Selective oxidation of methyl alpha-D-glucoside on carbon supported platinum III. Catalyst deactivation

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Selective oxidation of methyl α -D-glucoside on carbon supported platinum

III. Catalyst deactivation

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Abstract

Platinum supported on activated carbon and platinum supported on graphite were characterized before, during and after oxidation of methyl α -D-glucoside in water. Ex situ information was obtained by X-ray photoelectron spectroscopy, cyclic voltammetry, scanning transmission electron microscopy and carbon monoxide chemisorption. In situ information was obtained by cyclic voltammetry. Furthermore, the open circuit potential of a platinized platinum foil was monitored during reaction. A distinction could be made between a reversible deactivation, occurring on a time scale of 10 ks and an irreversible deactivation, occurring on a time scale of 100 ks. The reversible deactivation is attributed to a slowly increasing oxygen surface coverage rather than to the formation of platinum oxide. Chemisorption takes place beyond the steady-state degree of oxygen coverage expected from the intrinsic initial reaction kinetics and causes a reversible decrease of the reaction rate. The irreversible deactivation is caused by the dissolution and subsequent redeposition of platinum. The preferential dissolution of small platinum particles and redeposition on larger ones leads to a decrease of the fraction of exposed platinum atoms from 0.7 to 0.5. The effect of the irreversible decrease of the platinum surface area on the specific reaction rate is strongly attenuated by an antipathetic structure sensitivity. An increase of the average platinum particle diameter results in an increase of the turnover frequency.

Keywords: characterisation, deactivation, dissolution, glucoside, oxidation, platinum, redeposition.

INTRODUCTION

In previous papers [1,2], dealing with the kinetics of the oxidation of methyl α -D-glucoside (MGSD) on supported platinum, catalyst deactivation was reported.

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Several causes of deactivation of supported platinum applied in the liquid phase have been put forward: the oxidation of platinum [3-5], the blocking of active sites by carbonaceous deposits [6] and the growth of platinum crystallites [7,8].

The interaction between gaseous dioxygen and supported platinum crystallites has been studied intensively. Ratnasamy et al. [9] examined the oxidation of supported platinum catalysts by ambient air and found that an average platinum particle consists of 2 outer layers of platinum perturbed by the introduction of oxygen atoms in a 1:1 O-Pt ratio and of a core of unperturbed platinum. McCabe et al. [10] found that the oxidation of platinum by gaseous oxygen at 573 K was passivating, and limited to the first layer. This passivation was independent of the crystallite size. There is no full consensus in the literature on the stoichiometry of the platinum oxide layers nor on the nature of the interaction between oxygen and platinum.

The interaction between oxygen and platinum in water has hardly been studied, except in the context of the electrochemical oxidation of platinum [11,12]. It follows from the Pourbaix diagram of platinum [13] that at atmospheric oxygen pressure and 298 K, PtO_2 is the thermodynamically stable form in neutral saturated water. In alkaline aqueous solutions the formation of platinates, PtO_3^{2-} , is thermodynamically favoured.

During the electrochemical oxidation of small organic molecules, such as methanol, carbonaceous deposits were found to deactivate the platinum catalyst [6,14]. The electrode poisoning during the electrochemical oxidation of methanol in acid solutions is attributed to chemisorbed carbon monoxide species which are believed to be formed via the intermediate formyl. In alkaline solutions, however, electrode poisoning does not occur according to Beden et al. [15].

Sintering being a thermal process starting at temperatures above the Tamman temperature, i.e. above 600 K for platinum, does not seem to play a part in the deactivation of the platinum catalyst during oxidation of methyl α -D-glucoside. Several studies, however, indicate that recrystallisation processes are enhanced in the presence of a liquid [7,8]. In electrocatalysis dissolution of small particles and redeposition on larger ones is a well-known phenomenon, often referred to as Ostwald ripening [16]. The solvated ionic platinum species are transferred through the solution.

The aim of the present study is to obtain insight into the mechanism of the deactivation of supported platinum during the oxidation of polyalcohols by molecular oxygen in water. Platinum supported on activated carbon and platinum supported on graphite were characterized by X-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM), carbon monoxide chemisorption and cyclic voltammetry before and after reaction. Furthermore, in situ information was obtained by electrochemical techniques. In order to correlate the extent of the deactivation with the information from

the surface sensitive techniques, the activity of the catalysts for the oxidation of methyl α -D-glucoside to sodium 1-O-methyl α -D-glucuronate was measured before, during and after reaction.

Both platinum supported on activated carbon and platinum supported on graphite were used in this study. No dependence of the deactivation on the type of carbon support was observed. Hence, the following sections present only the results obtained with platinum supported on graphite.

EXPERIMENTAL

Catalyst

Platinum supported on high specific area graphite was prepared according to the method of Richard and Gallezot [17].

The starting materials consisted of graphite (Johnson Matthey, CH10213) with a BET surface area of $3.12 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ and a solution of tetrammine platinum hydroxide, $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ (Johnson Matthey). The graphite was activated by partial combustion in flowing air ($5 \times 10^{-3} \text{ N l s}^{-1}$) at 773 K for 5 h. Under these conditions 25% of the graphite was burned off. This was followed by stirring a suspension of this graphite in a solution of concentrated sodium hypochlorite (Janssen) for 24 h at room temperature.

