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Platinum Catalysis with Oxygen in Water

Catalyst characterization and kinetics of partial ethanol oxidation

J.A.A. van den Tillaart
Platinum Catalysis
with Oxygen in Water

Catalyst characterization and kinetics of partial ethanol oxidation

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof. dr. J.H. van Lint, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op maandag 4 juli 1994 om 16.00 uur

door

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SUMMARY

The partial oxidation of ethanol to ethanal and ethanoate over a well-defined platinum on graphite catalyst with oxygen in water was investigated as a model system for the oxidation of more complex molecules.

The catalyst preparation by a competitive cation exchange of platinumtetramine and ammonium ions on an activated graphite support, yielded a platinum on graphite catalyst with a metal loading of 3.5 to 4.9 wt% and a fraction of exposed platinum atoms, $\text{FE}$, from 0.66 up to 0.88.

Heating the catalyst to temperatures below 673 K at reducing conditions hardly influences the platinum particle size. The same holds for calcination at temperatures up to 600 K. Calcination at higher temperatures results in a growth of the particles. This growth is attributed to the mobility of platinum oxide at temperatures close to the melting point of 723 K.

The fraction of exposed platinum atoms could be varied systematically by calcination. Platinum particle sizes between 1.5 and 5.9 nm corresponding to fractions of exposed platinum atoms between 0.22 and 0.88 were obtained.

As oxygen is thought to play an important role in the deactivation of platinum catalysts during oxidation reactions, the oxidation and reduction of the platinum on graphite catalyst was investigated in various media with in-situ X-ray Absorption Spectroscopy. Extended X-ray Absorption Fine Structure analysis and white-line surface areas from XAS measurements showed that exposure to ambient air of small reduced platinum particles leads to a strong corrosive oxidation resulting in a particle consisting of a shell of PtO$_2$ and a core of metallic platinum.

Such an oxidized particle can be reduced easily by reduction at ambient temperatures in hydrogen gas or at 363 K in hydrogen saturated water or hydrogen saturated aqueous solutions. Contacting of the catalyst with hydrogen saturated water or a hydrogen saturated 0.1 M HClO$_4$ solution at 363 K for 20 hours lead to a small but significant growth of the platinum particles. This growth is equivalent to a change in the fraction of exposed platinum atoms from 0.75 to 0.69. Contacting with a hydrogen saturated 0.1 M NaOH solution at 363 K for 20 hours lead to a large growth of the platinum particles equivalent to a change in the fraction of exposed platinum atoms from 0.75 to 0.47.

Contacting of a reduced catalyst with oxygen saturated distilled water at 323 K for 20 hours did not lead not to a significant oxidation of the platinum particles. The observed
Pt-O contribution can be attributed to most probably an adsorbed hydroxide species. The Pt-C distance of the metal-support interaction was lowered from 2.6 \times 10^{-10} \text{ m} to approximately 2.2 \times 10^{-10} \text{ m} as a result of the oxidation of the hydrogen present in the metal-support interface after reduction.

Contacting of a reduced catalyst with an oxygen saturated 0.1 M HClO₄ or NaOH solution at 323 K for 20 hours did lead to a significant oxidation of the platinum particles. The structure of the particles is however not as disturbed as after contacting with ambient air. The presence of ions seems to enhance greatly the susceptibility of the platinum particle to oxidation. Also alkaline conditions seem to favor the oxidation of platinum more than acidic conditions.

Adsorption of ethanol on small reduced platinum particles leads to a significant change in the EXAFS signal. This change can be attributed qualitatively to the contribution of an extra shell of a light element at a distance close to the distance of the metal-support interaction of Pt-C at 2.6 \times 10^{-10} \text{ m}.

The kinetic investigation of the platinum catalyzed oxidation of ethanol to ethanal and ethanoate with oxygen dissolved in water was performed in a three-phase continuous stirred tank reactor. In this investigation the reaction temperature was varied from 293 to 344 K, the concentration ethanol was varied from 38 to 762 mol m⁻³, the partial oxygen pressure from 8 to 96 kPa, the pH from 7 to 10, and the ethanal and ethanoate concentration from 5 to 50 mol m⁻³.

The oxidation proceeds by a reaction sequence in which ethanal and ethanoate are formed successively. No effect of the pH on the disappearance rate of ethanol could be observed as could be expected from the low acidity of ethanol.

Regression analysis of the intrinsic kinetic data showed that the reaction kinetics of the platinum catalyzed oxidation of ethanol to ethanal in water can be described adequately over the experimental range of reaction conditions by the following relatively simple rate equation:

\[
\tilde{R}_w = \frac{2k_1c_{O_2}}{1 + \frac{2k_1c_{O_2}}{k_3\sqrt{K^2C_{ethanol}}} + 2\sqrt{K^2C_{ethanol}}} \times L_i
\]

This equation is based on an irreversible dissociative adsorption of oxygen and a equilibrated reversible dissociative adsorption of ethanol on the same type of sites.
These steps are followed by an irreversible surface reaction between these two adsorbed species in a so-called dual-site mechanism:

\[
\begin{align*}
(1) \quad O_2 + 2^* & \rightarrow 2O^* & \alpha = 1 \\
(2) \quad CH_3CH_2OH + 2^* & \rightarrow CH_3CH_2O^* + H^* & \beta = 2 \\
(3) \quad CH_3CH_2O^* + O^* & \rightarrow CH_3CHO + OH^* + ^* & \gamma = 2 \\
(4) \quad H^* + OH^* & \rightarrow H_2O + 2^* & \lambda = 2 \\
2CH_3CH_2OH + O_2 & \rightarrow CH_3CHO + H_2O
\end{align*}
\]

The dissociative adsorption of ethanol proceeds by abstraction of the hydroxyl hydrogen. The kinetic analysis itself however cannot distinguish between abstraction of the \( \alpha \)-carbon hydrogen or the hydroxyl hydrogen due to the ambiguity of the steady state kinetics. The kinetic analysis shows that the adsorption of ethanol is not rate-determining, however, and from literature it is known that the rate-determining step involves breaking the \( \alpha \)-carbon hydrogen bond.

The surface coverages calculated at typical reaction conditions, i.e. a temperature of 324 K, an ethanol concentration of 500 mol m\(^{-3}\) and an oxygen partial pressure of 50 kPa, amount to 0.25 for oxygen, 0.11 for both ethanol and hydrogen, and 0.52 for the free surface sites.

An assessment of the estimates of the kinetic parameters reveals that some of the steps in the reaction sequences are not true elementary reaction steps but are probably consisting of a reaction step preceded by an equilibrium reaction.

The absence of catalyst deactivation during most of the ethanol oxidation experiments results from the absence of poisoning or sequestering side products and from the relatively low fractional surface coverage of oxygen, typically 0.25, which prevents over-oxidation of the platinum surface and formation of ionic platinum. This low oxygen coverage is a result of the relative high rate coefficient of the surface reaction and the coverage with hydrogen atoms. The small deactivation of the platinum on graphite catalyst observed during an aqueous ethanol oxidation experiment of one week can at least partially be attributed according to the EXAFS analysis to a small but significant growth of the platinum particles.

The effect of the platinum particle size on the oxidation rate of ethanol was investigated by using a series of catalysts with a particle size ranging from 1.46 to 3.22 nm, equivalent to a FE ranging from 0.88 to 0.40. EXAFS measurements verified that reduced platinum particles as small as 1.48 nm retained the fcc structure on a graphite support and that such small particles could be reduced completely in water.
The particle size effect experiments were performed at a temperature of 303 K, a concentration ethanol of 260 mol m\(^{-3}\), a partial oxygen pressure 60 kPa, a pH of 9, and an ethanal and ethanoate concentration of 20 mol m\(^{-3}\). At these conditions the oxidation of ethanol with dioxygen over a well-reduced platinum on graphite catalyst showed a clear particle size effect on the turnover frequency but only for particle sizes smaller than 2 nm. Hence, the reaction shows a limited structure sensitivity. This indicates that the oxidation of ethanol on platinum does not need active sites consisting of special surface atoms or ensembles of surface atoms. Most probably only a few surface atoms are needed for this reaction. The particle size effect can be explained by the increased strength of the oxygen platinum bond with decreasing particle size, which is involved in some way in the rate-determining step. Probably the stronger bonded oxygen is less capable of abstracting a hydrogen atom from the adsorbed ethanol species thereby decreasing the rate of reaction.
SAMENVATTING

De partiële oxydatie van ethanol tot ethanal en ethanoaat over een goed gekarakteriseerde platina op grafiet katalysator met zuurstof in water is onderzocht als een modelsysteem voor de oxydatie van meer complexe moleculen.

De katalysator bereiding met behulp van een competitieve kationwisseling tussen platinatetramine en ammonium ionen op een geactiveerde grafiet drager, gaf een platina op grafiet katalysator met een metaal belading van 3.5 tot 4.9 m% en een fractie blootgestelde platina atomen, FE, van 0.66 tot 0.88. Verwarmen van deze katalysator tot temperaturen lager dan 673 K onder reducerende condities beïnvloedt de platina deeltjesgrootte nauwelijks. Hetzelfde geldt voor calcineren op temperaturen tot 600 K. Calcineren op hogere temperaturen geeft een duidelijke groei van de deeltjes. Deze groei wordt toegeschreven aan de mobiliteit van platinaoxyde op temperaturen dicht bij het smeltpunt van 723 K.

De fractie blootgestelde platina atomen kon systematisch worden gevarieerd door de katalysator te calcineren. Platina deeltjesgroottes tussen 1.5 en 5.9 nm, overeenkomend met een fractie blootgestelde platina atomen van 0.88 tot 0.22, werden op deze wijze verkregen.

Omdat zuurstof gedacht wordt een belangrijke rol te spelen in de desactivering van platina katalysatoren gedurende oxydatie reacties, werd de oxydatie en reductie van de platina katalysator onderzocht in verschillende milieus met behulp van in-situ röntgen absorptie spectroscopie.

Analyse van de "X-ray Absorption Fine Structure" en oppervlakten van de "white-line" tonen dat blootstelling van kleine gereduceerde platina deeltjes aan de buitenlucht leidt tot een sterk corrosieve oxydatie resulterend in een deeltje dat bestaat uit een schil van PtO$_2$ en een kern van metallisch platina.

Een dusdanig geoxideerd deeltje kan eenvoudig gereduceerd worden door reductie met waterstof gas op kamertemperatuur of met op 363 K met waterstof verzadigd water of waterige oplossing. Het in contact brengen van katalysator met waterstof verzadigd water of een met waterstof verzadigde 0.1 M HClO$_4$ oplossing op 363 K gedurende 20 uren resulteerde in een kleine maar significante groei van de platina deeltjes. Deze groei komt overeen met een verandering in de fractie blootgestelde platina atomen van 0.75 naar 0.69. Het in contact brengen met een met waterstof verzadigde 0.1 M NaOH oplossing op 363 K gedurende 20 uren resulteerde in een
sterke groei van de platina deeltjes overeenkomend met een verandering in de fractie blootgestelde platina atomen van 0.75 naar 0.47.

Het in contact brengen van een gereduceerde katalysator met zuurstof verzadigd gedestilleerd water op 323 K gedurende 20 uren resulteerde niet in een significante oxydatie van de platina deeltjes. De geobserveerde Pt-O bijdrage kan het meest waarschijnlijk worden toegeschreven aan een geadsorbeerde hydroxyde species. De Pt-C afstand van de metaal-drager interactie was verlaagd van 2.6 $10^{-10}$ m tot ongeveer 2.2 $10^{-10}$ m. Deze verandering wordt toegeschreven aan de oxydatie van het waterstof dat aanwezig is na reductie in het grensvlak tussen het metaal en de drager.

Het in contact brengen van een gereduceerde katalysator met een met zuurstof verzadigde 0.1 M HClO₄ of NaOH oplossing op 323 K gedurende 20 uren resulteerde wel in een significante oxydatie van de platina deeltjes. De structuur van de deeltjes was echter niet zo verstoord als na het contact met de buitenlucht. De aanwezigheid van ionen lijkt de gevoeligheid van de platina deeltjes voor oxydatie te versterken. Bovendien schijnen basische condities de oxydatie meer te versterken dan zure condities.

Adsorptie van ethanol op kleine gereduceerde platina deeltjes leidt tot een significante verandering van het EXAFS signaal. Deze verandering kan qualitatief worden toegeschreven aan de bijdrage van een extra omringingsschil van een licht element op een afstand dicht bij die van de metaal-drager interactie van Pt-C op 2.6 $10^{-10}$ m.

Het kinetisch onderzoek van de platina gekatalyseerde oxydatie van ethanol tot ethanal en ethanoaat met zuurstof opgelost in water werd gedaan in een drie-fasen continue geroerde tank reactor. In dit onderzoek werd de reactietemperatuur gevarieerd van 293 tot 344 K, de concentratie ethanol werd gevarieerd van 38 tot 762 mol m$^{-3}$, de partiële zuurstof druk van 8 tot 96 kPa, de pH van 7 tot 10 en de ethanal en ethanoaat concentratie van 5 tot 50 mol m$^{-3}$.

De oxydatie loopt volgens een reeks reactiestappen waarin ethanal en ethanoaat succesievelijk gevormd worden. Er was geen effect van de pH op de verdwijnsnelheid van ethanol zichtbaar, zoals verwacht kon worden van een zwak zuur als ethanol. Regressie analyse van de intrinsieke kinetische data toonde aan dat de reactiekinetiek van de platina gekatalyseerde oxydatie van ethanol in water adequaat beschreven kan worden binnen het gebied van de experimentele reactiecondities met de volgende relatief simpele reactiesnelheidsvergelijking:
Deze vergelijking is gebaseerd op een irreversibele dissociatieve adsorptie van zuurstof en een dissociatieve evenwichtsadsorptie van ethanol op dezelfde soort centra. Deze twee stappen worden gevolgd door een irreversibele reactiestap op het oppervlak tussen deze twee geadsorbeerde species volgens een zogenaamd dual-site mechanisme:

\[
\hat{R}_w = \frac{2k_1C_{O_2}}{\left(1 + \frac{2k_1C_{O_2}}{k_1\sqrt{K_2C_{ethanol}}} + 2\sqrt{K_2C_{ethanol}}\right)^2}L_{t}
\]

Deze vergelijking is gebaseerd op een irreversibele dissociatieve adsorptie van zuurstof en een dissociatieve evenwichtsadsorptie van ethanol op dezelfde soort centra. Deze twee stappen worden gevolgd door een irreversibele reactiestap op het oppervlak tussen deze twee geadsorbeerde species volgens een zogenaamd dual-site mechanisme:

\[
\begin{align*}
(1) \quad & O_2 + 2* \quad \rightarrow \quad 2O* \quad \sigma = 1 \\
(2) \quad & CH_3CH_2OH + 2* \quad \rightarrow \quad CH_3CH_2O* + H* \quad \sigma = 2 \\
(3) \quad & CH_3CH_2O* + O* \quad \rightarrow \quad CH_3CHO + OH* + * \quad \sigma = 2 \\
(4) \quad & H* + OH* \quad \rightarrow \quad H_2O + 2* \quad \sigma = 2 \\
& \quad 2CH_3CH_2OH + O_2 \quad \rightarrow \quad CH_3CHO + H_2O
\end{align*}
\]

De dissociatieve adsorptie van ethanol vindt plaats door het afstaan van het waterstofatoom aan de hydroxylfunctie. De kinetische analyse kan echter op zich zelf geen onderscheid maken tussen het afstaan van het waterstof aan het α-koolstofatoom of die van de hydroxylfunctie. De kinetische analyse toont echter wel aan dat de adsorptie van ethanol niet snelheidsbepalend is en uit de literatuur blijkt dat het breken van de waterstof-α-koolstofbinding wel snelheidsbepalend is.

De oppervlakte bedekkingsgraden die berekend zijn voor typische reactiecondities, d.w.z. een temperatuur van 323 K, een ethanolconcentratie van 500 mol m\(^{-3}\) en een zuurstof partiaaldruk van 50 kPa, bedragen 0.25 voor zuurstof, 0.11 voor zowel ethanol als waterstof en 0.52 voor de vrije oppervlakte plaatsen.

Een nadere beschouwing van de kinetische parameterschattingen leert dat sommige van de reactiestappen in de reeks niet werkelijk elementaire reactiestappen zijn maar waarschijnlijk zijn samengesteld uit een reactiestap voorafgegaan door een evenwichtsreactie.

