in the cyclic voltammogram, but from the change in the reduction of the platinum oxide in the cathodic scan, it can be clearly seen that platinum atoms which are covered by tin are not oxidized in the same way as uncovered platinum, and that the oxidation current in the anodic region is
Fig. 8. Voltammogram of platinized platinum, 0.1 N HClO₄ at 298 K. Full line: before deposition of tin. Dashed line: after deposition of tin. Degree of coverage of platinum by tin, Eq. (7), amounts to 0.74. Scan rate = 5 mV/s.

mainly determined by the oxidation of tin and not by the oxidation of platinum itself.

Metals can be reductively adsorbed on the platinum surface at potentials which can be 0.4 to 0.8 V higher than the potential as calculated from Nernst’s law [49], a phenomenon called ‘under potential deposition’ [50]. Hence, the standard potentials of the redox-couples of Sn/Sn²⁺ and Sn²⁺/Sn⁴⁺, amounting to −0.136 and 0.151 V [51], are not very helpful for the interpretation of the cyclic voltammogram. As tin can exist in three valency states, (0), (II) and (IV), it can be concluded that tin adsorbed on a platinum foil is in the zero-valent state at potentials below 0.5 V, in the (II) state between 0.5 and 1 V and in the (IV) state above 1 V. The oxidation state of tin after deposition from a SnSO₄ solution saturated with molecular hydrogen, is thus (0). This means that Sn²⁺ is reduced to zero-valent tin by molecular hydrogen, which corresponds to a deposition potential of 0 V vs. RHE. The formation of zero-valent tin at a deposition potential of 0 V is also measured by Lamy-Pitara et al. [39]. Bowles and Cranshaw demonstrated the formation of metallic tin on platinized platinum at a deposition potential of 0.1 V by Mössbauer Spectroscopy [52]. Even at 0.48 V the majority of the tin was measured to be in the metallic state.

Combination of Eq. (7), Eq. (8) and the total number of surface platinum atoms gives the adsorption stoichiometry of tin on platinum. In the unsupported tin/platinum catalyst the Sn:Pt stoichiometry amounts to 1:2, which is a well accepted value [38,39,53].

The tin-coverage remained unchanged upon cycling between 0 and 1 V, meaning that the Sn(II) adspecies, which are formed at 0.5 V, are stable. Cycling up to 1.3 V leads to a decrease of the tin-coverage, indicating that Sn(IV) which is formed above 1 V can be dissolved. The interaction between
the platinum surface with the Sn(0) and Sn(II) adspecies is thus strong enough to prevent desorption of these adspecies, whereas the interaction of Sn(IV) with platinum is too low to prevent its desorption at high potentials. This is in agreement with the much higher solubility of Sn(IV) species compared to Sn(II) species [54], which in general will lead to a stronger adsorption of Sn(II) than of Sn(IV) on platinum [55].

3.2.2. Interaction of tin with graphite supported platinum

3.2.2.1. Freshly prepared. Fig. 9 shows the cyclic voltammogram of a graphite supported platinum catalyst before and after the deposition of SnSO₄. The characterization scans of both the unpromoted and the promoted catalysts were started at 0.9 V in cathodic direction, in order to determine the degree of platinum coverage by tin. The presence of the graphite support makes the interpretation of the voltammogram of the supported tin/platinum less unambiguous than that of the unsupported tin/platinum catalyst. Especially the oxidation of tin at potentials higher than 1 V cannot be separated from the oxidation of both the platinum surface and the graphite support. Characterization of tin deposited on the platinum-free support pointed out that these tin-atoms do not take part in the electrochemical process, the cyclic voltammogram of tin/graphite being indistinguishable from the cyclic voltammogram of graphite without tin. Apparently the tin that is adsorbed on the graphite cannot be oxidized or reduced within the potential range of the voltammogram. The charge transferred by the oxidation of tin thus gives an indication on the amount of tin adsorbed on platinum. The amount of tin as determined by chemical analysis gives the amount of tin on both the graphite and the platinum surface. Compari-
son of these two amounts gives the ratio of tin adsorbed on platinum and on the support. In the freshly prepared catalyst only 20% of the total tin content is adsorbed on the platinum surface. The number of platinum atoms on which hydrogen can be adsorbed is clearly diminished after the deposition of SnSO₄. In the cathodic scan an extra reduction is measured at 0.5 V, which can be related to the reduction of oxidized tin adatoms. In the anodic scan the corresponding oxidation occurs at 0.7 V. In contrast to the unsupported tin/platinum catalyst, tin can be desorbed at potentials lower than 0.9 V. It is assumed that the oxidation of tin above 0.5 V, as in the case of unsupported tin/platinum, is a 2-electron process. Based on the desorption of tin below 0.9 V, it cannot be excluded that the oxidation of tin above 0.5 V represents a Sn(II) to Sn(IV) transition instead of a Sn(0) to Sn(II) transition, as is the case in the unsupported tin/platinum catalyst. The desorption of tin below 0.9 V was measured to be too slow to influence the degree of platinum coverage by tin as measured in the first scan.