A total of 100 g of a solution of tetrammine platinum hydroxide containing 8 wt-% Pt^{2+} was added dropwise to a suspension of 40 g graphite in 800 ml of a 1000 mol m^{-3} ammonia solution (Merck). Hereafter, the suspension was stirred for 25 h at room temperature and filtered on a Millipore filter of the HV type with a pore size of $0.45 \mu\text{m}$. The solids were washed with distilled water and dried at 373 K and 5 kPa. Reduction was performed by heating in flowing hydrogen (5 N ml s^{-1}) for 2 h at 573 K. The catalyst was stored after cooling. No special precautions to avoid air contact were taken.

After preparation the BET surface area was decreased to $1.17 \times 10^5 \text{ m}^2 \text{ kg}_{\text{cat}}^{-1}$. The total pore volume amounts to $1.05 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$, as determined by mercury porosimetry, applying pressures upto 200 MPa.

EQUIPMENT AND PROCEDURES

Start-up, reaction and regeneration

Unless specified otherwise, the oxidation reactions were carried out in the continuous three-phase agitated tank reactor as described previously [1]. Before reaction the catalyst was reduced with hydrogen in water at 363 K for one hour. Then, the water was removed while the reactor was purged with nitrogen and cooled down to reaction temperature. The reactor was filled with a nitrogen-purged solution containing an appropriate amount of methyl α -D-glucoside.

side and sodium 1-*O*-methyl α -D-glucuronate. To start an experiment, the nitrogen stream was replaced by an oxygen/nitrogen mixture and the stirrer was switched on. If a series of successive oxidations was performed with the same catalyst, a regeneration was applied in between at the temperature of the previous experiment, which consisted of changing the flow of oxygen to nitrogen for 10 min and purging with hydrogen for 10 min. Before the oxygen flow was restored, the reaction mixture was purged with nitrogen for another 10 min. At the end of an experiment the reaction mixture was removed through the membrane filter, leaving the catalyst in the reactor under the gas atmosphere applied during the reaction. Thereafter the catalyst was washed with water.

Besides the freshly prepared catalyst the following samples are examined: (1) after reduction with gaseous hydrogen at 473 K for 1 h; (2) after exposure to ambient air for 200 h; (3) after reduction in water with dihydrogen at 363 K for 1 h and subsequent immersion in an aqueous solution of methyl α -D-glucoside (MGSD); (4) after five successive oxidations at $C_{\text{MGSD}} = 200 \text{ mol m}^{-3}$, $p_{\text{O}_2} = 1.0 \times 10^5 \text{ Pa}$, $\text{pH} = 9$, $T = 323 \text{ K}$ and $X = 0.04$.

Sample transfer

After reaction or reduction the catalyst samples were washed with water and dried at 333 K and 5 kPa overnight. No special precautions were taken to prevent air contact, except for some of the catalyst samples which were transferred in a wet state to the cyclic voltammetry electrode. In the latter case oxygen diffusion through the water layer around the catalyst was calculated to be slow enough to avoid oxidation of the platinum particles.

In one case a catalyst sample was reduced in a glove box with gaseous hydrogen at 473 K and transferred under nitrogen into the XPS apparatus by means of a special insertion lock. This sample will be referred to as reduced in situ.

Determination of the platinum content

In a solution of excess chlorine ions platinum, with SnCl_2 present, forms a yellow stable complex with an absorption maximum at 403 nm [18,19]. To determine the platinum content of a catalyst the platinum metal is dissolved in aqua regia containing sodium chloride, followed by the formation of a complex of the platinum ions with SnCl_2 . In order to determine the extent of dissolution of platinum during reaction, three samples of 50 ml were filtered from the reaction mixture. To the first sample 12.5 ml of a solution of 12 mol m^{-3} HCl, 3.5 g NaCl and 20 ml of a solution of 1.27 mol m^{-3} SnCl_2 were added and made up to 100 ml. An additional and known amount of Pt^{4+} was added to the above for the second sample. An internal calibration method was used because some oxidation products, in particular sodium oxalate, interfered with the de-

termination of platinum ions. The third sample was used as a blank, to correct for the colour of the reaction mixture, by following the above procedure except for the addition of SnCl_2 .

XPS

The XPS spectra were obtained with a monochromatic spectrometer (VG Escalab 200) using $\text{Al K}\alpha$ as the excitation source and a hemispherical analyzer.

Dried catalyst powder was pressed into an indium template and mounted on a tantalum sample holder. The C 1s signal was used as internal reference and set at a value of 284.4 eV. The spectra were taken at a pass energy of 20 eV.

STEM

The micrographs were obtained with a Jeol 2000 CX microscope. An accelerating potential of 200 kV was used. The catalysts were examined in the conventional bright field detection mode.

The samples were ultrasonically dispersed in water and the suspension was collected on coated copper grids. Perforated lacey grids delivered by Biorad were used.

The following definition was used for the average particle diameter:

$$\overline{d_{\text{Pt}}} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

This equation gives the surface area average diameter which is also obtained from the carbon monoxide chemisorption data [20].