De afwezigheid van katalysatordesactivering gedurende de meeste ethanoloxdatie experimenten vloeit voort uit afwezigheid van vergiftigende of sequestrerende bijprodukten en uit de relatief lage zuurstofbedekkingsgraad, typisch 0.25, hetgeen de overoxydatie van het platina oppervlak en de vorming van platina ionen voorkomt. Deze lage zuurstofbedekkingsgraad is het resultaat van de relatief hoge reactiesnelheidscoëfficiënt van de oppervlaktereactie en de bedekking van het
oppervlak met waterstofatomen. De geobserveerde lichte desactivering van de platina op grafiet katalysator gedurende een ethanoloxydatie experiment in water van een week kan volgens de EXAFS analyse minstens gedeeltelijk toegeschreven worden aan een kleine maar significante groei van de platina deeltjes.

Het effect van de platina deeltjesgrootte op de oxydatiesnelheid van ethanol werd onderzocht door een serie katalysatoren te gebruiken met een deeltjesgrootte variërend van 1.46 tot 3.22 nm, overeenkomend met een fractie blootgestelde platina atomen van 0.88 tot 0.40. EXAFS metingen toonden aan dat zelfs gereduceerde platina deeltjes zo klein als 1.48 nm de fcc structuur behielden, en dat dergelijke kleine deeltjes geheel gereduceerd konden worden in water.

De metingen voor het effect van de deeltjesgrootte werden uitgevoerd op een temperatuur van 303 K, een ethanolconcentratie van 260 mol m⁻³, een zuurstofpartiaaldruk van 60 kPa, een pH van 9 en een ethanal en ethanoaatconcentratie van 20 mol m⁻³. De oxydatie van ethanol met moleculaire zuurstof over een goed gereduceerde katalysator toonde onder deze condities alleen een duidelijk effect van de deeltjesgrootte op de "turnover frequency" voor deeltjes kleiner dan 2 nm. De reactie toont dus een gelimiteerde structuur afhankelijkheid. Dit is een indicatie dat de oxydatie van ethanol over platina geen actieve plaatsen nodig heeft die bestaan uit speciale atomen aan het oppervlak of ensembles van atomen aan het oppervlak. Er zijn waarschijnlijk slechts enkele atomen aan het oppervlak nodig voor deze reactie. Het effect van de deeltjesgrootte kan worden verklaard door de toenemende sterkte van de zuurstof-platinabinding met afnemende deeltjesgrootte. Deze zuurstof-platinabinding is op de een of andere manier betrokken in de snelheidsbepalende stap. Waarschijnlijk is het sterker gebonden zuurstof minder in staat een waterstofatoom van het geadsorbeerde ethanol af te halen hetgeen leidt tot een lagere reactiesnelheid.
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NOTATION

CURRICULUM VITAE

DANKWOORD

ACKNOWLEDGEMENT
1. INTRODUCTION

There is a growing interest in obtaining valuable chemicals by selective oxidation from a relatively cheap and renewable feedstock such as carbohydrates. The catalytic oxidation of alcohols and aldehydes with oxygen over highly dispersed noble metal catalysts in aqueous media is a very useful and probably economical route to achieve a partial or even a selective oxidation. Several authors have reported recently on this topic. Gallezot et al. (1992) reported on the catalytic oxidation of aqueous glyoxal to glyoxylic acid. Schuurman et al. (1992a, 1992b and 1992c) studied the oxidation of methyl α-D-glucoside and Vinke et al. (1990) oxidized 5-hydroxymethylfurfural.

Deactivation of platinum catalysts during aqueous oxidation is a serious problem which is well documented. Dijkgraaf et al. (1988a and 1988b) observed catalyst deactivation during the oxidation of D-gluconate to D-glucarate. Mallat et al. (1992) investigated the catalyst deactivation which occurred during the oxidation of 1-methoxy-2-propanol. Schuurman et al. (1992c) studied the catalyst deactivation during the oxidation of methyl α-D-glucoside. All authors agree on the importance of the role of oxygen during deactivation.

To obtain further insight into mechanism, kinetics and catalyst deactivation concerning these oxidation reactions this work reports on the oxidation of ethanol over a platinum on graphite catalyst as model system.

The preparation and characterization of a highly dispersed platinum on graphite catalyst, to obtain finally a well-defined catalyst for the experiments described in this work, is discussed in chapter 2.

Chapter 3 deals with the structural changes in the local platinum environment of the platinum particles after reduction and oxidation treatments in gaseous and aqueous media as viewed by in-situ X-ray Absorption Spectroscopy.

The kinetics and mechanism of the oxidation of ethanol with oxygen over a platinum on graphite catalyst in water will be discussed, based on the regression analysis of intrinsic kinetic data, in chapter 4.

Chapter 5 deals with the effect of the platinum particle size on the reaction rate of the oxidation of ethanol.
1.1. References


2. CATALYST PREPARATION AND CHARACTERIZATION

2.1. Introduction

The platinum catalysts used in this work had to meet several physical and chemical criteria. The support needs to be resistant to strong acidic and basic aqueous solutions. Silica, SiO₂, and alumina, Al₂O₃, which are often used as catalyst supports, were rejected as they are not resistant to such conditions. Activated carbon is often used as a catalyst support which is resistant to strong acidic and basic conditions. In the present study graphite was chosen as support in order to have a support which is better defined than activated carbon. Additional advantages of graphite as support are the good electrical conductivity, which enables electrochemical characterization and reduces charging problems with techniques like Scanning Transmission Electron Microscopy, STEM, and X-ray Photoelectron Spectroscopy, XPS, and the relative low X-ray and electron absorption coefficients which enhance the applicability of several characterization techniques like X-ray Absorption Spectroscopy, XAS, and STEM. XAS is in principle a bulk characterization technique. As XAS will be used to investigate oxidation/reduction of the platinum surface and chemisorption on the platinum surface, most of the platinum must be present at the surface rather than in the bulk to receive any useful information on the platinum surface. Therefore the platinum particles must be smaller than 2 nm, which is equivalent to say that the fraction of exposed platinum atoms, FE, must be at least 0.65. To receive a useful signal during experiments in an aqueous environment at ambient temperatures a platinum content of 3 wt% is required. The catalyst will also be used to measure reaction rates in a three-phase slurry reactor. These reaction rates must be free of any mass transfer limitation in order to obtain intrinsic kinetic data. A well-defined catalyst powder size smaller than 20 μm is preferred for this type of experiments.

2.2. Preparation

A highly dispersed platinum on graphite catalyst was prepared following a method described by Richard and Gallezot (1987). High surface area graphite from Johnson Matthey (CH10213) was first activated by partial combustion of batches of 8 g in an air flow of 300 Nml min⁻¹ at 773 K for 5
hours. Under these conditions 25 wt% of the graphite was burned off. The amount of graphite burned off was not stoichiometrically limited by the total amount of air fed as this was sufficient to burn the graphite completely to CO$_2$. Subsequently the graphite was suspended at ambient temperature for 24 hours in a solution of concentrated sodium hypochlorite (13 wt% in active chlorine, Janssen p.a.). After this wet activation step the graphite was separated from the solution by filtration on a Millipore filter (HV 0.45μ), carefully rinsed with distilled water and dried in a vacuum oven at 373 K. These two activation steps create oxygen containing surface groups at the edges of the carbon layers (Richard and Gallezot, 1987). These groups will later act as anchoring sites for the platinum complex. A high concentration of such sites is necessary to obtain a highly dispersed platinum catalyst (Ehrburger, 1984), i.e. to obtain a catalyst with a high fraction of platinum atoms exposed at the surface. Richard and Gallezot (1987) tried several methods of support activation and concluded that the above method gave the best results.

Platinum was introduced on the activated support by a competitive cation exchange technique (Che and Bennet, 1989) of platinumtetramine and ammonium ions with the anchoring sites on the support to obtain a more uniform platinum distribution throughout the whole support. As Richard and Gallezot (1987) achieved a maximum platinum uptake in a suspension with 20 wt% platinum with respect to the amount of graphite, a calculated amount of a platinumtetramine hydroxide solution (100 g 8 wt% in platinum, Johnson Matthey or 50 g 16 wt% in platinum, Degussa) was added dropwise to a suspension of 40 graphite in 800 ml 1 M ammonia (Merck p.a.) and stirred at ambient temperature for 24 hours. The catalyst was separated from the suspension by filtration on a Millipore filter (HV 0.45μ), washed with distilled water and dried in a vacuum oven at 373 K. The dried catalyst was reduced in flowing hydrogen at 473 or 573 K for 2 hours and stored exposed to air before use.

Several batches of catalyst were prepared this way and will be referred to in this work as catalyst batch A, B, C and D, see Table 2.1. The platinum content is slightly different for these different batches as appears from Table 2.2.

### 2.3. Sintering of the platinum particles

To obtain catalyst samples with different platinum particle sizes, i.e. with different fractions of exposed platinum atoms, but which are similar with respect to platinum content and support, samples of freshly prepared catalyst batches were treated for 2 to 4 hours at temperatures ranging from 473 to 773 K in flowing hydrogen or air. The samples treated with air were subsequently reduced for 2 hours in flowing hydrogen at 473 K. All samples were stored before use exposed to ambient air.
An overview of catalyst samples can be found in Table 2.1. Catalyst batches A and B were mainly used in preliminary experiments and XAS-measurements, see chapter 3. Catalyst batch C was used during the kinetic study, reported in chapter 4. Catalyst batch D was used in the experiments concerning the platinum particle size-effect, see chapter 5. Catalyst batch E was used in XAS-measurements, see chapter 3.

### 2.4. Characterization

#### 2.4.1. Platinum content

The platinum content of the catalyst was determined by UV/VIS spectrophotometry at 403 nm of a stable yellow Sn-Pt complex formed by platinum ions and SnCl₂ in the presence of excess chlorine ions (Ayres and Meyer, 1951 and 1955; Charlot, 1961). The platinum is released and dissolved from the support by boiling the catalyst in aqua regia.

The platinum contents of the different prepared catalysts are given in Table 2.2. It is clear that the platinum content of these catalysts is often higher than the maximum of 3.3 wt% reported by Richard and Gallezot (1987). This is
probably an effect of the differences in the graphite support used. The differences in platinum content between the different prepared catalysts cannot be explained.

2.4.2. Platinum particle size distribution

Scanning Transmission Electron Microscopy micrographs were obtained on a JEOL 2000 CX microscope with an accelerating potential of 200 kV at a microscope magnification of $5 \times 10^5$. The resolution of this microscope was better than 1 nm at the conditions used. The final magnification on the micrographs was $2 \times 10^6$.

The catalyst samples were ultrasonically dispersed in water, brought, suspended in water, onto coated copper grids and finally dried by exposure to air. Different types of grids were tried but only self prepared grids and perforated "lacey" grids supplied by Biorad gave good results.

The platinum particle size distribution was obtained from the micrographs by using a computer equipped with a camera and image analysis software (TIM 3.35, TEA DIFA measuring systems). Sections of the micrograph were digitized and stored in the computer. Direct analysis of the particles on these digitized images was not possible because of the non-uniform background due to the non-uniform thickness of the graphite support. Therefore a defocused digitized image of the same section was subtracted from the original image. The defocused image contains only information on the average gray level distribution and so the particles become visible as dark spots on a more uniform light background. After noise filtering and contrast enhancement, the particles which were clearly the same in shape and size on both the original micrograph and on the final computer image were selected. The software subsequently determined the surface area of these selected particles. The geometric platinum particle diameter, $d$, was defined as the diameter of a circle with the same surface area as the platinum particle. The surface area averaged platinum particle size, $d_a$, was determined from the distribution according to Lemaître et al. (1984):

$$d_a = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$  \hspace{1cm} (2.1)

where the summation goes over all considered size classes, $i$, with a diameter $d_i$ and a number, $n_i$, of counted particles in that class.

The sample standard deviation for the surface area averaged platinum particle size, $s_a$, which contains information about the width of the distribution is then defined by:
Catalyst preparation and characterization

\[ s_s = \sqrt{\frac{\sum n_i d_i^2 (d_i - d_s)^2}{\sum n_i d_i^2}} \quad (2.2) \]

If sufficient data is present the 95% confidence interval for the surface averaged diameter is given by:

\[ d_s \pm \frac{1.96 s_s}{\sqrt{n}} \quad (2.3) \]

in which \( n \) is the total number of counted particles.

From the surface averaged diameter the fraction of the exposed platinum atoms, \( FE \), can be calculated assuming hemi-spherical particles and \( 1.42 \times 10^{19} \) platinum atoms per square meter for polycrystalline platinum by (Scholten et al., 1985):

\[ FE = \frac{1.29 \times 10^{-9}}{d_s} \quad (2.4) \]

The results of the micrograph analysis can be found in Figure 2.2 and in Table 2.3.

The results from Table 2.3 of catalyst series B0-B3 and D0-D6 clearly indicate that oxidizing conditions enhance sintering of the platinum particles. Starting both from a reduced catalyst, with a surface averaged platinum particle size of about 1.47 nm and a platinum content of 3.7 wt%, the platinum particles on the catalyst which was heated to 673 K at oxidizing conditions sintered to 2.20 nm. The particles on the to the same temperature heated catalyst sintered only to 1.63 nm at reducing conditions.

Figure 2.1 further illustrates that the platinum particles sinter when the catalyst is heated under oxidizing conditions. From 700 K on the particle size becomes strongly dependent on the temperature. This temperature is about 1/3 of the melting temperature of platinum, i.e. 2043 K (Weast, 1988), and is close to the melting point of PtO\(_2\), i.e. 723 K (Weast, 1988). Probably at this temperature the surface platinum oxide becomes mobile on the graphite surface.

Figure 2.1 Platinum particle size versus calcination temperature starting with sample D0.
Figure 2.2 Platinum particle size distribution of several catalyst samples as determined by STEM micrograph analysis.
Catalyst preparation and characterization

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$d_s$ [nm]</th>
<th>$s_s$ [nm]</th>
<th>n [-]</th>
<th>FE$_{TEM}$ [-]</th>
<th>FE$_{CO}$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>1.84±0.04</td>
<td>0.45</td>
<td>552</td>
<td>0.70</td>
<td>0.75</td>
</tr>
<tr>
<td>B0</td>
<td>1.48±0.05</td>
<td>0.31</td>
<td>182</td>
<td>0.87</td>
<td>-</td>
</tr>
<tr>
<td>B2</td>
<td>1.61±0.09</td>
<td>0.34</td>
<td>53</td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td>B3</td>
<td>1.63±0.04</td>
<td>0.40</td>
<td>394</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>C0</td>
<td>1.95±0.06</td>
<td>0.42</td>
<td>222</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>D0</td>
<td>1.46±0.03</td>
<td>0.34</td>
<td>530</td>
<td>0.88</td>
<td>0.54</td>
</tr>
<tr>
<td>D1</td>
<td>1.53±0.04</td>
<td>0.35</td>
<td>299</td>
<td>0.84</td>
<td>-</td>
</tr>
<tr>
<td>D2</td>
<td>1.59±0.04</td>
<td>0.38</td>
<td>322</td>
<td>0.81</td>
<td>-</td>
</tr>
<tr>
<td>D3</td>
<td>1.85±0.05</td>
<td>0.42</td>
<td>282</td>
<td>0.70</td>
<td>0.56</td>
</tr>
<tr>
<td>D4</td>
<td>2.20±0.07</td>
<td>0.61</td>
<td>277</td>
<td>0.59</td>
<td>0.51</td>
</tr>
<tr>
<td>D5</td>
<td>3.22*</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
<td>0.53</td>
</tr>
<tr>
<td>D6</td>
<td>5.86±0.66</td>
<td>2.19</td>
<td>42</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>E0</td>
<td>1.66±0.04</td>
<td>0.37</td>
<td>373</td>
<td>0.78</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 2.3 Summary of platinum particle size analysis of STEM micrographs giving the fraction of exposed atoms, the surface area averaged particle size with 95% confidence limit, the standard deviation of the particle size distribution and the total number of counted particles (*= estimated from Figure 2.1). Also included are the results from CO chemisorption measurements (see text).

The CO pulse chemisorption measurement on catalyst sample A0 was performed in a Quantachrome Quantasorb. Hydrogen was used as carrier gas. Before chemisorption, the catalyst was reduced overnight with hydrogen at ambient temperature. The other CO pulse chemisorption experiments were performed on a modified Carlo Erba gaschromatograph equipped with a thermal conductivity detector. The catalyst was dried overnight at 323 K and 5 kPa. Before chemisorption the catalyst was reduced at 373 K for one hour with hydrogen. Helium was used as carrier gas.