The Sn:Pt stoichiometry in the graphite supported tin/platinum catalyst was determined in the same way as for the unsupported platinum. For the tin/platinum/graphite catalyst it is calculated to amount to 1:2, as in the case of unsupported tin/platinum. Eq. (7) can only be applied in the absence of organic reactants. In the presence of organic reactants the amount of hydrogen adsorbed on platinum can be diminished by carbonaceous deposits, as has been shown in the preceding sections. The electrochemical oxidation of carbonaceous deposits was found to take place at higher potentials than the oxidation of tin adatoms. Hence the degree of coverage of platinum by tin adatoms can be determined most reliably from the anodic charge transfer accompanying the oxidation of tin adatoms at 0.7 V, i.e. by using Eq. (9) rather than Eq. (7):

\[
\theta_{Sn} = \frac{Q_{Sn}^{ox}}{Q_{H}^{0}}
\]

Eq. (9) follows from Eq. (8) by using the Sn:Pt stoichiometry of 1:2. All reported values of the degree of coverage of platinum by tin are calculated by Eq. (9).

3.2.2.2. Stability of tin-promoted catalysts during reaction. When using promoted platinum catalysts, it has to be kept in mind that most promoter metals are less noble than the platinum itself. Therefore, the possibility of dissolving the promoter metal during reaction is realistic.

The influence of oxygen in water with the absence of an organic reactant was studied first. The degree of coverage of platinum by tin atoms as obtained by cyclic voltammetry from Eq. (9) decreases from 0.60 to 0.41 after 5 h in water at 323 K, at a pH of 7 and an oxygen partial pressure of 100 kPa. The tin content of the catalyst decreased from 3.5 wt.-% to 2.7 wt.-%. Taking into
account the stability of Sn(0) and Sn(II) on the platinum surface, it can be concluded that tin is transformed to the Sn(IV) state in an oxygen saturated solution.

During reaction, i.e. in the presence of an organic reactant, the same effect can be expected as in the solution saturated with pure oxygen, except that the oxidative conditions are somewhat milder. The stability of the adsorbed tin was investigated during the oxidation of methyl-α-D-glucopyranoside, ethanol and ethylene glycol.

The degree of platinum coverage by tin as determined by cyclic voltammetry is given for the oxidation of methyl-α-D-glucopyranoside in Table 2 during various stages, i.e. after promotion, during reaction and after washing the catalyst. The degree of coverage of platinum by tin as measured by CO chemisorption can be calculated from Eq. (3). Deposition of carbonaceous species which was shown in the preceding sections to take place during reaction, leads to an overestimation of degree of platinum coverage by tin as calculated from Eq. (3). The specific determination of the tin-coverage by voltammetry is more reliable.

During the oxidation of methyl-α-D-glucopyranoside, the degree of platinum coverage by tin shows a sharp increase rather than a decrease during the first oxidative run, from 0.40 to 0.72. Apparently tin from the graphite support, which comprises 80% of the tin content of the catalyst, is deposited on the platinum surface. During reaction tin ions, adsorbed on the graphite support in the freshly prepared catalyst, are desorbed under the influence of oxygen. The dehydrogenation of methyl-α-D-glucopyranoside molecules on the platinum surface provides a source of hydrogen atoms, capable of reducing the tin ions which are desorbed from the graphite support on the platinum surface.

After the first oxidative run the reaction mixture was pumped off and the catalyst was washed at the reaction temperature with Millipore water at an oxygen partial pressure of 100 kPa. This led to a decrease of the degree of platinum coverage by tin from 0.72 to 0.09 and to a decrease of the tin content of the catalyst from 1.5 wt.-% to 0.9 wt.-%, indicating a large loss of tin during oxidative conditions in the absence of an organic reactant. During the second oxidative run, the degree of platinum coverage by tin can be regarded as being
constant. As the amount of tin on the graphite support is still in the order of 0.9 wt.-%, this means that only a small fraction of the tin on the graphite support can be deposited on the platinum surface, possibly those tin atoms that are in the direct vicinity of a platinum particle.