Carbon monoxide chemisorption

The carbon monoxide pulse chemisorption was performed in a Quantachrome Quantasorb. Hydrogen was used as carrier gas. A prereduction was performed with hydrogen at 293 K overnight. The platinum surface area was determined from the amount of chemisorbed carbon monoxide assuming a 1:1 stoichiometry [21]. The relation between the fraction of platinum atoms exposed (FE), and the surface area average diameter, assuming 1.42×10^{19} platinum atoms per square meter, is given by Scholten et al. [21]:

$$\overline{d_{\text{Pt}}} = \frac{1.3 \times 10^{-9}}{\text{FE}} \quad (2)$$

Ex situ cyclic voltammetry

From ex situ cyclic voltammetry information can be obtained about the platinum surface area, the oxidation state of platinum and the presence of adsorbates. Cyclic voltammetry analysis was performed with the catalyst as the working electrode and Hg/HgO as a reference electrode ($E = +0.96$ V versus the reversible hydrogen electrode). In the present study the electric potentials are reported with respect to the reversible hydrogen electrode. A platinum foil was used as an auxiliary electrode. The working electrode consisted of the catalyst powder using Teflon as a binder. The procedure for the preparation of this electrode is described in detail by de Bruijn et al. [22]. All cyclic voltammetry characterization studies were carried out at 298 K in an aqueous solution of 1000 mol m^{-3} NaOH as the electrolyte. De Bruijn et al. [22] also describe the two different procedures which were applied depending on whether the aim was to detect the presence of platinum oxides or to determine the platinum surface area.

In situ electrochemical methods

The in situ characterization of supported platinum, was carried out in an electrochemical cell, in which a semi-batch oxidation of methyl α -D-glucoside was performed. The electrochemical cell was constructed of glass and had a volume of 40 ml and a thermostat with an accuracy of less than 0.1 K was used. The cell could be purged with a gas of choice. The catalyst was pressed on the electrode which was covered with a layer of Leit C paste (Neubauer Chemikalien). In this way a long-term stable electrode was obtained. Analogous procedures to those for the ex situ cyclic voltammetry were applied to detect the presence of adsorbates and to determine the platinum surface area [22].

The reaction conditions were comparable to those applied in the three-phase agitated tank reactor. In order to obtain sufficient conductance of the solution, a pH of 12 was applied and NaClO_4 was added. It was shown in separate experiments that NaClO_4 had no significant influence on the oxidation of methyl α -D-glucoside. In contrast to the reactions carried out in the three-phase agitated tank reactor, the pH was not kept constant during the experiments. The conversion was limited to 2% and did not lead to a decrease of the pH below 11.

Open circuit potential measurements were performed on a platinized platinum foil. The platinum foil, with a geometric surface area of $6 \times 10^{-4} \text{ m}^2$, was immersed in a solution of platinum hexachloric acid while applying a cathodic current of 100 A m^{-2} leading to the deposition of small platinum particles on the platinum foil. In this way a platinum surface area of 1.7 m^2 was obtained as determined by the anodic oxidation of hydrogen atoms. This corresponds to platinum particles with diameters between 15 and 20 nm [23,24]. The use of

a platinized platinum foil is the best compromise between a good measurement of the open circuit potential and a platinum surface similar to that of platinum supported on graphite. It must be kept in mind, however, that oxygen chemisorption in particular, is stronger on small platinum particles than on larger ones [25,26].

RESULTS

Specific reaction rate versus time

Fig. 1 shows the specific reaction rate versus time during five successive oxidations of methyl α -D-glucoside. The discontinuities correspond to regenerations.

The reaction rate decreases rapidly during an experiment and is restored only partially after regeneration with hydrogen. Fig. 1 shows that a distinction can be made between a reversible decrease of the reaction rate, i.e. a deactivation which is restored after regeneration with hydrogen and an irreversible decrease. The extent of the reversible deactivation can be represented by the ratio of the specific reaction rate to the reaction rate observed immediately after regeneration, $R_{W,R}^0$. The extent of the irreversible deactivation can be represented by the ratio of the reaction rate immediately after regeneration to the initial reaction rate on a freshly reduced catalyst, R_W^0 . The reversible deac-

Fig. 1. Specific reaction rate versus time. Continuous flow experiment (cf. ref. 1). Reaction conditions: $C_{\text{MGSD}} = 200 \text{ mol m}^{-3}$, $p_{\text{O}_2} = 1.0 \times 10^5 \text{ Pa}$, $\text{pH} = 9$, $T = 323 \text{ K}$, $X = 0.04$.

Fig. 2. Extent of reversible deactivation. Relative specific reaction rate versus time. Conditions: see Fig. 1.

tivation occurs on a time scale of 10 ks and the irreversible deactivation on a time scale of 100 ks. Fig. 2 shows the extent of the reversible deactivation based upon the five deactivation curves presented in Fig. 1. The coincidence of the five curves shown in Fig. 2, indicates that the reversible deactivation occurs at a relative rate which is independent of the number of regenerations. The curvature indicates a second-order process. It was observed that the reaction rate was restored to the same level by substitution of hydrogen by nitrogen in the regeneration procedure. Apparently, the regeneration of the catalyst by methyl α -D-glucoside is possible as soon as oxygen is excluded.