The number of platinum surface atoms was determined from the amount of chemisorbed CO assuming a 1:1 stoichiometry (Scholten et al., 1985). The fraction of exposed platinum atoms, FE, could then be calculated as the ratio of the amount of adsorbed CO molecules to the total amount of platinum atoms in the sample. The relation between the fraction of exposed platinum atoms and the surface area averaged platinum particle size is already given in Equation 2.4.

The fraction exposed platinum atoms on catalyst sample A0 amounted to 0.75. This is in good agreement with the FE of 0.70 found by STEM micrograph analysis, see Table 2.3. The other results of the pulse CO chemisorption measurements are not in good
agreement with the results from STEM micrograph analysis. These results were all obtained on samples which had been stored for almost a year. The kinetic experiments with these catalysts were done immediately after preparation. For this reason the STEM micrograph analysis results obtained on fresh catalysts will be used in this work.

2.4.3. Catalyst powder size distribution

![Figure 2.3 Powder size distribution by weight of catalyst A0.](image)

The powder size distribution of catalyst A0 was measured with a Malvern 2600 particle sizer equipped with a 100 mm focal length lens. Figure 2.3 shows that only a very small weight fraction of the particles is larger than 20 μm. The volume mean diameter of the catalyst powder particles amounts to 9.5 μm. As the catalyst powder size distribution is determined by the powder size distribution of the activated support, the other catalyst samples are assumed to show the same powder size distribution.

2.4.4. BET surface area

A standard method for the determination of the specific surface area of porous materials is the Brunauer, Emmet and Teller method, better known as the BET-method. The equipment used for this method was a Strohlein Area-meter.

The changes of the BET surface area have been followed during the preparation steps of catalyst sample A0. The BET surface area of the graphite, as received, amounted to $3.12 \times 10^5$ m$^2$ kg$^{-1}$. This is a quite high specific surface area for graphite as normal graphite has a specific surface area in the order of $10^3$ m$^2$ kg$^{-1}$. Special etched graphites can have specific surface areas up to $3 \times 10^4$ m$^2$ kg$^{-1}$. Activated carbon consists of strongly disturbed micro crystallites with a diameter of approximately 10 nm and a specific surface area in the order of $10^6$ m$^2$ kg$^{-1}$. The high surface area graphite used in this work as support can thus better be labeled as a well-structured activated carbon or as a strongly disturbed graphite.

After activation of the support with air the BET surface area is significantly decreased to $1.82 \times 10^5$ m$^2$ kg$^{-1}$ as the more disturbed graphitic structures are more vulnerable to complete oxidation than the better structured regions. The specific surface area is somewhat further decreased after the wet activation step to $1.43 \times 10^5$ m$^2$ kg$^{-1}$. The specific surface area of sample A0 after reduction and exposure to ambient air amounts to $1.17 \times 10^5$ m$^2$ kg$^{-1}$. 
2.4.5. Pore size distribution

The catalyst pore size distribution has been determined by mercury porosimetry on a Carlo-Erba porosimeter. As is shown by Figure 2.4 a large contribution to the total pore volume stems from macro pores with a radius of approximately 0.8 μm. The increase of the cumulative pore volume at a pore radius smaller than 0.01 μm is attributed to the compressibility of the support material. The total specific pore volume is therefore taken as \(0.94 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}\). Using a volumetric mass of graphite of 2250 kg m\(^{-3}\) the catalyst powder porosity, \(\varepsilon_p\), amounts to 0.68.

2.5. Conclusions

The catalyst preparation according to the recipe of Richard and Gallezot (1987) yielded a platinum on graphite catalyst with a metal loading of 3.5 to 4.9 wt% and a fraction of exposed platinum atoms from 0.66 up to 0.88. Heating the catalyst to temperatures lower than 673 K at reducing conditions does hardly influence the particle size. The same holds for calcination at temperatures up to 600 K.

The fraction of exposed platinum atoms could be varied systematically by calcining. Platinum particle sizes between 1.46 and 5.9 nm corresponding to fractions of exposed platinum atoms between 0.22 and 0.88 could be obtained in this way.

The catalyst samples which were prepared are useful for as well X-ray absorption measurements as for intrinsic kinetic studies in a three-phase slurry reactor as they meet the criteria discussed in the introduction.

2.6. References

3. X-RAY ABSORPTION SPECTROSCOPY

3.1. Introduction

Bulk platinum is the thermodynamically stable form of platinum in air at ambient conditions as the standard Gibbs energy of formation of platinum oxide, PtO₂, amounts to 167 kJ mol⁻¹ (Weast, 1988). Surface platinum atoms and platinum atoms in very small particles however are less noble than platinum atoms in bulk metal because of their incomplete coordination. The standard Gibbs energy of formation of a single platinum atom amounts to 520 kJ mol⁻¹ at 298 K (Weast, 1988). Hence, there exists a critical coordination below which platinum is no longer stable in ambient air.

The literature on the oxidation of highly dispersed platinum in gaseous media agrees on the relative ease of oxidation at even ambient conditions. It was shown, using techniques such as EXAFS, Small and Wide Angle X-ray Scattering, chemisorption and Temperature Programmed Reduction, that the oxidation of platinum is passivating and limited to about two platinum layers (Bassi et al., 1976; Joyner, 1980; McCabe et al., 1988; Nandi et al., 1982; Ratnasamy et al., 1973). For highly dispersed catalysts this leads to an almost complete oxidation of the platinum as almost all platinum atoms are at the surface.

The thermodynamically stable form of bulk platinum in oxygen saturated water at ambient conditions is the completely hydrated platinum(IV)oxide, PtO₂·4H₂O, also referred to as platinic acid H₂Pt(OH)₆ (Burke and Lyons, 1986; Pourbaix, 1966) with a standard Gibbs energy of formation of -84 kJ mol⁻¹. The formation of this compound will be even more favored in the case of incompletely coordinated platinum.

The literature on the oxidation of platinum in aqueous media is essentially limited to the electrochemical oxidation of bulk platinum. Angerstein-Kozlowska et al. (1973) investigated the initial stages of electrochemical oxidation in 0.5 M H₂SO₄ at room temperature. It was concluded by deconvolution of the fine structure in the broad anodic oxidation peak of a cyclic voltammogram that the oxidation proceeds by formation of different surface lattices of hydroxide species. Part of the adsorbed hydroxide rearranges, according the authors, to a form of subsurface hydroxide. Ross (1977) however attributed the observed fine structure to sulfate anion adsorption as it is not present with HF as electrolyte. Peuckert and Bonzel (1984) concluded from XPS measurements that an electrochemically grown oxide film on platinum (111) in acid medium consists of Pt(OH)₄ (PtO₂·2H₂O), which was confirmed by Wagner and Ross (1985) for Pt (100) using AES, XPS and Temperature Programmed Desorption. In al-
kaline media a compound with stoichiometry PtO(OH)$_2$ was proposed on Pt (111) (Peuckert and Bonzel, 1984). Burke and Lyons (1986) explained anodic charging curves, measured on polycrystalline platinum in different aqueous buffers, giving a pH ranging from 1 to 12, by initial formation of a charged anionic species such as [Pt$_2$O·OH]$^-\cdot$

According to Burke and Roche (1984) the electrochemical formation of a hydrous oxide film is easily achieved in acid and alkaline media but is difficult to achieve at intermediate pH values. The film formed in base could, however, not be reduced easily (Burke and Roche, 1984; Burke and O'Dwyer, 1992).

It is clear that the oxidation of platinum proceeds by different routes and leads to different stable compounds when comparing the oxidation of highly dispersed platinum by oxygen gas and the aqueous electrochemical oxidation of bulk platinum. In this chapter the extent to which the effects of exposure of highly dispersed platinum to oxygen depend on the medium will be investigated by means of X-ray Absorption Spectroscopy. Part of this work has been published earlier (van den Tillaart, 1993). For this work all data has been analyzed again, which resulted in some small quantitative and qualitative changes. These changes did, however, not influence the main conclusions of the publication.

### 3.1.1. Background of X-ray Absorption Spectroscopy

The absorption coefficient for X-ray radiation decreases generally with increasing photon energy. When however the photon energy is sufficient to eject an electron out if its orbital, the absorption coefficient increases sharply. This sharp increase of the absorption coefficient is called an absorption edge. As the energy levels of electrons are element specific, edges are also specific for a certain element. Figure 3.1 shows the platinum L$_{III}$ and L$_{II}$ edges measured on a sample of catalyst B0. The L$_{III}$ edge arises from absorption of the photon by a 2p$_{3/2}$ core state electron, the L$_{II}$ edge from absorption by a 2p$_{1/2}$ core state electron.

The feature visible in Figure 3.1 as a very sharp increase of the absorption coefficient on top of the L$_{III}$ platinum edge is called the white-line. Such a white-line is also present at the L$_{II}$ platinum edge, but is less pronounced. The white-line results from the excitation of a core state electron to a vacant energy level just above the Fermi level.
of the metal (Mansour et al., 1984). The dipole selection rules, $\Delta l = \pm 1$ and $\Delta J = 0, \pm 1$, enable the transition from the $2p_{3/2}$ core state to the empty states above the Fermi level of the $5s_{2s}$, $5d_{2p}$, and $5d_{2p}$ bands, and from the $2p_{3/2}$ core state to the empty states of the $5s_{2s}$ and $5d_{2p}$ bands. The contribution to the absorption by the final s-states is much smaller than the contribution of the final d-states as the density of s-states is much lower. As the density of vacant $5d_{2p}$ states in metallic platinum is much higher than the density of vacant $5d_{2p}$ states, the white-line of the $L_{III}$ edge is less pronounced than the white-line of the $L_{II}$ edge.

The $L_{III}$ and $L_{II}$ edge white-line surface area of 5d metals is thus a measure for the d-band occupancy, or better the d-band vacancy (Lyttle et al., 1988). As small reduced platinum and iridium clusters were reported to be electron deficient compared to the bulk metal (Lyttle et al., 1988) the white-line surface area can only provide information on the relative degree of oxidation of the metal when the platinum particle size does not change.

Another important feature visible in Figure 3.1 is the fine structure starting just after the platinum $L_{III}$ absorption edge and extending to about 1 keV after the edge. This region is called the Extended X-ray Absorption Fine Structure, or EXAFS for short. The observed oscillation is the result of a modulation of the absorption probability by interference of the outgoing photoelectron wave from the absorber atom with the back-scattered wave from a surrounding atom. Hence, the oscillation contains information on the average local environment of the absorber atom in the form of atom type, coordination number, interatomic distance, and disorder of the different shells of surrounding atoms.

3.2. Experimental

3.2.1. The in-situ XAS-cell

The in-situ XAS-cell was designed to contact catalyst samples with aqueous as well as gaseous media. Figure 3.2 shows the construction of this cell.

The cell consists of 2 flanges, a front and a back flange, a housing and a sample holder. The front flange keeps the sample holder with catalyst sample together with the two mylar windows at its place in the housing. The catalyst in the sample holder can be contacted with liquid or gas by two connections on the top and the bottom of the housing. The housing can be kept at a certain temperature by a flow of water from a warm water bath through a tubular channel along the front and back side of the housing. The connections for this channel are situated on the front and back flange.
3.2.2. XAS measurements

Catalyst samples were pressed as a wafer in the stainless steel or perspex sample holder. The amount of catalyst was determined to give a total absorption of 2.5, leading to samples of about 100 mg. It was calculated that, due to diffusion limitations, the aqueous samples needed at least 11 hours pretreatment in order to attain monolayer coverage of the platinum with oxygen or hydrogen throughout the sample (see Appendix A.1). A pretreatment time of 20 hours was chosen.

The X-ray absorption measurements were performed at station 9.2 of the SRS at Daresbury (UK) with an electron beam energy of 2 GeV and a stored current varying between 290 and 160 mA. The wiggler was operational at 5.0 Tesla. Data were collected in the transmission mode from 11.37 keV to 13.43 keV (Pt L\textsubscript{III}-edge: 11.564 keV, Pt L\textsubscript{II}-edge: 13.273 keV) with a Si (220) monochromator detuned to 50% of the maximum intensity for harmonic rejection. The ion chambers were filled with gas mixtures optimized to suit the measuring conditions. Energy calibration was monitored using a gold foil or a platinum foil and a third ion chamber, and was set at 11.919 keV at the Au L\textsubscript{III}-edge or 11.564 keV for the Pt L\textsubscript{III}-edge. The spot size was reduced with the entrance slits to give a spot of 1 mm height and 10 mm width. Energy
resolution was estimated to be 2.2 eV. Samples were scanned 8 times to determine the error in the data and to improve the data quality by averaging.

3.2.3. XANES data analysis

There is no generally accepted method for the determination of the white-line surface area of platinum. The methods proposed by Gallezot et al. (1979) and Mansour et al. (1984) are sensitive to the local environment of the absorber. This becomes especially evident when oxidized samples are compared with reduced samples. Horsley (1982), however, used a deconvolution based on absorption theory, which is quite insensitive to the local structure of the central absorber. This method is therefore more appropriate to compare the white-line surface areas of platinum samples with a different local structure and will be followed in this work.

The white-line surface area was determined using the data of a single XAS measurement. The Pt L_{III} and L_{II} edge region (-100 to 100 eV relative to edge) were isolated, the energy rescaled relative to the edge, the pre-edge background was subtracted by using a Victoreen approximation and the data were finally normalized by the edge jump.

The data were subsequently deconvoluted to the sum of an arctangent and a Lorentzian function as described by Horsley (1982):

\[ \hat{\mu} = \frac{1}{2} + \frac{1}{\pi} \arctan \left( \frac{p_1 (E - p_2)}{1 + p_4 (E - p_5)^2} \right) + \frac{p_3}{1 + p_4 (E - p_5)^2} \]  

(3.1)

in which \( \hat{\mu} \) is the calculated normalised absorption coefficient, \( E \) is the energy relative to the edge and \( p_1 \) to \( p_5 \) are the adjustable regression parameters. Maximum likelihood parameter estimates were obtained by applying a Marquardt algorithm to minimize the sum of squared residuals between the calculated and observed normalised absorption coefficient.

The white-line surface area was obtained as the integrated Lorentzian part of the regression function:

\[ A = \int_{-\infty}^{\infty} \frac{p_1}{1 + p_4 (E - p_5)^2} dE = \frac{p_1 \pi}{\sqrt{p_4}} \]  

(3.2)

The L_{II} surface area was corrected to the same scale as the L_{III} surface area by multiplication with the quotient of the specific edge jumps.
3.2.4. EXAFS data analysis

Data analysis was performed with software developed at the Laboratory of Inorganic Chemistry and Catalysis of the Eindhoven University of Technology (Vaarkamp, 1993) and follows mainly the procedure described by Sayers and Bunker (1988).

The pre-edge background was subtracted by using a Victoreen approximation. Glitches and jumps were removed by using a spline approximation through the neighboring data. The edge energy, $E_0$, was taken as the position of the inflection point in the absorption edge. The energy scale, $E$, was transposed to the photoelectron wave number scale, $k$, according to:

$$ k = \sqrt{\frac{8m\pi^2}{h^2}(E - E_0)} $$

(3.3)

in which $m$ is the electron mass, $h$ is Planck's constant and $E$ is the photon energy.

To isolate the EXAFS oscillations, the background absorption was subtracted using a flexible spline approximation, $\tilde{\mu}(k)$, and chi-data, $\chi(k)$, were produced after normalization of the data by the edge jump, $\Delta\mu$:

$$ \chi(k) = \frac{\mu(k) - \tilde{\mu}(k)}{\Delta\mu} $$

(3.4)

Replicate chi-data were averaged to yield the final chi-data and an estimate of the experimental error in the data: the standard deviation, $s$.

A Fourier filter was used to isolate the shells of interest. The filter was applied on the $k^2$ weighted final chi-data. For the reduced samples a $k$-range of $3.1 \times 10^{10}$ m$^{-1}$ to $16 \times 10^{10}$ m$^{-1}$ was used for the forward Fourier transformation. Such a Fourier transformation transposes the $k$-axis with a dimension of reciprocal meters to a $R$-axis with a dimension of meters. This $R$ value is close to but not equal to the interatomic distance. A $R$-range of $1.3 \times 10^{-10}$ m to $3.3 \times 10^{-10}$ m was used for the backward transformation. For the oxidized samples a $k$-range of $2.8 \times 10^{10}$ m$^{-1}$ to $13 \times 10^{10}$ m$^{-1}$ and a $R$-range of $0.6 \times 10^{-10}$ m to $3.1 \times 10^{-10}$ m was used.