The oxidation rate of methyl-α-D-glucopyranoside during run I and run II is shown in Fig. 10, together with the oxidation rate without the addition of tin. As can be seen, the degree of platinum coverage by tin has a large negative influence on the oxidation rate. After the washing of the catalyst between run I and II, the degree of platinum coverage by tin decreased from 0.72 to 0.09, leading to an initial oxidation rate in run II which is almost a factor 10 higher than that in run I.

The effects during the oxidation of ethanol were similar to those observed during the oxidation of methyl-α-D-glucopyranoside. During the oxidation of ethylene glycol however, the coverage by tin as measured by voltammetry decreased to zero, while the tin content of the catalyst decreased from 0.7 wt.-% to 0.2 wt.-%. As the conversion of ethylene glycol to sodium glycolate was high, this glycolate possibly acted as a tin-complexing agent.

An alternative explanation for the increase of the degree of platinum coverage by tin observed during the first oxidative run of methyl-α-D-glucopyranoside and ethanol oxidation is the spreading of multilayer tin islands towards submonolayer tin, leading to an increased coverage of the platinum surface by tin. However, oxidation on unsupported tin/platinum did not lead to an increase of the tin coverage. Moreover, all tin layers adsorbed on platinum do contribute to the electrochemical signal. In the supported tin/platinum catalysts no multilayers of tin existed at the start of the oxidation of alcohol.
4. Conclusions

The application of voltammetry on graphite supported platinum catalysts allows the quantitative determination of both the platinum particle diameter and the degree of platinum coverage by carbonaceous species during liquid phase reactions. It renders at least the same information as the combination of CO chemisorption and TEM. As the characterization can be performed at different stages of reaction and regeneration, a better insight in the deactivation process can be obtained. The characterization can be regarded as an in-situ technique, as no transfer of the catalyst from the liquid phase to the gas phase is needed.

During the oxidation of methyl-α-D-glucopyranoside an increase of the platinum particle diameter occurs only during reductive treatments. This increase of the platinum particle diameter is accompanied by an increase of the coverage of the platinum surface by carbonaceous species. Under oxidizing conditions, the adsorbed carbonaceous species are only partially removed from the platinum surface.

The characterization of tin/platinum/graphite catalysts by voltammetry gives specific information on the tin adsorbed on platinum. Under reaction conditions the coverage of the platinum surface by tin-atoms changes with respect to the tin-coverage in the freshly promoted catalysts. The in-situ characterization of promoted catalysts is thus essential for a meaningful relation between coverage by promoter metal and catalyst activity.

5. Notation

5.1. Roman symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{pt}$</td>
<td>platinum particle diameter</td>
<td>nm</td>
</tr>
<tr>
<td>$E$</td>
<td>electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$FE$</td>
<td>fraction of exposed platinum atoms</td>
<td>–</td>
</tr>
<tr>
<td>$I$</td>
<td>current</td>
<td>A</td>
</tr>
<tr>
<td>$M_{Pt}$</td>
<td>molar mass of platinum</td>
<td>g/mol</td>
</tr>
<tr>
<td>$n$</td>
<td>number of moles</td>
<td>–</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$Q$</td>
<td>charge transferred</td>
<td>C</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$V_{CO}$</td>
<td>volume of adsorbed CO</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$W_{cat}$</td>
<td>mass of catalyst</td>
<td>g</td>
</tr>
<tr>
<td>$w_{Pt}$</td>
<td>weight fraction of platinum in catalyst</td>
<td>–</td>
</tr>
</tbody>
</table>
5.2. Greek symbols

\( \Theta \)  
degree of platinum coverage

5.3. Subscripts

0  
before tin-deposition

C  
carbonaceous species

H  
hydrogen atom

O  
oxide

ox  
oxidation

Sn  
tin, after tin deposition

CO  
as determined by CO chemisorption

5.4. Superscripts

1  
first scan in cyclic voltammetry

CO  
as determined by CO pulse chemisorption

CV  
as determined by cyclic voltammetry

F  
final scan in cyclic voltammetry

Sn  
after tin-deposition

References