Effect of the reaction conditions on the deactivation

Fig. 3 shows that the reversible catalyst deactivation strongly depends on the oxygen partial pressure. A higher oxygen partial pressure results in an increase of the reversible deactivation rate.

Fig. 4 shows the extent of the irreversible deactivation versus the amount of sodium 1-*O*-methyl α -D-glucuronate produced per kg of catalyst for different applied reaction conditions. No correlation was observed between the extent of irreversible deactivation and the time of reaction nor with the concentration of sodium 1-*O*-methyl α -D-glucuronate nor with the amount of liquid passed through the reactor. Fig. 4 also shows that the extent of irreversible deactivation decreases with decreasing pH.

Fig. 3. Extent of the reversible deactivation versus time for different oxygen partial pressures. Reaction conditions: $C_{\text{MGSD}}=200 \text{ mol m}^{-3}$, $\text{pH}=9$, $T=323 \text{ K}$, $X=0.04$, $C_{\text{cat}}=1.8 \text{ kg m}^{-3}$ and ($\square$) $p_{\text{O}_2}=1.0 \times 10^3 \text{ Pa}$, ($\circ$) $p_{\text{O}_2}=1.0 \times 10^4 \text{ Pa}$, ($\triangle$) $p_{\text{O}_2}=1.0 \times 10^5 \text{ Pa}$.

Fig. 4. Extent of irreversible deactivation versus the amount of sodium 1-*O*-methyl α -D-glucosiduronate produced per kg of catalyst. Reaction conditions: ($\circ$) ($C_{\text{MGSD}}=200 \text{ mol m}^{-3}$, $p_{\text{O}_2}=1.0 \times 10^5 \text{ Pa}$, $\text{pH}=9$, $T=323 \text{ K}$, $X=0.04$, $C_{\text{cat}}=1.8 \text{ kg m}^{-3}$) ($\triangle$) idem except $X=0.08$, (∇) idem except $C_{\text{cat}}=1.0 \text{ kg m}^{-3}$, ($\square$) idem except $p_{\text{O}_2}=1.0 \times 10^3 \text{ Pa}$, ($\diamond$) idem except $C_{\text{MGSD}}=100 \text{ mol m}^{-3}$, ($\bullet$) idem except $\text{pH}=7$.

Platinum content

The platinum content of the catalyst as prepared amounted to 4.9 wt-%. The platinum content of the catalyst after five oxidations was decreased to 4.7 wt-%.

A platinum ion concentration in the range of 10–20 mmol m^{-3} was found

after batchwise oxidation of methyl α -D-glucoside at various reaction conditions. Re-use of the catalyst resulted in a new loss of platinum.

STEM and carbon monoxide chemisorption

The platinum particle diameter distributions, based upon micrographs, are shown in Fig. 5. The average diameter of the platinum particles on the catalyst as-prepared amounts to 1.85 nm which is in good agreement with that of the catalyst examined by Richard and Gallezot [17].

The particle diameter distribution of the catalyst after five successive oxidations is also shown in Fig. 5 and indicates the appearance of larger particles at the expense of the smallest platinum particles. The fraction of platinum atoms exposed obtained by carbon monoxide chemisorption and from the micrographs are listed in Table 1.

XPS

XPS spectra of the investigated catalyst samples have been reported by de Bruijn et al. [22]. No significant shift of the binding energies of the Pt 4f

Fig. 5. Platinum particle diameter distribution: (1) as prepared, (2) after 5 successive oxidations.

TABLE 1

Fraction of platinum atoms exposed of the catalyst samples investigated as obtained by STEM and CO chemisorption

Catalyst sample	STEM	CO chemisorption
As prepared	0.70	0.75
After 5 successive oxidations	0.53	0.54

electrons after exposure to ambient air was observed with respect to the binding energy of in situ reduced platinum. In the case of platinum supported on carbon, the O 1s core level cannot be used for the identification of chemisorbed oxygen because the O 1s electrons originating from chemisorbed oxygen and from oxygen present in the functional groups at the surface of the carbon support have similar binding energies [27,28]. Hence, it was not possible to clarify the presence or absence of chemisorbed oxygen on the catalyst by using XPS.

To verify whether it is at all possible to observe highly dispersed platinum oxides by XPS, spectra were collected of a non-prereduced platinum supported on activated carbon (Degussa F196 N/W) and of platinum supported on graphite, oxidized electrochemically at a potential of 1.5 V for 15 min. The latter procedure was reported to result in a platinum oxide of a few monolayers thickness [29]. The spectra of these samples could be distinguished easily from the previously obtained spectra of the catalysts. The binding energy of the doublet of the Pt 4f electrons of the non-prereduced platinum supported on activated carbon was 1 eV higher than the binding energy for platinum reduced in situ. The Pt 4f XPS spectrum of the electrochemical oxidized platinum supported on graphite showed a broad signal at a binding energy which is 2 eV higher than the corresponding energy of the in situ reduced platinum. After five successive oxidations the same binding energy of the Pt 4f electrons was observed as for platinum reduced in situ [22]. Hence, the supported platinum can be considered to be in a metallic state even after reaction.