The Fourier filtered chi-data was finally used to estimate the adjustable parameters in the EXAFS model equation. Phase shift and amplitude functions were extracted from reference compounds according to Table 3.1.
Table 3.1 Crystallographic data for the reference compounds with used filter parameters. References for Pt-Pt: Wyckoff, 1963; Pt-O: Trömel and Lupprich, 1975 and Pt-C: Koch et al., 1977.

This allows to simplify the EXAFS model equation for an unoriented sample with small or Gaussian disorder to (Sayers and Bunker, 1988):

\[
\hat{\chi}(k) = \sum_j \frac{N_j}{kR_j^2} F_j(k) \exp\left(-2k_j^2(\Delta\sigma^2)_j\right) \sin\left(2k_jR_j + \delta_j(k)ight)
\]

(3.5)

in which \(\hat{\chi}(k)\) is the calculated EXAFS oscillation, \(N_j\) is the number of atoms in the \(j\)th shell, \(R_j\) is the mean distance between the central absorber and the \(j\)th shell, \(F_j(k)\) and \(\delta_j(k)\) are respectively the amplitude function and the phase shift function for the atom in the \(j\)th shell and \((\Delta\sigma^2)_j\) is the relative mean square displacement of an atom in the \(j\)th shell. The amplitude function, \(F_j(k)\), is defined as:

\[
F_j(k) = S_0^2 e^{(-2R/\lambda)} e^{-2k^2\sigma^2} F(k)
\]

(3.6)

in which \(S_0^2\) accounts for the relaxations and multi-electron excitations, \(\lambda\) is the free path length of the photoelectron, \(\sigma^2\) the mean square displacement and \(F(k)\) the backscattering amplitude. The photoelectron wave number, \(k\), is defined for the \(j\)th shell as:

\[
k_j = \sqrt{\frac{8\pi n^2}{h^2}} (E - E_0 - E_{e,j})
\]

(3.7)

in which \(m\) is the electron mass, \(h\) is Planck's constant, \(E\) is the photon energy, \(E_0\) is the edge energy and \(E_{e,j}\) is the energy correction for the \(j\)th shell.

The best regression was determined using a minimization routine incorporated into the program which minimized the sum of squared residuals between the calculated and ob-
served EXAFS oscillation, $\hat{\chi}(k)$ and $\chi(k)$. The minimization was usually done using $k^2$-weighted chi data to compensate for the lower amplitude of the oscillations at higher $k$ values. The result was visually verified by comparing the $k^1$ and $k^3$ weighted Fourier transforms of the regression and the contributions of each regressed shell separately to the acquired data.

As most shells contribute to the total EXAFS signal with a different frequency, Fourier transformation of the EXAFS signal reveals the contribution of a single shell as a peak. This peak is mostly not symmetric and is not correctly located at the interatomic distance as results of the $k$-dependency of the amplitude function and the phase shift function. Correcting the Fourier transform with a amplitude function and phase shift function, which are of course element specific, results in more symmetric peaks which are located at the correct interatomic distance for the contributions of that specific element.

The maximum number of degrees of freedom, $n_r$, of the oscillating signal was estimated by the program using the Nyquist theorem:

$$n_r = \frac{2\Delta k \Delta R}{\pi} + 1 \quad (3.8)$$

This maximum number of degrees of freedom amounts for the reduced samples in this work to 14 and for the oxidized samples to 17. The large difference is mainly caused by the large $R$ range used for the back transformation of the data for the oxidized samples.

The goodness of fit, $\varepsilon^2$, was determined by the program using:

$$\varepsilon^2 = \frac{n_r}{n_{obs}(n_r - n_{par})} \sum_{s=1}^{n_{par}} \left( \frac{\chi_s - \hat{\chi}_s}{s} \right)^2 \quad (3.9)$$

in which $n_{obs}$ is the actual number of observations in the $k$-range used for regression, typically 200, and $n_{par}$ is the number of estimated parameters.

3.2.5. Sample treatment

The following sample treatments were used for the XAS characterization.

- The basic catalyst samples, referred to as O2G, received no further treatment as they were already exposed to ambient air in the preparation process of the catalyst.
- Samples, referred to as H2G, were treated in-situ with flowing hydrogen gas at atmospheric pressure and room temperature.
The aqueous samples, H2L and O2L, were all exposed ex-situ to hydrogen saturated distilled water at atmospheric pressure and 363 K for 20 hours prior to further treatment. The pH of the water after contacting with the catalyst sample amounted to 5 due to the presence of acidic groups on the graphite support.

- The sample, H2L, was subsequently contacted in-situ with hydrogen saturated distilled water at atmospheric pressure and ambient temperature.
- The sample, O2L, was exposed ex-situ to oxygen saturated distilled water at atmospheric pressure and 323 K for 20 hours and subsequently contacted in-situ with oxygen saturated distilled water at atmospheric pressure and ambient temperature. By using a perspex sample holder for this sample absence of cathodic protection was assured.

Other aqueous samples were prepared as described above except that they were prepared in an acidic solution of 0.1 M HClO4 (pH=1) or an alkaline solution of 0.1 M NaOH (pH=13). The labels for these samples are extended with an "a" for the acidic samples and with a "b" for alkaline samples, e.g. H2La refers to a sample that received the same treatment as sample H2L except that was done in 0.1 M HClO4 rather than in water.

3.3. Results and discussion

3.3.1. Structure of the catalyst in ambient air

The sample from which all other samples are derived, sample O2G, is discussed first.

<table>
<thead>
<tr>
<th>sample</th>
<th>e^2</th>
<th>shell</th>
<th>N [-]</th>
<th>R [10^-10 m]</th>
<th>Δσ^2 [10^-23 m²]</th>
<th>E_c [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2G</td>
<td>21.1</td>
<td>O</td>
<td>2.72±0.09</td>
<td>2.075±0.004</td>
<td>412±51</td>
<td>2.47±0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>3.03±1.16</td>
<td>2.735±0.020</td>
<td>685±328</td>
<td>4.85±2.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt*</td>
<td>0.60±0.97</td>
<td>3.085±0.080</td>
<td>200±965</td>
<td>5.00±9.80</td>
</tr>
<tr>
<td>H2G</td>
<td>0.4</td>
<td>C</td>
<td>1.61±0.34</td>
<td>2.660±0.018</td>
<td>375±425</td>
<td>-2.61±1.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.03±0.45</td>
<td>2.757±0.003</td>
<td>390±031</td>
<td>5.28±0.47</td>
</tr>
<tr>
<td>H2L</td>
<td>0.5</td>
<td>C</td>
<td>1.56±0.26</td>
<td>2.626±0.014</td>
<td>193±248</td>
<td>-0.98±1.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.56±0.43</td>
<td>2.757±0.002</td>
<td>418±029</td>
<td>5.16±0.40</td>
</tr>
</tbody>
</table>

Table 3.2 Parameter estimates with standard deviation from the EXAFS analysis of samples O2G, H2G and H2L of catalyst A0 (*= not all parameters regressed simultaneously).

This sample consists of catalyst which was stored after preparation exposed to ambient air. The results for the EXAFS analysis of sample O2G of catalyst A0 in Table 3.2 show a Pt-O coordination of 2.7 neighbors at an interatomic distance of 2.08 10^-10 m
and a Pt-Pt coordination of 0.6 at a distance of \( 3.1 \times 10^{-10} \) m which distances are both typical for PtO$_2$.

Another large contribution to the EXAFS of sample O2G consists of a shell of Pt with a coordination number of 3 at a distance of 2.74 \( 10^{-10} \) m. This distance is somewhat shorter than the interatomic distance of 2.775 \( 10^{-10} \) m in bulk fcc platinum.

The white-line surface area determination, see Table 3.3 and Figure 3.6, clearly shows the high surface area of sample O2G compared to the white-line surface area of the reduced samples, H2G and H2L. This indicates a high degree of oxidation.
These observations on sample O2G are consistent with oxidized platinum particles made up of a core of metallic platinum covered by a shell of platinum oxide, PtO₂, as has already been discussed in the introduction.

3.3.2. Structure of the reduced catalyst

The structure of reduced catalyst was investigated by exposing the sample discussed in the previous section, sample O2G, to hydrogen gas at ambient temperature, sample H2G. Figure 3.4 shows the k²-weighted Fourier transform of samples H2G and O2G of catalyst A0. It is clear from this figure that the local structure around platinum has changed drastically upon exposure to hydrogen. The maximum for sample O2G at 1.6 × 10⁻¹⁰ m, arising from a Pt-O interaction at an interatomic distance of about 2.05 × 10⁻¹⁰ m, is shifted to 2.5 × 10⁻¹⁰ m, arising from a Pt-Pt interaction at a distance of about 2.77 × 10⁻¹⁰ m, for sample H2G.

The results of the EXAFS analysis of these samples are given in Table 3.2 and in Figure 3.3. Sample H2G shows a Pt-C interaction, resulting from the support, with a coordination of 1.6 at a distance of about 2.6 × 10⁻¹⁰ m and a Pt-Pt coordination of 8.0 at a distance of 2.76 × 10⁻¹⁰ m. The high Pt-C coordination number indicates an intimate contact of the platinum crystallite with the graphite support. This coordination number is even high compared to that found for very small platinum particles on oxidic supports (Vaarkamp, 1993) and indicates that platinum in the interface is coordinated to 6 carbon neighbors in contrast to the 3 oxygen neighbors on oxidic supports.

The first shell Pt-Pt distance of 2.76 × 10⁻¹⁰ m is in good agreement with the interatomic distance of 2.775 × 10⁻¹⁰ m in bulk fcc platinum. An elongation of the first shell Pt distance, due to electron transfer from the graphite support to the metal, as was earlier reported for highly dispersed Pt/graphite catalysts, FE=0.8, by Richard et al. (1988) cannot be observed. The obverse, the contraction of the Pt-Pt distance, cannot be concluded either from the data as the uncertainty in distances determined with EXAFS amounts to approximately 1%.

Kip et al. (1987) correlated the first shell Pt-Pt coordination number with the hydrogen to metal ratio H/M as determined with H2 chemisorption. They also made calculations to correlate the H/M ratio to the fraction of exposed surface atoms assuming spherical particles and raft-like particles. Using their data a first shell Pt-Pt coordination number of 8.0 amounts to a fraction exposed of about 0.75 for spherical particles. With STEM
Chapter 3.

micrograph analysis a FE of 0.70 and with CO pulse chemisorption a FE of 0.75 was determined for this catalyst sample. The white-line surface area determination, see Table 3.3 and Figure 3.6, clearly shows the low surface area of sample H2G compared to the white-line surface area of the oxidized sample, O2G. This clearly illustrates the reduction of sample O2G to sample H2G upon exposure to hydrogen gas at ambient temperature.

There is some discussion in literature about the preferred crystal structure of small platinum particles. Renouprez et al. (1980) concluded from EXAFS measurements that the structure of a Pt/SiO2 catalyst with platinum particles of 1.8 nm could be well described with a 5% contracted fcc structure, whereas a Pt/zeolite catalyst with platinum particles of 1.1 nm could be better described by a 7% contracted icosahedron, which is not a fcc structure. Joyner and Meehan (1983) studied EUROPT-1, a 6.3 wt% Pt/SiO2 catalyst, and a 2.5 wt% Pt/C catalyst with platinum particles larger than 1.8 nm. They concluded for both catalysts that the fcc structure is maintained even in platinum particles as small as 1.8 nm.

Their conclusion is also supported by this work. Figure 3.5 shows the for the platinum-platinum interaction phase and amplitude corrected Fourier transforms of the EXAFS of a platinum foil, sample H2G of catalyst B0, and sample H2G of catalyst B3. It is clear from this figure that even in platinum particles as small as in catalyst B0, with an average platinum particle size of 1.48 nm, the same fcc structure as in the platinum foil is maintained with interatomic distances quite close to the fcc Pt-Pt distances in bulk platinum of 2.775, 3.934, 4.806 and 5.550 10-10 m.

3.3.3. Reduction of the catalyst in aqueous media

The reduction of catalyst in hydrogen saturated distilled water was investigated by comparing the results of samples H2G and H2L of catalyst sample A0. The results of
the EXAFS analysis are shown in Table 3.2. Samples H2L and H2G are quite similar with the exception of the somewhat higher Pt-Pt coordination number of sample H2L. The results of the white-line regression can be found in Table 3.3 and in Figure 3.6. It is quite clear from these results that sample H2L is as well-reduced as sample H2G.

The observations on samples H2G and H2L show the ease of reduction of oxidized platinum particles. Exposure to hydrogen gas at room temperature or to hydrogen saturated water at 363 K is sufficient to reduce the platinum particles completely.

<table>
<thead>
<tr>
<th>treatment</th>
<th>LIII-edge [eV]</th>
<th>LII-edge [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2G</td>
<td>7.66</td>
<td>0.48</td>
</tr>
<tr>
<td>H2L</td>
<td>7.62</td>
<td>0.35</td>
</tr>
<tr>
<td>O2G</td>
<td>9.93</td>
<td>4.27</td>
</tr>
<tr>
<td>O2L</td>
<td>7.35</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table 3.3 White-line surface areas from deconvolution of the platinum L-edges for various samples of catalyst A0.

Figure 3.6 Typical results of white-line regression of the normalised platinum L-edges. Results are shown for various samples of catalyst A0. Boxes: experimental data; full lines: contributions of Lorentzian part and arctangent part and the total regression according to equation 3.1.

The effect of the pH of the hydrogen saturated solution on the reduction was investigated by comparing the results of samples H2La, H2Lb and H2G of catalyst sample E0. Figure 3.7 shows the for the platinum-platinum interaction phase and amplitude corrected Fourier transforms of the EXAFS of these samples. It is clear from this figure that the distance and type of interaction in all three samples are equal.
Only the coordination number is increased significantly when going from sample H2G to sample H2La and H2Lb. This observation is confirmed quantitatively by the results of the EXAFS analysis in Table 3.4.

It is clear from Table 3.4 that the first shell platinum coordination number increases from 8.0 for the sample reduced with hydrogen in the gas phase at an ambient temperature to 8.7 for the sample reduced with hydrogen dissolved in a 0.1 M solution of HClO4 at 363 K and even to 9.7 for the sample reduced with hydrogen dissolved in a 0.1 M solution of NaOH at 363 K. The other regression parameters do not significantly differ between the different samples.

The same trend is visible when the results for sample H2G and H2L of catalyst A0 in Table 3.2 are examined more closely. The first shell platinum coordination number increased slightly from 8.0 to 8.6, whereas the other regression parameters did not significantly change.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\varepsilon_\gamma^2$ [-]</th>
<th>shell</th>
<th>N [-]</th>
<th>R $[10^{-10}$ m$]$</th>
<th>$\Delta \sigma^2 [10^{-25}$ m$^2]$</th>
<th>$E_c$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2G</td>
<td>0.6</td>
<td>C</td>
<td>1.28±0.26</td>
<td>2.571±0.016</td>
<td>0.02±0.016</td>
<td>6.97±1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.02±0.42</td>
<td>2.745±0.002</td>
<td>4.26±0.29</td>
<td>5.40±0.42</td>
</tr>
<tr>
<td>H2La</td>
<td>0.6</td>
<td>C</td>
<td>1.14±0.29</td>
<td>2.551±0.019</td>
<td>1.02±0.24</td>
<td>7.41±2.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.66±0.43</td>
<td>2.750±0.002</td>
<td>4.20±0.28</td>
<td>5.31±0.39</td>
</tr>
<tr>
<td>H2Lb</td>
<td>0.8</td>
<td>C</td>
<td>1.30±0.22</td>
<td>2.604±0.013</td>
<td>0.31±0.19</td>
<td>-0.64±1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>9.74±0.39</td>
<td>2.751±0.002</td>
<td>3.90±0.23</td>
<td>5.26±0.32</td>
</tr>
</tbody>
</table>

Table 3.4 Parameter estimates with standard deviation from the EXAFS analysis of samples H2G, H2La and H2Lb of catalyst E0.

It is quite clear from these results that the platinum particles grow during the 20 hours of reduction with dissolved hydrogen at 363 K. This growth is also dependent on the pH of the solution. In the acidic solution pH=1, and the slightly acidic solution, pH=5, the first shell platinum coordination number increased from 8.0 to 8.6 which is according Kip et al. (1987) equivalent to a change in FE from 0.75 to 0.69. In the
alkaline solution, pH=13, the first shell platinum coordination number increased dramatically from 8.0 to 9.7 equivalent to a change in FE from 0.75 to 0.47. This extra growth in alkaline media can probably be attributed to the formation of platinum hydroxide complexes which are responsible for the net transport of platinum ions from small to large particles.