Ex situ cyclic voltammetry

Fig. 6 shows the cyclic voltammogram of a platinum foil in a sodium hydroxide solution of 1000 mol m^{-3} . The first two peaks in the anodic scan, between 0.25 and 0.4 V, correspond to the oxidation of hydrogen atoms chemisorbed on different adsorption sites [30]. These peaks enable the calculation of the platinum surface area, assuming that the oxidation of hydrogen atoms corresponds to the transfer of 2.1 C per square meter platinum surface area [31]. In the region between 0.4 and 0.5 V the surface is free of adsorbed species. This region is referred to as the double-layer region. Above 0.5 V the chemisorption of oxygen occurs, followed by the formation of oxidic platinum and at potentials higher than 1.4 V by the evolution of dioxygen. If the potential scan is reversed the oxidic platinum will be reduced whereby a net cathodic current is generated. The first peak in the cathodic scan, at 0.68 V, corresponds to the reduction of platinum surface oxide or oxygen adatoms [25,32,33]. The potential at which this cathodic reduction occurs depends on the nature of the interaction between oxygen and platinum. Reduction of small oxidic platinum particles occurs at potentials lower than 0.68 V, because of the stronger oxygen–platinum bond [25]. The reduction of bulk platinum oxide also requires stronger reducing conditions than platinum surface oxide or oxygen adatoms

Fig. 6. Cyclic voltammogram of a platinum foil in a sodium hydroxide solution of 1000 mol m^{-3} , with a scan rate of 10 mV s^{-1} .

[32,33]. At potentials below 0.4 V, peaks corresponding to the adsorption and reduction of protons are observed.

The paper of de Bruijn et al. [22] deals with the analysis of the investigated catalyst samples by ex situ cyclic voltammetry. The cyclic voltammogram of the catalyst exposed to ambient air showed, in the first cathodic scan, a peak corresponding to the reduction of oxidic platinum. It was found that the platinum was covered with approximately a monolayer of oxygen adatoms, upon exposure to ambient air.

No significant peak corresponding to the reduction of oxidic species was observed in the cyclic voltammogram of the catalyst after reduction in water. A cyclic voltammogram of the catalyst after five successive oxidations did not show any reduction of oxidic species either. It was believed that methyl α -D-glucoside, still present after washing the sample, reacted with the chemisorbed oxygen atoms. Oxidation of organic compounds was indeed observed around 0.8 V during the first anodic scan on such a sample.

The cyclic voltammogram of the dried catalyst after five successive oxidations showed a decrease of the platinum surface area to the same extent as observed by STEM and carbon monoxide chemisorption.

In situ cyclic voltammetry

The oxidation of methyl α -D-glucoside with molecular oxygen was carried out in the electrochemical cell with the catalyst as electrode. The following initial oxidation conditions were applied: $C_{\text{MGSD}}^0 = 500 \text{ mol m}^{-3}$, $p_{\text{O}_2} = 1.0 \times 10^5 \text{ Pa}$, $\text{pH}^0 = 12$ and $T = 323 \text{ K}$. Fig. 7 shows the cyclic voltammogram of the catalyst recorded in the reaction mixture after 45 ks and after substitution of oxygen by nitrogen.

Fig. 7. In situ cyclic voltammogram of the catalyst after 45 ks of oxidation of methyl α -D-glucoside (298 K, helium atmosphere, $C_{\text{NaClO}_4} = 990 \text{ mol m}^{-3}$, scan rate of 10 mV s^{-1}). Full line: first scan; dashed line: second scan.

The electrochemical cell was cooled down to 298 K before the cyclic voltammogram was recorded to suppress the electrochemical oxidation of the methyl α -D-glucoside present in the solution. In the first cathodic scan a small peak at 0.65 V corresponding to the reduction of oxygen adatoms is found. Apparently, the low temperature and the quick analysis of the catalyst prevented that all the chemisorbed oxygen reacts with adsorbed methyl α -D-glucoside. In the first anodic scan a peak at a potential of 0.94 V is observed corresponding to the oxidation of adsorbed organic species. In the second scan the peak corresponding to the reduction of oxidic platinum is absent, the peak corresponding to the oxidation of hydrogen atoms increases and the peak corresponding to the oxidation of organic species decreases.

A cyclic voltammogram of the catalyst after 70 ks of reaction was compared to that of the catalyst before reaction. A platinum surface area loss of 50% was observed.

Open circuit potential

By monitoring the open circuit potential of the platinum during reaction, information can be gained about the adsorbed species. The open circuit potential of platinum is mainly determined by the presence of adatoms of hydrogen or oxygen. The open circuit potential of a platinized platinum foil in water with a pH of 12 saturated with dihydrogen at atmospheric pressure and 323 K amounted to 0.0 V. The potential immediately increased to 1.12 V when dihydrogen was substituted by dioxygen. A typical time scale of the process is 100 s.

Fig. 8 shows the open circuit potential of the platinized platinum foil as monitored during oxidation of methyl α -D-glucoside with molecular oxygen in

Fig. 8. Open circuit potential of a platinized platinum foil versus time during the oxidation of methyl- α -D-glucoside. Oxidation conditions: $C_{\text{MGSD}}^0 = 200 \text{ mol m}^{-3}$, $p_{\text{O}_2} = 1.0 \times 10^5 \text{ Pa}$, $\text{pH}^0 = 12$ and $T = 323 \text{ K}$. Batch oxidation.

the electrochemical cell. The following initial reaction conditions were applied: $C_{\text{MGSD}}^0 = 200 \text{ mol m}^{-3}$, $p_{\text{O}_2} = 1.0 \times 10^5 \text{ Pa}$, $\text{pH}^0 = 12$ and $T = 323 \text{ K}$. Under these reaction conditions no oxygen transfer limitation occurred.

Before the reaction the cell and reaction mixture were saturated with nitrogen. The open circuit potential of the platinized foil covered with methyl α -D-glucoside amounted to 0.26 V. Substitution of nitrogen by oxygen resulted in an increase of the potential from 0.26 to 0.66 V within a few minutes. During the oxidation further increase to 1.16 V occurred. Purging with nitrogen for 10 min resulted in a potential drop from 1.16 to 0.66 V. Reduction with hydrogen resulted in a further decrease of the open circuit potential back to 0.26 V. When comparing Figs. 2 and 8, it appears that the change in potential runs parallel to the reversible decrease in oxidation rate.

Cyclic voltammograms of the platinized platinum foil before and after the experiment did not show the presence of bulk platinum oxide. The platinum surface area was decreased by 50%.

Comparison of platinum supported on graphite and platinum supported on activated carbon

A comparison of the activities of the investigated graphite-supported platinum to the platinum supported on activated carbon which was used for the study of the oxidation kinetics [1,2], is only fair and meaningful when performed in terms of turnover frequencies, i.e. based on the same amount of exposed platinum atoms. The turnover frequencies have been calculated from the observed specific reaction rates and the fractions of exposed platinum atoms as obtained from STEM.

Table 2 lists the observed intrinsic initial reaction rates and the calculated

TABLE 2

Surface area weighed average platinum particle diameters, initial intrinsic reaction rates and TOFs

Catalyst sample	d_{Pt} (nm)	R_w^0 ($10^{-3} \text{ mol kg}_{cat}^{-1} \text{ s}^{-1}$)	TOF (10^{-3} s^{-1})
<i>Activated carbon</i>			
As received ^a	2.20 ± 0.08	2.2	22
After 1 batch experiment ^a	3.20 ± 0.22	1.8	27
After 25 batch experiments ^a	8.00 ± 0.58	1.0	31
<i>Graphite</i>			
As prepared ^b	1.85 ± 0.04	2.4	20
After 5 successive oxidations ^b	2.45 ± 0.15	1.8	22

^a $T=303 \text{ K}$, $\text{pH}=7.0$, $C_{\text{MGSD}}=500 \text{ mol m}^{-3}$, $p_{\text{O}_2}=1 \times 10^5 \text{ Pa}$, $C_{\text{cat}}=2 \text{ kg m}^{-3}$.^b $T=323 \text{ K}$, $\text{pH}=7.0$, $C_{\text{MGSD}}=500 \text{ mol m}^{-3}$, $p_{\text{O}_2}=1 \times 10^5 \text{ Pa}$, $C_{\text{cat}}=1 \text{ kg m}^{-3}$.

turnover frequencies for both platinum supported on graphite and platinum supported on activated carbon together with the surface area average particle diameters.

The activity of platinum supported on graphite for the oxidation of methyl α -D-glucoside was low compared to platinum supported on activated carbon. Hence, a reaction temperature difference of 20 K was necessary to obtain comparable reaction rates for both catalysts.

DISCUSSION

A distinction is made between the reversible deactivation and the irreversible deactivation.

Reversible deactivation

The establishment of a steady-state after a change of the reaction conditions requires a certain time. For a two-stage catalytic reaction, the intrinsic relaxation time is related to the steady-state turnover frequency (TOF), by ref. 34:

$$\tau \leq \frac{1}{4} \frac{1}{\text{TOF}} \quad (3)$$

Eqn. (3) is related to an intrinsic relaxation process, i.e. determined by the mechanism of the reaction itself. During the relaxation the surface concentrations of the adsorbed reaction intermediates adapt to the reaction conditions. Intrinsic relaxation should be considered in contrast to extrinsic (or side) relaxation processes of which catalyst deactivation is an example.

The steady-state TOF of the selective oxidation of methyl α -D-glucoside is

in the order of 0.01 s^{-1} . Hence, a steady-state oxidation rate is expected after 100 s, if extrinsic relaxation processes can be excluded. As was shown in a previous paper [2], the rate-determining step for the oxidation of methyl α -D-glucoside is the surface reaction between adsorbed oxygen atoms and adsorbed methyl α -D-glucoside. Hence, the oxidation rate can be written as:

$$\text{TOF} = k_3 \theta_{\text{O}^*} \theta_{\text{MGSD}^*} \quad (4)$$

According to eqn. (4) the oxidation rate reaches a maximum at $\theta_{\text{O}^*} = \theta_{\text{MGSD}^*} = 0.5$.