3.3.4. Oxidation of the catalyst in aqueous media

The oxidation of small platinum particles in water was investigated by contacting a H2L sample of catalyst A0 with oxygen saturated water at 323 K for 20 hours to obtain sample O2L. Figure 3.8 shows the k²-weighted Fourier transform of samples H2L, O2G and O2L of catalyst A0. It is clear from this figure that EXAFS of sample O2L is quite different from the EXAFS of both sample H2L and sample O2G. There is no peak present at 1.6 10⁻¹⁰ m as is the case for sample O2G. As this peak is attributed to the presence of an oxidic Pt-O shell it is clear that sample O2L is not strongly oxidized. This is also indicated by the white-line surface areas given in Table 3.3. The white-line surface areas are not significantly different for samples H2G, H2L and O2L, but these do significantly differ from those of sample O2G.

<table>
<thead>
<tr>
<th>sample</th>
<th>r²</th>
<th>shell</th>
<th>N</th>
<th>R [10⁻¹⁰ m]</th>
<th>Δσ² [10⁻²⁵ m²]</th>
<th>Eₜ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2G</td>
<td>21.1</td>
<td>O</td>
<td>2.72±0.09</td>
<td>2.075±0.004</td>
<td>412±051</td>
<td>2.47±0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>3.03±1.16</td>
<td>2.735±0.020</td>
<td>685±328</td>
<td>4.85±2.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt*</td>
<td>0.60±0.97</td>
<td>3.085±0.080</td>
<td>200±965</td>
<td>5.00±9.80</td>
</tr>
<tr>
<td>H2L</td>
<td>0.5</td>
<td>C</td>
<td>1.56±0.26</td>
<td>2.626±0.014</td>
<td>193±248</td>
<td>-0.98±1.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.5±0.43</td>
<td>2.757±0.002</td>
<td>418±029</td>
<td>5.16±0.40</td>
</tr>
<tr>
<td>O2L</td>
<td>2.3</td>
<td>O</td>
<td>0.59±0.43</td>
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<td>520±532</td>
<td>1.34±6.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C*</td>
<td>0.74±1.06</td>
<td>2.207±0.071</td>
<td>400±959</td>
<td>-2.04±15.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.12±0.41</td>
<td>2.752±0.003</td>
<td>518±034</td>
<td>3.10±0.54</td>
</tr>
</tbody>
</table>

Table 3.5 Parameter estimates with standard deviation from the EXAFS analysis of samples O2G, H2L and O2L of catalyst A0 (*= not all parameters regressed simultaneously).
The amplitude of the peak at $2.5 \times 10^{-10}$ m is lowered significantly with respect to the peak of sample H2L. This could be the result of a lower first shell Pt coordination number. However, close examination of the shoulder at $2.1 \times 10^{-10}$ m reveals that this shoulder is not lowered in proportion to the main peak. It is thus more probable that the Pt-C interaction at an estimated interatomic distance of $2.6 \times 10^{-10}$ m, see Table 3.2, has shifted to a shorter distance.

![Figure 3.9 EXAFS analysis of sample O2L of catalyst A0. Full lines: observed; dotted lines: regressed with equation 3.5. A) $k^2$-weighted chi, B) $k^3$-weighted Fourier transform, and C) $k^3$-weighted Fourier transform.](image)

These observations are substantiated by the regression analysis results in Table 3.5 and Figure 3.9. The results for sample H2L and O2G are repeated from Table 3.2.

The EXAFS analysis reveals a small contribution from a Pt-O shell with a coordination number of 0.6 at an interatomic distance of $2.03 \times 10^{-10}$ m. The Pt-C coordination stemming from the particle support interaction is indeed shifted to an interatomic distance of $2.2 \times 10^{-10}$ m and the coordination number is somewhat lowered compared to the Pt-C coordination number in sample H2L. Such a shift of the metal-support distance has been reported more often in literature according to the recent review of EXAFS studies on the metal-support interface by Koningsberger and Gates (1992). Short metal-support distances of about $2.15 \times 10^{-10}$ m and long metal-support distances between $2.5$ and $2.7 \times 10^{-10}$ m have been observed for the metal-O bond on oxidic supports. This long metal-support distance was present only after reduction at temperatures up to 573 K. Reduction at higher temperatures resulted irreversibly in a short metal-support distance. Vaarkamp (1993) attributes these different distances to the absence or presence of interfacial hydrogen, i.e. a layer of hydrogen between the metal particle and the support. When this interfacial hydrogen is present the metal-
support Pt-O bond is elongated. Interfacial hydrogen can also explain the observed difference in the metal-support Pt-C distance as the interfacial hydrogen present in sample H2L, and resulting in a long Pt-C distance of $2.6 \times 10^{-10}$ m, can be easily removed by platinum catalyzed oxidation with oxygen to water, resulting in a Pt-C distance of $2.2 \times 10^{-10}$ m. Moreover, the observed Pt-C distance in sample O2L compares quite well to the Pt-C distance of $2.25 \times 10^{-10}$ m for benzene adsorption on platinum according to Somorjai (1990).

As sample O2L contains a contribution of 0.6 Pt-O at a typical distance for PtO$_2$ and the white-line surface area indicates no significant degree of oxidation, this contribution is most probably the result of a chemisorbed oxide or hydroxide species. The first shell Pt-Pt coordination number of sample O2L appears to be somewhat lowered compared to sample H2L. This difference could indicate a restructuring of the platinum surface with the adsorbed oxide or hydroxide species into a rearranged subsurface species as was reported by Angerstein-Kozlowska et al. (1973). These conclusions are in agreement with the literature on the electrochemical oxidation of bulk platinum in aqueous media (Angerstein-Kozlowska et al., 1973; Burke and Lyons, 1986; Peuckert and Bonzel, 1984; Wagner and Ross, 1985; Weber et al., 1988).

The effect of the pH of the oxygen saturated solution on the oxidation was investigated by comparing the results of samples O2La, O2Lb and O2G of catalyst E0. The $k^2$-weighted Fourier transforms of the EXAFS of these samples are shown in Figure 3.10. Both in samples O2La and O2Lb the peak for the first platinum shell is more markedly present at $2.5 \times 10^{-10}$ m than in sample O2G. This confirms that the gas phase oxidation is more destructive for the structure of the particle. Also a peak is clearly present in both these samples at $2.10^{-10}$ m. This peak consists most probably of a shoulder of the main Pt-Pt peak at $2.5 \times 10^{-10}$ m and a Pt-C contribution at an interatomic distance of about $2.2 \times 10^{-10}$ m. Sample O2G and O2Lb show an almost equal contribution of a Pt-O shell at $1.6 \times 10^{-10}$ m. The contribution of the Pt-O shell in sample O2La is much lower.

The results of the regression analysis of the EXAFS of these samples are, together with the data for samples H2G, H2La and H2Lb from Table 3.4, given in Table 3.6 and Figure 3.11.
The above observations are confirmed by the regression results. Sample O2G is clearly oxidized as is indicated by the presence of 2.2 Pt-O at an interatomic distance of 2.02 $10^{-10}$ m, the lower Pt-Pt coordination of 5.4, relative to the reduced sample H2G, and the relatively high Debye-Waller factor of 880 $10^{-25}$ m$^2$.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\varepsilon^2$ [-]</th>
<th>shell</th>
<th>N [-]</th>
<th>R [$10^{-10}$ m]</th>
<th>$\Delta\sigma^2$ [$10^{-25}$ m$^2$]</th>
<th>$E_e$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2G</td>
<td>0.6</td>
<td>C</td>
<td>1.28±0.26</td>
<td>2.571±0.016</td>
<td>062±193</td>
<td>6.97±1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.02±0.42</td>
<td>2.745±0.002</td>
<td>426±029</td>
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<tr>
<td>O2G</td>
<td>3.4</td>
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<td>H2La</td>
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<td>C</td>
<td>1.14±0.29</td>
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<td>7.41±2.10</td>
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<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.66±0.43</td>
<td>2.750±0.002</td>
<td>420±028</td>
<td>5.31±0.39</td>
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<td>O2La</td>
<td>1.8</td>
<td>O</td>
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<td>C*</td>
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<tr>
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<td></td>
<td>Pt</td>
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<td>517±039</td>
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<td>0.8</td>
<td>C</td>
<td>1.30±0.22</td>
<td>2.604±0.013</td>
<td>031±198</td>
<td>-0.64±1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>9.74±0.39</td>
<td>2.751±0.002</td>
<td>390±023</td>
<td>5.26±0.32</td>
</tr>
<tr>
<td>O2Lb</td>
<td>6.6</td>
<td>O</td>
<td>2.48±0.31</td>
<td>2.062±0.006</td>
<td>497±097</td>
<td>2.47±1.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C*</td>
<td>1.88±1.38</td>
<td>2.280±0.033</td>
<td>487±552</td>
<td>0.98±4.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>5.84±0.41</td>
<td>2.767±0.004</td>
<td>503±046</td>
<td>0.23±0.80</td>
</tr>
</tbody>
</table>

Table 3.6 Parameter estimates with standard deviation from the EXAFS analysis of samples H2G, O2G, H2La, O2La, H2Lb and O2Lb of catalyst E0 (*= not all parameters regressed simultaneously).

Sample O2La contains a Pt-O contribution with a coordination number of 1.1 at a distance of 2.03 $10^{-10}$ m, a short metal-support bond of 2.24 $10^{-10}$ m with a coordination number of 2.2, and a Pt-Pt contribution of 6.9 at 2.76 $10^{-10}$ m. The presence of the Pt-O contribution and the lowered Pt-Pt coordination from 8.7 to 6.9 indicate also a corrosive oxidation. The structure is however not as much disturbed as is the case for sample O2G as can be observed from the low Debye-Waller factor of 517 $10^{-25}$ m$^2$.

Sample O2Lb is even more oxidized than sample O2La as appears from the higher Pt-O coordination of 2.5 at a distance of 2.06 $10^{-10}$ m, and the very dramatic decrease in the Pt-Pt coordination number from 9.7 to 5.8. The Debye-Waller factor for the Pt-Pt shell indicates however that the structure is less disturbed than in sample O2G.
Figure 3.11 EXAFS analysis of oxygen and hydrogen exposed samples of catalyst E0. Full lines: observed; dotted lines: regressed with equation 3.5. Sample O2G: A) $k^2$-weighted chi, B) $k^1$-weighted Fourier transform, and C) $k^3$-weighted Fourier transform. Sample O2La: D) $k^2$-weighted chi, E) $k^1$-weighted Fourier transform, and F) $k^3$-weighted Fourier transform. Sample O2Lb: G) $k^2$-weighted chi, and H) $k^1$-weighted Fourier transform.
The results of the EXAFS analysis are verified with the results of the white-line surface area determination as given in Table 3.7. It is clear from this table that the number of d-band vacancies, or the degree of oxidation, is increasing when going from sample O2La via O2Lb to O2G.

The total of results for the oxidation of small platinum particles seem to indicate that the presence of ions greatly enhances the susceptibility of the platinum particle to oxidation. In distilled water saturated with oxygen the particles are not significantly oxidized as is shown previously, whereas in a solution of 0.1 M HClO₄ or 0.1 M NaOH saturated with oxygen the particles are clearly oxidized. Also alkaline conditions seem to favor the oxidation of platinum more than acidic conditions. This is all in good agreement with the observations of Burke and Roche (1984) and Burke and O'Dwyer (1992) discussed in the introduction.

### 3.3.5. Adsorption of ethanol

The adsorption of ethanol was studied by contacting a H2L sample of catalyst A0 with a solution of 0.5 M ethanol in water at 323 K. The solution was purged with nitrogen to remove oxygen. The results of the EXAFS analysis are given in Table 3.8. The results of sample H2L before adsorption of ethanol are repeated from Table 3.2. The regression of the sample after adsorption of ethanol is graphically shown in Figure 3.12.

### Table 3.7 White-line surface areas from deconvolution of the platinum L-edges for various samples of catalyst E0.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>LIII-edge [eV]</th>
<th>LII-edge [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2G</td>
<td>7.33</td>
<td>0.54</td>
</tr>
<tr>
<td>O2La</td>
<td>7.98</td>
<td>3.02</td>
</tr>
<tr>
<td>O2Lb</td>
<td>9.30</td>
<td>3.86</td>
</tr>
<tr>
<td>O2G</td>
<td>9.71</td>
<td>4.15</td>
</tr>
</tbody>
</table>

### Table 3.8 Parameter estimates with standard deviation from the EXAFS analysis of samples H2L of catalyst E0 before and after ethanol adsorption.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \varepsilon^2 )</th>
<th>Shell</th>
<th>N [-]</th>
<th>R ([10^{-10} \text{ m}])</th>
<th>( \Delta \sigma^2 ) ([10^{-25} \text{ m}^2])</th>
<th>( E_c ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before ads.</td>
<td>0.5</td>
<td>C</td>
<td>1.56±0.26</td>
<td>2.626±0.014</td>
<td>193±248</td>
<td>-0.98±1.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.56±0.43</td>
<td>2.757±0.002</td>
<td>418±029</td>
<td>5.16±0.40</td>
</tr>
<tr>
<td>After ads.</td>
<td>0.3</td>
<td>C</td>
<td>3.59±0.57</td>
<td>2.627±0.015</td>
<td>1210±339</td>
<td>-0.04±1.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>8.52±0.44</td>
<td>2.753±0.003</td>
<td>453±030</td>
<td>6.44±0.51</td>
</tr>
</tbody>
</table>

The results clearly show that the coordination number for the Pt-C interaction has increased from 1.6 to 3.6 and that the relative Debye-Waller factor has increased from 193 to 1210 \(10^{-25} \text{ m}^2\). This relative Debye-Waller factor is so high that these results can be better explained by assuming an extra contribution of a light element like carbon or oxygen at a distance close to the original distance of the Pt-C interaction of the
support at $2.6 \times 10^{-10}$ m in sample H2L. The results thus show a clear qualitative difference between a catalyst before and after ethanol adsorption. It is however not possible to estimate simultaneously the parameters corresponding to two shells when the differences in distance and scatter behavior are small.

![Figure 3.12 EXAFS analysis of sample H2L of catalyst A0 after ethanol adsorption. Full lines: observed; dotted lines: regressed with equation 3.5. A) $k^2$-weighted chi, B) $k^4$-weighted Fourier transform, and C) $k^3$-weighted Fourier transform.](image)

The white-line surface areas do not change significantly upon adsorption of ethanol. This indicates that the adsorption of ethanol does not involve a significant electron transfer to or from the metal.

When a sample O2G of catalyst B0 was contacted with nitrogen gas, which was saturated with ethanol vapor at ambient temperature, the catalyst is partially reduced as is shown by a decrease in the white-line surface areas from 9.66 to 8.70 eV for the Pt L$_{III}$ edge and from 3.85 to 1.05 eV for the Pt L$_{II}$ edge. However, as many different shells are present between 2 $10^{-10}$ m and 3.5 $10^{-10}$ m EXAFS analysis of that sample failed.

### 3.3.6. Structure of the reduced catalyst after reaction

The structure of the catalyst after the oxidation of ethanol was studied by comparing a H2L sample of fresh catalyst A0 with a H2L sample of catalyst A0 which was used during a continuous flow experiment lasting a week at a temperature of 303 K, a partial oxygen pressure of 20 kPa, a pH of 9, and an ethanol concentration of 400 mol m$^{-3}$. The activity of the catalyst decreased by less than 10% during this experiment. The results of the EXAFS analysis are given in Table 3.9 and Figure 3.13. The results of the fresh catalyst are repeated from Table 3.2.
Table 3.9 Parameter estimates with standard deviation from the EXAFS analysis of a fresh and used sample H2L of catalyst A0.

It is clear from the results in Table 3.9 that the used catalyst has a higher coordination number for both the Pt-C and the Pt-Pt interaction. All other parameters are equal within the 66% confidence limits.

The Pt-C interaction is increased from 1.6 to 3.1. This increase can be the result of a stronger interaction of the platinum particles with the support or of platinum particles partially covered with carbon residues.

The slight increase in the coordination number of the first platinum shell of 8.6 to 8.9 indicates a growth of the platinum particle during the reaction. This finding is in agreement with the work of Schuurman et al. (1992) who found that the deactivation of a highly dispersed platinum on activated carbon catalyst, FE=0.60, and a platinum
X-ray absorption spectroscopy

on graphite catalyst, FE=0.70, during the oxidation of methyl \(\alpha\)-D-glucoside could be partially attributed to the growth of the platinum particles during reaction.