At the start of an oxidation experiment, the reduced catalyst is suspended into the aqueous solution of methyl α -D-glucoside saturated with nitrogen. According to the value of the Langmuir adsorption coefficient for methyl α -D-glucoside [2], a surface coverage with methyl α -D-glucoside of $\theta_{\text{MGSD}^*} = 0.4$ is established ($C_{\text{MGSD}} = 200 \text{ mol m}^{-3}$, $\text{pH} = 7$, $p_{\text{O}_2} = 0 \text{ Pa}$). The oxidation is started by substitution of nitrogen by oxygen. Upon admission of molecular oxygen, dissociative chemisorption on the free platinum sites occurs. On the time scale of the reaction, i.e. 100 s, a stationary oxygen coverage will be established. The latter amounts to 0.8 according to the reported value of the Langmuir adsorption coefficient [2] ($C_{\text{MGSD}} = 200 \text{ mol m}^{-3}$, $\text{pH} = 7$, $p_{\text{O}_2} = 1.0 \times 10^5 \text{ Pa}$). The corresponding stationary surface coverage with methyl α -D-glucoside decreases over the same lapse of time to $\theta_{\text{MGSD}^*} = 0.08$. The increase within a few minutes of the open circuit potential from 0.26 V to 0.66 V upon switching from nitrogen to oxygen, shown in Fig. 8, corresponds to the establishment of these surface coverages.

The further increase of the open circuit potential during oxidation, occurring on a time scale of 10 ks, indicates that the oxygen surface coverage further increases until the platinum surface is almost completely covered by oxygen, as indicated by the potential reached, cf. Fig. 8. A parallel decrease of the reaction rate is shown in Fig. 1. Hence, a distinction can be made between the establishment of an oxygen coverage upto $\theta_{\text{O}^*} = 0.8$ according to an intrinsic relaxation process, and the establishment of oxygen coverages above $\theta_{\text{O}^*} = 0.8$ caused by an extrinsic relaxation process. The latter cannot be attributed to the formation of a platinum oxide. Firstly, neither XPS nor cyclic voltammetry show the presence of platinum oxide. Secondly, it can be seen from Fig. 8 that the open circuit potential decreases, within a few minutes, to a value corresponding with a low oxygen surface coverage, as soon as the oxygen feed is interrupted. Apparently, all adsorbed oxygen then reacts with methyl α -D-glucoside.

When assuming a linear relation between the open circuit potential and the oxygen surface coverage, it can be estimated from Fig. 8 that after 10 ks an oxygen surface coverage of approximately 0.98 is established which corresponds to a surface coverage with methyl α -D-glucoside of 0.008. Substitution of the above-mentioned values of the degrees of coverages in eqn. (4) allows to calculate the extent of reversible deactivation after 10 ks:

$$\frac{R_w}{R_{w,R}^0} = \frac{0.98 \times 0.008}{0.8 \times 0.08} = 0.12$$

This calculated decrease of the specific reaction rate agrees with the observed decrease after 10 ks of oxidation of methyl α -D-glucoside, cf. Fig. 2.

The results of the present study indicate that the nature of the oxygen–platinum interaction is limited to chemisorption, but do not provide an explanation for the increasing oxygen coverage beyond the levels expected from the Langmuir isotherm nor for the time scale of this phenomenon. Within the scope of this discussion it must be noticed that it follows from the Pourbaix diagram that PtO_2 is the thermodynamically stable bulk form of platinum in neutral water saturated with oxygen at atmospheric pressure and 298 K. It appears that the presence of methyl α -D-glucoside does not prevent the platinum from becoming almost completely covered by oxygen, but only slows down the process. It may be possible that the high time-scale of the further increase of the oxygen coverage in the presence of methyl- α -D-glucoside, is due to a rearrangement of the platinum surface comparable to the electrochemical oxidation of platinum where a change in the oxygen–platinum interaction was observed by maintaining the electrode at a certain potential for half an hour [11]. Briot et al. [26] observed a sharp decrease of the adsorption enthalpy of oxygen on supported platinum at near monolayer coverages. This could also lead to a strong decrease of the chemisorption rate. A similar phenomenon has been observed for the chemisorption of oxygen on silver [35].

Finally the two-stage oxygen adsorption process also could be caused by the occurrence of two different oxygen species i.e. $^*\text{OH}$ and $^*\text{O}$. A likely sequence could be that initial adsorption of oxygen on the hydrated platinum surface, also partly covered with hydrogen and methyl- α -D-glucoside, results in a high coverage with surface hydroxyls and high activity, followed by a slow process of further oxygen adsorption, where surface hydroxyl has to be displaced simultaneously, resulting in low activity.

Further studies are needed to discriminate between the explanations given.

Irreversible deactivation

The platinum particle diameter distribution of the used catalyst shows the appearance of larger particles at the expense of the smaller ones, i.e. recrystallization occurs during reaction. The presence of platinum ions in solution during oxidation indicates that recrystallization occurs via the dissolution and subsequent redeposition of platinum, rather than by migration of platinum over the support. It appears that this process involves the preferential dissolution of the small platinum particles. The extent of the irreversible deactivation is correlated with the amount of methyl α -D-glucoside converted per amount of catalyst, cf. Fig. 4. But no correlation is observed with the product

concentration. Apparently, one of the intermediates or products of the oxidation of methyl α -D-glucoside is able to extract and complex platinum on desorption. Several studies indicate that platinum covered by oxygen can be extracted into the liquid phase by I^- and Cl^- ions [36,37]. A positive correlation between the fraction of platinum atoms exposed and the concentration of platinum ions in solution was observed by these authors indicating that platinum surface atoms covered by oxygen are the intermediate in the dissolution process. The pH dependence of the irreversible deactivation, cf. Fig. 4, is expected on the basis of the Pourbaix diagram [13] which states that the dissolution of oxidic platinum increases with increasing pH. Also the concentration of anionic species, which can more easily complex with platinum cations, increases with increasing pH.