### 3.4. Conclusions

Exposure to ambient air of small reduced platinum particles leads to a strong corrosive oxidation resulting in a particle consisting of a shell of PtO\(_2\) and a core of metallic platinum. Such an oxidized particle can be reduced easily by reduction at ambient temperatures in hydrogen gas or at 363 K in hydrogen saturated water or hydrogen saturated aqueous solutions. Contacting of the catalyst with hydrogen saturated water or a hydrogen saturated 0.1 M HClO\(_4\) solution at 363 K for 20 hours leads to a small but significant growth of the platinum particles. This growth is equivalent to a decrease of the fraction of exposed platinum atoms from 0.75 to 0.69. Contacting with a hydrogen saturated 0.1 M NaOH solution at 363 K for 20 hours leads to a large growth of the platinum particles equivalent to a decrease of the fraction of exposed platinum atoms from 0.75 to 0.47.

In reduced platinum particles as small as 1.48 nm the fcc structure is retained on a graphite support. Contacting of the catalyst with oxygen saturated distilled water at 323 K for 20 hours did not lead to a significant oxidation of the platinum particles. The observed Pt-O contribution can most probably be attributed to an adsorbed hydroxide species. The Pt-C distance of the metal-support interaction was lowered from 2.6 \(10^{-10}\) m to approximately 2.2 \(10^{-10}\) m. This change could be attributed to the oxidation of the interfacial hydrogen according to Vaarkamp (1993). Contacting of the catalyst with an oxygen saturated 0.1 M HClO\(_4\) or NaOH solution at 323 K for 20 hours leads to a significant oxidation of the platinum particles. The structure of the particles is however not as disturbed as after contacting with ambient air. The presence of ions seems to enhance greatly the susceptibility of the platinum particle to oxidation. Also alkaline conditions seem to favor the oxidation of platinum more than acidic conditions.

Adsorption of ethanol on small platinum particles leads to a significant change in the EXAFS signal. This change can be attributed qualitatively to the contribution of an extra shell of a light element at a distance close to the distance of the metal-support interaction distance of Pt-C at 2.6 \(10^{-10}\) m.

The small deactivation of the platinum on graphite catalyst during the aqueous oxidation of ethanol can at least partially be attributed to a small but significant growth of the platinum particles.
3.5. References


Bassi I.W., Lyttle F.W. and Parravano G. *J. Catal.*, 42 (1976), 139


Ross P.N., *J. Electroanal. Chem.*, 76 (1977), 139


4. KINETICS OF ETHANOL OXIDATION

4.1. Introduction

The selective catalytic oxidation of alcohols and aldehydes with oxygen over highly dispersed noble metal catalysts in aqueous media has been discussed by several authors recently. Gallezot et al. (1992) reported on the catalytic oxidation of aqueous glyoxal to glyoxylic acid, Mallat and Baiker (1991a and 1991b) and Mallat et al. (1992) investigated the oxidation of 1-methoxy-2-propanol, Schuurman et al. (1992a, 1992b and 1992c) studied the oxidation of methyl α-D-glucoside and Vinke et al. (1990) oxidized 5-hydroxymethylfurfural. To obtain further insight into mechanism, kinetics and catalyst deactivation concerning these oxidation reactions this work reports on the oxidation of ethanol over a platinum on graphite catalyst as model system.

The stoichiometry of the oxidation of ethanol to ethanoate via ethanal in basic aqueous media is given by:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} + \frac{1}{2}\text{O}_2 & \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2\text{O} \\
\text{CH}_3\text{CHO} + \text{OH}^- + \frac{1}{2}\text{O}_2 & \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_2\text{O}
\end{align*}
\] (4.1)

The first stoichiometric equation corresponds to an oxidative dehydrogenation reaction while the second equation corresponds to a selective oxidation. The equilibria for both reactions are far to the right. The above equations are not only stoichiometric equations for the oxidation of ethanol to ethanoate but are also generally believed to correspond to two separate consecutive reaction paths consisting of the oxidative dehydrogenation of ethanol to ethanal and of the selective oxidation of ethanal to ethanoate.

4.1.1. Mechanism of the aqueous alcohol oxidation

Much has been written on the mechanism of the oxidation of alcohols and aldehydes with dioxygen over noble metal catalysts after the discovery of this catalytic reaction by Döbereiner (1845). Wieland (1912a, 1912b, 1913 and 1921) showed that finely divided Pd catalyzed the oxidation of alcohols and aldehydes in the presence of hydrogen acceptors like dioxygen, methylene blue and quinone. This led to the hypothesis that this reaction is essentially a dehydrogenation reaction. This was later confirmed by Müller and Schwabe (1928, 1930) who conducted open circuit potential measurements on noble metal wires during the oxidation of ethanol to acetate in the presence of
excess sodium hydroxide. The potential of the wire during reaction was strongly on the hydrogen side, proving that the noble metal surface was mainly covered with hydrogen during reaction.

It was shown by Rottenberg and Baertschi (1956) by conducting experiments with labeled $^{18}$O$_2$ in unlabeled H$_2$O and with unlabeled O$_2$ in labeled H$_2^{18}$O that the oxygen introduced into acetic acid originated from water and not from dioxygen. As oxygen is introduced in the reaction step from acetaldehyde to acetic acid the most probable intermediate in this reaction is a hydrated acetaldehyde species.

Kolotusha et al. (1978) concluded from open circuit potential measurements on a platinum wire in the presence of a Pt/SiO$_2$ catalyst during the adsorption and reaction of n-propanol that the alcohol adsorbs dissociatively on the platinum with abstraction of a hydrogen atom.

Willsau and Heitbaum (1985) studied the adsorption of ethanol and the electrooxidation in 0.5 M H$_2$SO$_4$ on Pt with isotope labeling and Differential Electrochemical Mass Spectroscopy, DEMS. They concluded that the direct electrooxidation of ethanol yields acetaldehyde as product, whereas electrooxidation of preadsorbed ethanol results in carbon dioxide. The direct oxidation proceeds at potentials of 0.3 V vs. the Reversible Hydrogen Electrode, RHE. As the potential at which hydroxide species are formed on the Pt is much higher, it is most improbable that this reaction proceeds by reaction with a PtOH species. The oxidation of the preadsorbed species proceeds not until the formation of PtOH at a potential of about 0.7 V vs. RHE. The mechanism of the direct electrooxidation of ethanol consists according to these authors of a dissociative adsorption of ethanol with abstraction of the $\alpha$-carbon hydrogen followed by the abstraction of the hydrogen atom from the hydroxyl function as is illustrated in Figure 4.1.A. They conclude that both the hydroxyl hydrogen and the $\alpha$-carbon hydrogen are abstracted in this reaction from the observation that when CD$_3$CD$_2$OD is oxidized in unlabeled water only CD$_3$CDO is observed as product. When CD$_3$CD$_2$OD is dissolved in unlabeled water the deuterium from the hydroxyl function will easily be exchanged with hydrogen from water. If both $\alpha$-carbon hydrogens were abstracted some CD$_3$CHO would be expected as reaction product because otherwise a H atom from either the hydroxyl group or from water would have to shift to the $\alpha$-carbon.

DiCosimo and Whitesides (1989) studied the oxidation of 2-propanol with dioxygen in an electrochemical cell which enabled open circuit potential measurement during reaction on platinized Pt gauze. They observed in this system an isotope effect of $k_H/k_D=3.2$ in a competitive reaction of CH$_3$CHOHCH$_3$ and CD$_3$CDODCD$_3$. A similar isotope effect ($k_H/k_D=1.9$) was earlier observed by these authors in a competitive reaction of CH$_3$CHOHCH$_3$ and CH$_3$CDOHCH$_3$ over platinum black. These ob-
servations clearly indicate that the abstraction of the α-carbon hydrogen atom is the rate-limiting step of the reaction. DiCosimo and Whitesides propose therefore the following mechanism for the oxidation; dissociative adsorption of 2-propanol on the surface most probably by abstraction of the hydroxyl hydrogen followed by a rate-limiting abstraction of the α-carbon hydrogen. This sequence is illustrated in Figure 4.1.B.

\[
\begin{align*}
\text{A)} & \quad \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}_3\text{C} & \quad \text{H} & \quad \text{CH}_3\text{OH} \rightarrow \text{H}_3\text{C} & \quad \text{H} & \quad \text{CH}_3\text{O} & \quad \text{H} & \quad \rightarrow \text{CH}_3\text{CHO} \\
\text{B)} & \quad \text{CH}_2\text{CDOHCH}_3 \rightarrow \text{RDS} \quad \text{H}_3\text{C} & \quad \text{CH}_3 & \quad \text{H} & \quad \text{O} & \quad \text{CD} & \quad \rightarrow \text{CH}_3\text{COCH}_4 \\
\text{C)} & \quad \text{CD}_3\text{OH} \quad \text{RDS} \quad \text{D} & \quad \text{CDOH} & \quad \rightarrow \text{D} & \quad \text{CD} & \quad \text{O} & \quad \text{D} & \quad \rightarrow \text{CD}_3\text{O} \end{align*}
\]

**Figure 4.1** Schematic representation of the mechanism of the direct oxidation in water of alcohols to aldehydes according to: A) Willsau and Heithaum (1985) for the electrochemical oxidation, B) DiCosimo and Whitesides (1989) for the oxidation with oxygen, and C) Franaszczuk et al. (1992) for the electrochemical oxidation. The Rate-Determining Step is marked RDS.

Recently Franaszczuk et al. (1992) reported on the differences of electrochemical oxidation of methanol on Pt and decomposition in vacuum, i.e. in the absence of oxygen, of methanol on Pt. In the electrochemical decomposition in 0.1 M H\textsubscript{2}SO\textsubscript{4} they showed by chronoamperometry during oxidation at 0.4 V vs. RHE an isotope effect of $k_{\text{H}}/k_{\text{D}}=3.2$ between CH\textsubscript{3}OH and CD\textsubscript{3}OH and a secondary isotope effect of $k_{\text{H}}/k_{\text{D}}=1.6$ between CH\textsubscript{3}OH in H\textsubscript{2}O and CH\textsubscript{3}OH in D\textsubscript{2}O. An even larger isotope effect could be observed between CH\textsubscript{3}OH in H\textsubscript{2}O and CD\textsubscript{3}OH in D\textsubscript{2}O. Franaszczuk et al. (1992) explain the isotope effect as a result from a rate-determining step involving C-H bond scission. They propose as this step the dissociative adsorption of methanol as is illustrated in Figure 4.1.C. The secondary isotope effect is explained as a solvent effect.

The decomposition rates in absence of oxygen as determined by Franaszczuk et al. (1992) from Temperature Programmed Desorption measurements in Ultra High Vacuum showed a clear isotope effect of $k_{\text{H}}/k_{\text{D}}=1.6$ between CH\textsubscript{3}OH and CH\textsubscript{3}OD while no isotope effects could be observed between CH\textsubscript{3}OH and CD\textsubscript{3}OH nor between CH\textsubscript{3}OD and CD\textsubscript{3}OD. These observations indicate a rate-determining step involving scission of the hydroxyl O-H bond. Also with EELS methoxy intermediates could be detected on the surface by Franaszczuk et al. (1992) which indicates that the hydroxyl O-H bond is broken during or just after adsorption. This is quite surprising as
thermodynamics predict that the C-H bond of 393 kJ mol\(^{-1}\) in methanol would rather be broken than the O-H bond of 435 kJ mol\(^{-1}\) (Davis and Barteau, 1987). Moreover, forming a platinum-carbon bond is energetically more favoured than forming a platinum-oxygen bond. Bond dissociation enthalpies calculated from organometallic complexes and fragments amount for the platinum-carbon bond to 631 kJ mol\(^{-1}\), whereas the bond dissociation enthalpy for the platinum-oxygen bond amounts to only 414 kJ mol\(^{-1}\) (Martinho Simões and Beauchamp, 1990). According to Franaszczuk et al. (1992) the scission of the hydroxyl O-H bond during adsorption could possibly be explained by the proximity of the hydroxyl-H to the surface as methanol is adsorbed with its hydroxyl-O to the surface. It is clear that literature has not reached general consensus on the type of hydrogen involved in the initial dissociative adsorption of alcohols. The fact that during aqueous oxidation a strong isotope effect has been observed between \(\alpha\)-carbon deuterated and non-deuterated alcohols suggests that the abstraction of an \(\alpha\)-carbon hydrogen is the rate determining step during oxidation. Whether this rate-determining step is the initial adsorption of the alcohol or the subsequent surface reaction of an adsorbed dissociated alcohol is not yet clear. It is also clear from literature that electrochemical oxidation of preadsorbed alcohol yields another product, namely carbon dioxide, and proceeds at higher oxidative potentials than the direct oxidation of the alcohol which yields the corresponding aldehyde. In this case spectroscopic studies of platinum surfaces after adsorption or during oxidation of alcohols do not necessarily yield information on the type of surface intermediates involved in the direct oxidation as a large part of the surface will probably be occupied with other surface species.

4.1.2. Side reactions
One possible side reaction of the heterogeneous ethanol oxidation is the homogeneous base or acid catalyzed aldol condensation of ethanal to form 3-hydroxybutanal (\(\beta\)-hydroxybutyraldehyde) (Morrison and Boyd, 1983):

\[
2\text{CH}_3\text{CHO} + \text{OH}^+ \rightarrow \text{CH}_3\text{CHOHCH}_2\text{CHO}
\]  \hspace{1cm} (4.2)

As the product of the aldol condensation is another aldehyde it can undergo further condensations leading to polymers. The generally accepted mechanism for the base catalyzed aldol condensation proceeds by the slow formation of a carbanion by abstraction of a \(\alpha\)-hydrogen by the base. This formed carbanion then performs a nucleophilic attack on the carbonyl-carbon to form
the deprotonized 3-hydroxybutanal which will form 3-hydroxybutanal by abstraction of a proton from water.

Ethanal will not undergo the Cannizzaro reaction to yield ethanol and ethanoate as ethanal contains a α-hydrogen and therefore undergoes aldol condensation much faster at much lower base concentrations.

4.1.3. Catalyst deactivation
Deactivation of platinum catalysts during selective aqueous oxidation is a serious problem which is well documented.

Dijkgraaf et al. (1988a and 1988b) observed catalyst deactivation during the oxidation of D-gluconate to D-glucarate which was attributed to dissolution of oxygen into the platinum particles.

Mallat et al. (1992) investigated the catalyst deactivation which occurred during the oxidation of 1-methoxy-2-propanol. They distinguished two different types of deactivation; deactivation due to strong adsorption of by-products, chemical deactivation or more commonly called poisoning, which could be eliminated by applying sufficient oxidizing conditions, and a deactivation originating from over-oxidation of the surface, oxygen poisoning, which could be eliminated by applying reducing conditions.

Schuurman et al. (1992c) studied the catalyst deactivation during the oxidation of methyl α-D-glucoside. They observed a reversible deactivation due to an increasing coverage of oxygen at the platinum surface which could be eliminated by temporarily applying reducing conditions, i.e. stopping the oxygen feed. They observed also a much slower irreversible deactivation which was shown to be due to growth of the platinum particles on the support leading to a lower platinum surface area. This growth was attributed to a net transport of platinum ions, which can be sequestered by by-products of the methyl α-D-glucoside oxidation, from the less stable small particles to the more stable larger particles.

In contrast with these reports on catalyst deactivation during selective aqueous oxidation Gallezot et al. (1992) report no catalyst deactivation during the oxidation of glyoxal. This was attributed to the strong reductive capacity of glyoxal and glyoxylic acid.

4.2. Experimental

4.2.1. Choice and description of set-up
To enable the study of the kinetics and the deactivation of the catalyst in selective catalytic oxidation reactions in aqueous media with gaseous reactants as oxygen, a three-phase laboratory reactor set-up is needed.
### Table 4.1 Summary of ratings for different types of three-phase catalytic laboratory reactors with deactivating catalyst (Weekman 1974). Ratings: G=good, F=fair and P=poor.

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Mass transfer limitations</th>
<th>Sampling/ Product analysis</th>
<th>Iso-thermal-ity</th>
<th>Residence- contact time</th>
<th>Selectivity disguise</th>
<th>Construction</th>
<th>Data- analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential</td>
<td>P</td>
<td>P-F</td>
<td>F-G</td>
<td>F</td>
<td>P</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Fixed bed</td>
<td>P</td>
<td>G</td>
<td>P-F</td>
<td>F</td>
<td>P</td>
<td>G</td>
<td>P</td>
</tr>
<tr>
<td>Stirred batch</td>
<td>G</td>
<td>F</td>
<td>G</td>
<td>G</td>
<td>P</td>
<td>G</td>
<td>F</td>
</tr>
<tr>
<td>Stirred contained solids</td>
<td>P</td>
<td>G</td>
<td>G</td>
<td>F-G</td>
<td>P</td>
<td>F-G</td>
<td>G</td>
</tr>
<tr>
<td>Continuous stirred tank</td>
<td>G</td>
<td>F</td>
<td>G</td>
<td>F-G</td>
<td>G</td>
<td>P-F</td>
<td>G</td>
</tr>
<tr>
<td>Straight-through transport</td>
<td>G</td>
<td>F-G</td>
<td>P-F</td>
<td>F-G</td>
<td>G</td>
<td>F-G</td>
<td>G</td>
</tr>
<tr>
<td>Recirculating transport</td>
<td>G</td>
<td>F-G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>P-F</td>
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</tr>
<tr>
<td>Pulse</td>
<td>P</td>
<td>G</td>
<td>F-G</td>
<td>F</td>
<td>P-G</td>
<td>G</td>
<td>F</td>
</tr>
</tbody>
</table>

Figure 4.2 Reactor set-up. (1) mass flow controller, (2) HPLC pump, (3) pressurized vessel, (4) on/off valve, (5) reactor, (6) pH-probe, (7) backward-pressure regulator, (8) H2/O2 sensor, (9) on-line GC, (10) proportional valve, (11) differential pressure sensor, (12) cooling coil and (13) liquid outlet filter.
In literature many different types of laboratory reactors are described. Weekman (1974) reviews the most popular of these types and evaluates them on several important criteria (see Table 4.1).

The reactor which was used for this work is a continuous stirred three-phase slurry reactor, CSTR, in which the catalyst was retained. This type of reactor offers an intimate well-mixed contacting of the three phases and assures thus good isothermality, a well-defined space time, and, when using sufficiently fine catalyst powder, absence of mass transfer limitations.

The CSTR set-up consists of three main sections from the left to the right in Figure 4.2: the inlet section, the reactor section, and the outlet section.

The gas inlet consists of three mass flow controllers (HiTec F-201C-FA-22). Two parallel controllers enable feeding different mixtures O2/N2 and H2/N2. The third one splits a constant flow from the N2 feed for the level measurement. The liquid inlets consist of a HPLC pump (LKB 2150) to fill the reactor and of a pressurized vessel, which contains all aqueous feed and feeds into the reactor via an on/off regulated valve.

The reactor is a 500 ml internal volume autoclave (Autoclave Engineers Zipperclave AZC 0050 ss 01) with two internal baffles, thermowell, cooling coil, 2 separate liquid inlets, a liquid outlet with catalyst filter (filter type: Millipore HV 0.45 µ), immersion-pipe for level measurement, pH-probe (Ingold 765-31-BY with electrode 405-60-RB), and a gas dispersion impeller. The reactor is kept at constant temperature within 0.3 K between 303 and 373 K by a heating element around the reactor, which is controlled by a PID-controller (Pyreg). To obtain a stable control cooling water is supplied through the cooling coil. The pH is set by using the pH-controlling unit (Knick Type 70) to drive the on/off valve connected to the pressurized vessel. The liquid concentrations of all reactants and products, except the oxygen concentration, are kept constant in the reactor by feeding these together with the NaOH solution from the pressurized vessel. The concentration of NaOH in the feeding mixture is such that NaOH is the stoichiometric limiting reactant. As the feed rate of the NaOH in this mixture is controlled by the pH-controller to match the formation rate of acid products, the reactant and product concentrations will be kept constant in the reactor as long as no selectivity changes occur in time. The oxygen concentration in the liquid is kept constant by maintaining the partial oxygen pressure in the reactor constant.

The gas outlet of the reactor is controlled by a backward pressure regulator (Grove mity-mite S90W) to maintain the reactor pressure between 1 and 60 bar. The outlet gas composition is monitored by an H2/O2 sensor (Orbisphere 2641) and an on-line GC. The H2/O2 sensor gives a signal to a PID-controller (Eurotherm 815S) which
kept the oxygen concentration in the gas outlet at a constant level by controlling the mass flow of oxygen into the reactor. 

The liquid outlet of the reactor consists of a proportional valve which is controlled by a PID-controller (Eurotherm 815S). This controller takes as input the differential pressure (Fischer & Porter 50DPF110-3) between the head space and the bottom (tip of immersion-pipe) of the reactor and keeps the reactor level constant within a few millimeters. The outgoing liquid can be sampled for off-line HPLC analysis.

All available signals are monitored and recorded by an acquisition program written in Asyst running on a Personal Computer equipped with a Labmaster data acquisition card. The recorded data is after the end of an experiment available as a Lotus 123 worksheet for further data analysis and treatment.

4.2.2. Starting procedure

At the start of an experiment the reactor is filled with catalyst and 350 ml water. After closure, the reactor is purged with nitrogen to remove the oxygen, while maintaining the stirring speed at 18 s⁻¹. The reactor temperature is brought to 363 K. As soon as no more oxygen is detected in the outgoing gas and the temperature in the reactor has reached 363 K the nitrogen is replaced with hydrogen for half an hour to reduce the catalyst in-situ. After this period the reactor is again purged with nitrogen to remove the hydrogen and the reactor temperature is brought to the reaction temperature. As the reactor has reached this temperature the reactor pressure is increased to the reaction pressure. By manually operating the proportional valve in the liquid outlet, 175 ml water is removed from the reactor. This amount is replaced with the HPLC pump with a mixture prepared to give, after dilution, concentrations in the reactor which are close to the expected steady-state concentrations. The reactor contents are subsequently brought at the reaction pH by starting the pH-control. The stirring speed is reduced to 4 s⁻¹ and oxygen is introduced into the reactor. The reaction is started as soon as the detected outgoing oxygen concentration is close to the desired reactor oxygen concentration, typically 10 minutes after starting the oxygen introduction, by increasing the stirrer speed to 18 s⁻¹.

4.2.3. Reaction conditions

The catalyst used in the kinetic experiments is catalyst C0. The preparation and characterization of this catalyst have already been discussed in Chapter 2. The specific concentration of surface platinum atoms, $L_1$, amounted for this catalyst to 0.15 mol kg⁻¹.
The reaction conditions were varied between the limits given in Table 4.2. Most of the experiments however resulted in ethanal and ethanoate concentrations of 20 mol m\(^{-3}\). The total pressure was 600 kPa and the amount of catalyst used 350 mg in all experiments.

It was established that under these reaction conditions the obtained production rates were free of any mass or heat transfer limitations and represented thus the true intrinsic kinetics (see Appendix A.3).

4.2.4. Chemical analysis

The aqueous oxidation of ethanol produces mainly ethanal (acetaldehyde) and ethanoic acid (acetic acid) which will be, in the pH range used, completely ionized and present as ethanoate (acetate). At higher pH (pH>9) or at high ethanal concentrations also some 3-hydroxybutanal (β-hydroxybutyraldehyde) is formed as a by-product of the homogeneous aldol condensation. Other products like methanal, methanoic acid (formic acid) and carbon dioxide have not been detected and are most probably absent.

The components to detect and to quantify with the analysis are therefore ethanol, ethanal, and ethanoate in the aqueous phase and oxygen, nitrogen, water, and traces of ethanol and ethanal in the gas phase.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration ethanol</td>
<td>38-936 mol m(^{-3})</td>
</tr>
<tr>
<td>Concentration ethanal</td>
<td>5-55 mol m(^{-3})</td>
</tr>
<tr>
<td>Concentration ethanoate</td>
<td>5-212 mol m(^{-3})</td>
</tr>
<tr>
<td>Oxygen partial pressure</td>
<td>7-101 kPa</td>
</tr>
<tr>
<td>pH</td>
<td>7-10</td>
</tr>
<tr>
<td>Temperature</td>
<td>293-344 K</td>
</tr>
<tr>
<td>Conversion of ethanol</td>
<td>0.04-0.28</td>
</tr>
</tbody>
</table>

Table 4.2 Investigated range of reaction conditions.

![Diagram of GC analysis](image-url)
Chapter 4.

The gas phase composition was determined with an on-line GC (HP 5890A Series II) equipped with a 10 μl sample loop injection, a 10 m mol sieve 5A wide bore column (Chrompack), a 25 m poraplot Q wide bore column (Chrompack), and a thermal conductivity detector. The flow of helium carrier gas was set at 5 ml min⁻¹. The two columns were mounted on valves which enabled parking of each column separately (see Figure 4.3). The poraplot column was mounted upstream of the mol sieve column.

The analysis starts with an injection on the poraplot column at an oven temperature of 353 K. After 2.5 min. the permanent gases O₂ and N₂ will already have eluted from the poraplot column. At this time the poraplot column is parked and O₂ and N₂ are separated on the mol sieve column. At 4.5 min. O₂ and N₂ have eluted from the mol sieve column and the mol sieve column is parked. The other components are separated on the poraplot column. After 7.5 min. water has eluted from the poraplot column and the GC oven is heated to 453 K at a rate of 50 K min⁻¹ to accelerate the elution of ethanol and ethanal.

The quantification of the analysis was performed by an integrator (Milton Roy CI-10B LDC) using the 100% method and the relative molar response factors (Dietz, 1967) from Table 4.3.

The liquid phase composition was determined with a HPLC set-up (Spectra Physics) which consists of a HPLC pump (SP 8800), an auto sampler (SP 8775), a column heater (SP 8790), a differential refractometer (Waters R401) and an integrator (SP 4290). Data acquisition and set-up control was performed by the Autolab program (Spectra Physics) running on a PC. The separation of the components was achieved on a 280x4.6 ID mm Lichroma SS column slurry packed with a Benson type of cation-exchange resin (BC-X8, 7-10 μ), having sulphonic acid groups attached to the PS/DVB (8%) lattice. This column was brought into the H⁺-form by pumping overnight with a 0.025 M H₂SO₄ solution in water. Analysis was done with a flow of 0.7 ml min⁻¹.

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention time [min]</th>
<th>Relative molar response [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen</td>
<td>2.80</td>
<td>1.18*</td>
</tr>
<tr>
<td>nitrogen</td>
<td>3.00</td>
<td>1.41*</td>
</tr>
<tr>
<td>water</td>
<td>6.98</td>
<td>0.92</td>
</tr>
<tr>
<td>ethanol</td>
<td>9.80</td>
<td>1.82</td>
</tr>
<tr>
<td>ethanol</td>
<td>11.00</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 4.3 Retention times and relative molar response factors with respect to methane for the GC analysis as used in this work. The factors marked with an asterisk (*) are determined experimentally, the others are given by Dietz (1967).

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanoate</td>
<td>4.46</td>
</tr>
<tr>
<td>ethanol</td>
<td>5.34</td>
</tr>
<tr>
<td>ethanol</td>
<td>6.17</td>
</tr>
</tbody>
</table>

Table 4.4 Retention times for the HPLC analysis.
0.025 M H₂SO₄ at a temperature of 343 K. The injection volume of the auto sampler was set at 20 µl.

The quantification was performed by the integrator using a one point external standard method. After 5 samples the external standard was injected to recalibrate the molar response factors. The RI detector gave a linear response in the used concentration range for all components. The external standard was prepared from absolute ethanol (Merck P.A.), acetaldehyde (Fluka P.A.), and sodium acetate tri-hydrate (Merck extra pure).

The mass balance based on carbon at steady state was verified after every experiment and amounted typically to 98-100%:

\[
\text{C - balance} \% = \frac{\sum C_i n_{c,i}}{\sum C_i^0 n_{c,i}} \times 100 \% \tag{4.3}
\]

in which \(n_{c,i}\) is the number of carbon atoms in a molecule \(i\). Equation 4.3 can be used as mass balance only if the flow of liquid in and out of the reactor are equal and if the carbon containing components are not significantly present in the gas phase. These conditions are fulfilled during the experiments reported here.

Experiments with a carbon mass balance which deviated more than 2% were rejected.

4.2.5. Data analysis

From the recorded supply vessel volume and the analysis results the steady state net specific disappearance rate of ethanol and the net specific production rate of ethanoate were calculated by:

\[
R_{W,\text{CH}_2\text{OH}} = \frac{F_{V,L}}{W} \left( C^0_{\text{CH}_2\text{OH}} - C_{\text{CH}_2\text{OH}} \right) \tag{4.4}
\]

\[
R_{W,\text{CH}_2\text{COO}^-} = -\frac{F_{V,L}}{W} \left( C^0_{\text{CH}_2\text{COO}^-} - C_{\text{CH}_2\text{COO}^-} \right) \tag{4.5}
\]

The aqueous oxygen concentration was calculated using a semi-empirical correlation given by Battino (1981) for the mole fraction oxygen in pure water at a partial oxygen pressure of 101.325 kPa from 273 to 373 K:

\[
x_{O_2} = \exp(-179.3439 + 8747.547 / T + 24.45264 \ln(T)) \tag{4.6}
\]

The oxygen concentration can be calculated as:

\[
C_{O_2} = 0.55 \times x_{O_2} P_{O_2} \tag{4.7}
\]
It was verified that the correlation of Battino (1981) was also valid for the ethanol concentrations used in this work (see Figure 4.4). The other concentrations were, in all here reported experiments, much lower and will probably not significantly influence the solubility of oxygen.

The hydroxyl concentration in the reactor was calculated from the pH and the dissociation constant of water, $K_w$, at the reactor temperature.

In the regression analysis of the proposed rate equations concentrations were used instead of activities as it was verified with several thermodynamic interaction models that the activity coefficients for the components in the investigated concentration range were constant and deviated from one by not more than 20%.

![Figure 4.4 Oxygen solubility in water at an oxygen partial pressure of 101.325 kPa. Full line: correlation of Battino; ◯: experimental data in pure water; ■: experimental data in 2 wt% aqueous ethanol solution (experimental data from Battino 1981).](image)

The regression analysis was performed as outlined by Froment and Hosten (1981). The regression of the obtained production rate data to the proposed rate equations, to obtain maximum likelihood estimates $\hat{b}$ for the kinetic parameters $\beta$, was performed by minimization of the sum of squared residuals (least squares criterion) of the observed and calculated production rates:

$$SRS(b) = \sum_{i=1}^{n} \left[ R_{w,i} - \hat{R}_w(x_i, b) \right]^2 \rightarrow \text{Min}$$

(4.8)
in which \( n_{\text{obs}} \) is the number of observations, \( R_{w,i} \) is the observed specific production rate of observation \( i \) and \( \hat{R}_{w}(x_i, \beta) \) is the calculated specific production rate at the reaction conditions \( x_i \) of observation \( i \) and with parameter estimates \( \beta \).

This minimization was performed using the Marquardt algorithm (Marquardt, 1963).

The significance of the global regression was expressed by the F-ratio, the ratio of the mean regression sum of squares to the mean residual sum of squares:

\[
F - \text{ratio} = \frac{(n_{\text{obs}} - n_{\text{per}}) \sum_{i=1}^{n_{\text{obs}}} \hat{R}_{w,i}^2}{n_{\text{per}} \sum_{i=1}^{n_{\text{per}}} [R_{w,i} - \hat{R}_{w}(x_i, \beta)]^2}
\]  

(4.9)

in which \( n_{\text{per}} \) is the number of parameters. A high value of this F-ratio, which is distributed according to the in statistics known F distribution (Draper and Smith, 1966), indicates a high significance of the global regression.

The significance of the individual parameter estimates is expressed as a calculated t-value which is given by the ratio of the parameter estimate, \( b_i \), and the estimated standard error of the parameter estimate, \( s(b_i) \):

\[
t_i = \frac{b_i}{\sqrt{\text{variance}(b_i)}} = \frac{b_i}{s(b_i)}
\]  

(4.10)

As a rule of thumb these calculated t-values should be larger than 2 to indicate a parameter estimate significantly different from 0. The two sided \( 1-\alpha \) confidence intervals for the parameters were calculated from tabulated critical t-values as:

\[
b_i - t_c (n_{\text{obs}} - n_{\text{per}}, 1 - \frac{1}{2} \alpha) s(b_i) \leq \beta_i \leq b_i + t_c (n_{\text{obs}} - n_{\text{per}}, 1 - \frac{1}{2} \alpha) s(b_i)
\]  

(4.11)

To facilitate the simultaneous estimation of standard activation entropies, \( \Delta^s S^0 \), and enthalpies, \( \Delta^s H^0 \), or standard reaction entropies, \( \Delta S^0 \), and enthalpies, \( \Delta H^0 \), the following reparametrizations were applied:

\[
k = \mathcal{A}^0 \exp \left( \frac{\Delta^s H^0}{RT} \right) = \frac{zRT}{2N_e h} \exp \left( \frac{\Delta^s S^0}{R} - \frac{\Delta^s H^0}{RT} \right) \exp \left( -\frac{\Delta^s H^0}{R} \left( \frac{1}{T} - \frac{1}{\bar{T}} \right) \right)
\]  

(4.12)

and
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\[ K = K^0 \exp \left( -\frac{\Delta H^0}{RT} \right) = \exp \left( \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \right) \exp \left( -\frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right) \] (4.13)

in which \( \bar{T} \) is the average temperature of the experiments (in this work 324.4 K), \( z \) is the number of neighboring sites, taken to be 6 for the platinum surface, \( N_{av} \) is the constant of Avogadro, and \( h \) is the constant of Planck.