Particle size effect

It is shown in Table 2 that a temperature of 323 K for platinum supported on graphite rather than 303 K was required to obtain specific reaction rates comparable to those obtained on activated carbon as support. It is not expected that support factors would have such large effect on the reaction rate. To allow a better comparison of the two catalysts, the TOFs for the platinum on activated carbon were extrapolated to a temperature of 323 K based on the Arrhenius and Langmuir parameter estimates reported previously [2].

Fig. 9 shows the TOF at 323 K versus the surface area average particle diameter obtained by STEM. Fig. 9 indicates that the oxidation of methyl α -D-glucoside over supported platinum shows some antipathetic structure sensitivity: the TOF increases with increasing particle diameter [38,39]. The TOF for

Fig. 9. Turnover frequency versus the average platinum particle diameter. (○) Platinum supported on activated carbon, calculated from the data in Table 2 and the Arrhenius and van 't Hoff parameters as reported by Schuurman et al. [2], (△) platinum supported on graphite. Reaction conditions: $T = 323$ K, $pH = 7.0$, $C_{MGS} = 500 \text{ mol m}^{-3}$, $p_{O_2} = 1 \times 10^5 \text{ Pa}$.

the electrochemical reduction of oxygen at platinum electrodes has been reported to present a similar behaviour [25,40]. Briot et al. [26] attributed an analogous phenomenon for the oxidation of methane over platinum to a decrease of the adsorption enthalpy for oxygen with increasing platinum particle diameter. It is indeed known that the activation energy for the desorption of oxygen from platinum to the gas phase increases with decreasing particle diameter [10,41]. Peuckert et al. [25] also observed that the reduction potential for platinum oxide in aqueous media is shifted to lower potentials with decreasing particle size. The increasing oxygen-platinum bond strength with decreasing platinum particle diameter has been attributed to geometrical [40] as well as to electronic effects [42].

If the decrease of the TOF with decreasing platinum particle diameter is attributed to the stronger oxygen-platinum bond, the reaction conditions have to be such that the reaction rate decreases with an increasing oxygen coverage. For the conditions at which the particle size effect of the oxidation of methyl α -D-glucoside was investigated this condition is fulfilled because the oxygen partial pressure was 1.0×10^5 Pa during the oxidation, corresponding to an oxygen surface coverage of more than 0.5.

Hence, the observed increase of the initial TOF with increasing platinum particle diameter can indeed be attributed to a decrease of the oxygen surface coverage towards the optimal one.

An alternative Sabatier type of explanation can be given if it is assumed that the oxygen-platinum bond is broken in the rate-determining step [43] and that for the investigated platinum particle diameters the bond strength is higher than the optimal bond strength. If the former explanation is correct, the particle size effect would have an opposite direction if the oxygen coverage is below 0.5.

It is not clear from the kinetic analysis whether the oxygen-platinum bond is broken in the rate-determining step or in a step thereafter [2]. The structure sensitivity of the oxidation of methyl α -D-glucoside is not very pronounced and therefore it is believed that it has to be attributed to the decrease of the oxygen surface coverage with increasing platinum particle size, towards the more optimal value of 0.5, rather than to the decrease of the activation energy for the breaking of the oxygen-platinum bond. A more pronounced structure sensitivity would be expected in the latter case.

CONCLUSIONS

The combination of surface-sensitive techniques, especially those performed in situ, in conjunction with the examination of the reaction rates has provided a better insight in the deactivation mechanism of platinum supported on carbon during the oxidation of methyl α -D-glucoside.

A distinction has to be made between the reversible deactivation, occurring

on the time scale of 10 ks and the irreversible deactivation, occurring on the time scale of 100 ks.

After the establishment of the surface coverages with oxygen and methyl α -D-glucoside, on the time scale of the reaction, the oxygen surface coverage increases further. This increase of the oxygen coverage is not attributed to the formation of platinum oxide, but by further chemisorption. The resulting decrease of the surface coverage with methyl α -D-glucoside explains the observed decrease of the reaction rate.

The irreversible deactivation is caused by the dissolution and redeposition of platinum. This process involves the preferential dissolution of small platinum particles and leads to a catalyst with larger platinum particles.

The oxidation of methyl α -D-glucoside over freshly reduced supported platinum can be classified as a structure-sensitive reaction, although the structure sensitivity is not very pronounced.

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NOTATION

C	Concentration, mol m ⁻³
d	Diameter, m
FE	Fraction exposed
k	Reaction rate coefficient, arbitrary
n	Number
p	Partial pressure, Pa
R_w	Production rate, mol kg _{cat} ⁻¹ s ⁻¹
T	Temperature, K
t	Time, s
TOF	Turnover frequency, s ⁻¹
X	Conversion

Greek symbols

θ	Degree of surface coverage
τ	Relaxation time, s

Subscripts

MGSD	Methyl- α -D-glucoside
R	Reversible

Superscripts

0	Initial
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