Standard conditions are for the liquid phase a concentration 1 mol dm\(^{-3}\) and for the adsorbed phase a degree of coverage of \( \frac{1}{2} \). The form of the preexponential factor in Equation 4.12 is derived from the transition state theory (Barrow, 1973; Boudart and Djéga-Mariadassou, 1984). The calculation of the rate and equilibrium coefficients for the different models from the estimated entropies and enthalpies is illustrated in appendix A.4.

4.3. Results and discussion

4.3.1. Multiplicity

One of the first striking features in the acquired data is the existence of two different activity levels at certain reaction conditions as illustrated in Figure 4.5. This multiplicity was only observed at ethanol concentrations between 150 to 400 mol m\(^{-3}\). This feature cannot simply be explained by errors in the measurement as the reaction rates at both activity levels are quite reproducible (within approx. 1 mmol kg\(^{-1}\) s\(^{-1}\)). It was not possible to predict whether the low or high activity level would be attained at the start of an experiment in the multiplicity range. However, only transitions from low activity to high activity have been observed in experiments in which one or more of the reaction conditions were changed in the course of the experiment. As the data at the low activity level is scarce the kinetic analysis in this work will be limited to the high activity level.

![Figure 4.5 Net specific disappearance rate of ethanol vs. ethanol concentration.](image)
4.3.2. Catalyst deactivation

Another striking feature in the acquired data is the absence of catalyst deactivation during most experiments, as illustrated in Figure 4.6, in contrast with the many literature reports on catalyst deactivation during selective aqueous oxidations (Dijkgraaf et al., 1988a and 1988b; Mallat et al., 1992; Schuurman et al., 1992c).

![Figure 4.6 Net specific disappearance of ethanol vs. time at a temperature of 325 K, an oxygen partial pressure of 58 kPa and an ethanol concentration of 165 mol m⁻³. A) pH=7. B) pH=10.](image)

Deactivation could only be observed at conditions favoring the aldol condensation reaction i.e. at pH values higher than 9.5 and/or ethanal concentrations higher than 50 mol m⁻³. The liquid samples taken during reactions at these conditions were lightly yellow colored and on the HPLC chromatograms a small peak could be detected at a position at which homogeneously prepared 3-hydroxybutanal also gave a peak. These observations suggest that the catalyst deactivation is caused by poisoning of the platinum surface by 3-hydroxybutanal, or larger polymers formed by aldol condensation reactions. It could also be possible that 3-hydroxybutanal, or one or more of the larger polymers, is capable of sequestering Pt ions thereby inducing growth of the larger Pt particles at the expense of the smaller particles (Schuurman et al., 1992c).

The absence of catalyst deactivation at conditions not favoring the aldol condensation can thus be ascribed to the absence of poisoning or sequestering side products. Another possible explanation for the absence of catalyst deactivation could be a strong adsorption of ethanol to the Pt surface or a stronger reducing capacity of ethanol. This would result in a surface covered with less oxygen and lead to a slower formation of ionic platinum which is an intermediate in the dissolution process (Schuurman et al., 1992c) or, in other words, would less easily lead to an over-oxidation of the platinum surface (Mallat et al., 1992).
4.3.3. Reaction network

For the global oxidation reaction of ethanol to ethanal and ethanoate different reaction paths are possible. The most simple of these is a reaction path in which ethanal is formed from ethanol and ethanoate is formed successively from ethanal. Another possibility is that ethanal and ethanoate are both formed in parallel from ethanol. A more difficult case is the so called desorption disguised kinetics. In this case the desorption of ethanal and ethanoate, which are formed in series, are relatively slow compared to the surface reaction. This leads to a situation which is hard to distinguish from the parallel formation of ethanal and ethanoate.

To discern between these different reaction networks a concentration vs. space time (W/F°) curve was obtained and is shown in Figure 4.7. Clearly ethanal is formed from ethanol before ethanoate is formed. Also it is clear that the ethanal concentration reaches a maximum while the ethanoate concentration continually increases. These observations are in agreement with a reaction network in which ethanal is formed from ethanol and ethanoate is successively formed from ethanal. Ethanal is thus an intermediate in the ethanol oxidation towards ethanoate.

This conclusion is also supported by the observation that ethanal oxidation in the absence of ethanol yields ethanoate. Moreover and as important for the further kinetic analysis, it is clear from these observations that the desorption of the reaction products is not rate-determining as would be the case for desorption disguised kinetics.

4.3.4. Rate equation for the ethanol disappearance

In principle a full kinetic analysis of the data should be based on the simultaneous analysis of both the net disappearance rate of ethanol and the net production rate of ethanoate, i.e. should take into account explicitly the existence of ethanal as intermediate. As the variation in ethanal concentration is very small and within the error of the determination at the observed concentration levels, such a regression analysis failed. Deactivation by products of the aldol condensation did not allow to obtain data at high ethanal concentrations.
A few experiments with high ethanoate concentration in the feed indicate a clear product inhibition. Hence the data corresponding to ethanol conversion levels higher than 0.3 were not involved in the regression.

At low ethanal and ethanoate concentrations the surface coverage of species involved in the oxidation of ethanal to ethanoate is considered also small, and a separate analysis of the net disappearance rate of ethanol from the net production rate of ethanoate is possible. Hence, the present kinetic analysis is limited to the ethanol disappearance rate. The latter can be accounted for completely by considering only the oxidative dehydrogenation towards ethanal because of the consecutive nature of the reaction network.

The final data set used in the regression analysis consisted of 42 selected points (see Appendix A.2). A summary of the range of reaction conditions at which the ethanol disappearance rate was modeled is given in Table 4.5.

From Figure 4.8 it is clear that the rate increases as both the ethanol concentration and the partial oxygen pressure increase but also that this increase levels off at higher concentrations.

<table>
<thead>
<tr>
<th>condition</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration ethanol</td>
<td>38-762 mol m⁻³</td>
</tr>
<tr>
<td>concentration ethanal</td>
<td>5-40 mol m⁻³</td>
</tr>
<tr>
<td>concentration ethanoate</td>
<td>5-51 mol m⁻³</td>
</tr>
<tr>
<td>oxygen partial pressure</td>
<td>8-96 kPa</td>
</tr>
<tr>
<td>pH</td>
<td>7-10</td>
</tr>
<tr>
<td>temperature</td>
<td>293-344 K</td>
</tr>
<tr>
<td>conversion of ethanol</td>
<td>0.05-0.28</td>
</tr>
<tr>
<td>volumetric flow of feed</td>
<td>1-10 ml min⁻¹</td>
</tr>
</tbody>
</table>

Table 4.5 Range of reaction conditions for which the ethanol disappearance rate was modeled.

![Figure 4.8 Net specific disappearance rate of ethanol vs.](image)

This indicates that both reactants are adsorbed on the surface. Most probably both reactants are in some way involved in the rate-determining step and occupy the same type of active sites, a so-called dual-site mechanism as is depicted with step 3 in Table
4.6. Models in which only one absorbed reactant is involved in the rate-determining step, a so-called single-site mechanism, cannot explain a increase of the ethanol disappearance rate for both an ethanol and an oxygen concentration increase together with the observed level-off at higher concentrations.

No strong dependence of the rate on the pH, as was reported by Schuurman et al. (1992a) for the oxidation of methyl α-D-glucoside, could be found. This pH dependence was attributed by Schuurman et al. to the existence of a reaction path starting from the methyl α-D-glucoside anion. The lack of pH dependence for the oxidation rate of ethanol is consistent with the fact that the acidity of ethanol, $pK_a = 16$ (Ballinger and Long, 1960), is lower than the acidity of methyl α-D-glucoside, $pK_a = 13.7$ (Schuurman et al., 1992a).

As during the experiments no hydrogen was detected at the gas outlet, dehydrogenation of ethanol could be eliminated as possible reaction path in the proposed reaction sequences.

Taking the above observations into account several reaction sequences were proposed. The adsorption isotherm was assumed to be of the Langmuir type.

Reaction sequences in which the ethanol adsorption was not equilibrated could not describe the data adequately. This indicates that ethanol adsorption will not be the rate-determining step of the oxidation. Literature clearly states that the rate-determining step during the oxidation of an alcohol involves breaking the α-carbon to hydrogen bond (DiCosimo and Whitesides, 1989; Franaszczuk et al., 1992). Hence, adsorption of ethanol during the oxidation does not involve breaking the α-carbon to hydrogen bond. Therefore ethanol is most probably adsorbed reversibly during reaction and if the adsorption is dissociative the O-H bond will be involved.

Two sequences in which ethanol is adsorbed associatively are given in Table 4.6. The stoichiometric numbers, $\sigma$, indicate the multiplicity of the corresponding elementary step which is required to obtain a closed sequence leading to the global reaction (Temkin, 1971).

Table 4.6 Sequences of proposed elementary steps for the oxidation of ethanol to ethanal involving associative adsorption of ethanol and equilibrated (AE) or irreversible (AI) oxygen adsorption.
Applying the steady-state approximation to the reactive surface intermediates and assuming that the affinity of the reversible reactions is almost zero, i.e. that these reactions are virtually in equilibrium, the following rate equations can be obtained:

\[ \hat{R}_{W,\text{AE}} = \frac{k_3 \sqrt{K_{i} C_{O_2} K_{2} C_{\text{ethanol}}}}{\left(1 + \sqrt{K_{i} C_{O_2} + K_{2} C_{\text{ethanol}}} \right)^2} \left[ \frac{L_i}{1} \right] \]  

(4.14)

and:

\[ \hat{R}_{W,\text{AI}} = \frac{2k_1 C_{O_2}}{\left(1 + \frac{2k_1 C_{O_2}}{k_3 K_{2} C_{\text{ethanol}}} \right)^2} L_i \]  

(4.15)

The regression results for these two models can be found in Tables 4.7 and 4.8. It can be seen clearly from the F-ratio's that both models with associative adsorption of ethanol can describe the experimental data adequately. One of the parameter estimates in model AI, \( \Delta^\circ H^0 \), is not significantly different from zero, however, as can be seen from the 95% confidence limit. All other parameter estimates are significantly different from zero.

<table>
<thead>
<tr>
<th>parameter estimate</th>
<th>parameter estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta S^0 ) [J mol(^{-1}) K(^{-1})] -200±133</td>
<td>( \Delta S^0 ) [J mol(^{-1}) K(^{-1})] -197±52</td>
</tr>
<tr>
<td>( \Delta S^0 ) [J mol(^{-1}) K(^{-1})] -90±51</td>
<td>( \Delta S^0 ) [J mol(^{-1}) K(^{-1})] -148±48</td>
</tr>
<tr>
<td>( \Delta S^0 ) [J mol(^{-1}) K(^{-1})] -77±52</td>
<td>( \Delta S^0 ) [J mol(^{-1}) K(^{-1})] -94±39</td>
</tr>
<tr>
<td>( \Delta H^0 ) [kJ mol(^{-1})] -78±42</td>
<td>( \Delta H^0 ) [kJ mol(^{-1})] 4.6±17</td>
</tr>
<tr>
<td>( \Delta H^0 ) [kJ mol(^{-1})] -32±17</td>
<td>( \Delta H^0 ) [kJ mol(^{-1})] -48±16</td>
</tr>
<tr>
<td>( \Delta H^0 ) [kJ mol(^{-1})] 58±16</td>
<td>( \Delta H^0 ) [kJ mol(^{-1})] 52±12</td>
</tr>
<tr>
<td>F-ratio 616</td>
<td>F-ratio 503</td>
</tr>
</tbody>
</table>

Table 4.7 Parameter estimates with 95% confidence limits for the model with associative adsorption of ethanol and equilibrated dissociative adsorption of oxygen; model AE (rate equation 4.14).

Table 4.8 Parameter estimates with 95% confidence limits for the model with associative adsorption of ethanol and irreversible dissociative adsorption of oxygen; model AI (rate equation 4.15).

The sequences involving dissociatively adsorbed ethanol are given in Table 4.9. These sequences start all with the dissociative adsorption of oxygen, step 1, which is taken to be equilibrated, DE and DE', or irreversible, DI and DI'. The dissociation of ethanol, step 2, is assumed to proceed by abstraction of the hydroxyl hydrogen rather
than the \( \alpha \)-carbon hydrogen as this in agreement with the observation that the ethanol adsorption is not rate-determining. This choice does however not influence the corresponding rate equation.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{(1)} & \text{O}_2 + 2^* & \rightleftharpoons & 2O^* \\
\hline
\text{(2)} & \text{CH}_3\text{CH}_2\text{OH} + 2^* & \rightarrow & \text{CH}_3\text{CH}_2\text{O}^* + \text{H}^* \\
\hline
\text{(3)} & \text{CH}_3\text{CH}_2\text{O}^* + \text{O}^* & \rightarrow & \text{CH}_3\text{CHO} + \text{OH}^* + ^* \\
\hline
\text{(3')} & \text{H}^* + \text{O}^* & \rightarrow & \text{OH}^* + ^* \\
\hline
\text{(4)} & \text{H}^* + \text{OH}^* & \rightarrow & \text{H}_2\text{O} + 2^* \\
\hline
\text{(4')} & \text{CH}_3\text{CH}_2\text{O}^* + \text{OH}^* & \rightarrow & \text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2^* \\
\hline
\end{array}
\]

Table 4.9 Sequences of proposed elementary steps for the oxidation of ethanol to ethanal involving dissociative adsorption of ethanol, adsorbed oxygen in the surface reaction step and equilibrated (DE) or irreversible (DI) oxygen adsorption. The sequences DE' and DI' are different from sequences DE and DI but lead to the same rate equation.

In sequence D the \( \alpha \)-carbon hydrogen is irreversibly abstracted from the adsorbed ethanol by adsorbed oxygen to form an adsorbed hydroxyl species and ethanal, step 3. The adsorbed hydroxyl species reacts very fast with adsorbed hydrogen to yield water, step 4. Alternatively, the reaction could also proceed as is depicted in sequence D'. An adsorbed hydroxyl species is formed by the irreversible combination of adsorbed oxygen and hydrogen, step 3'. This hydroxyl species reacts with adsorbed ethanol to yield ethanal and water, step 4'. Both sequences D and D' result in the same equation for the ethanol disappearance rate but the former sequence is considered more likely. Both sequences can of course occur in parallel. This would, however, not result in a mathematically different form of the rate equation.

The rate equations which can be derived from these sequences, assuming that reaction step 4 or 4' are very fast, i.e. that the surface coverage of species \( \text{OH}^* \) can be neglected compared to the surface coverages of the other surface species in the reaction sequence, and that the adsorption of oxygen, step 1, is considered equilibrated:

\[
\hat{R}_{\text{w,DE}} = \frac{k_3\sqrt{K_{\text{C,O}_2} \sqrt{K_{\text{C,ethanol}}}}}{(1 + \sqrt{K_{\text{C,O}_2} + 2\sqrt{K_{\text{C,ethanol}}}})^2} L_i \quad (4.16)
\]

and when the adsorption of oxygen, step 1, is considered irreversible:
The terms in the denominator of the rate equations give the relative fractions of the different surface species with respect to the number of vacant sites. Some of these terms are expressed as an adsorption equilibrium, others are expressed as a ratio of production to disappearance rates. For instance the first term in the denominator of the rate equation for model DI (Equation 4.17) represents the relative fraction of vacant sites, obviously being 1. The second term is the relative fraction of O* given as the ratio of the rate of reaction step 1 to that of reaction step 3. The last term represents the species CH₃CH₂O* and H* which are in equilibrium with the ethanol concentration in the liquid phase. As they are both formed in equilibrium 2 and both disappear with the same rate, i.e. the rate of step 3, the coverages of these two species will be equal, hence the factor 2. Indeed, the OH* produced in step 3 will be immediately converted into H₂O by reaction 4. Hence for each CH₃CH₂O* converted by reaction 3, one H* will be converted by reaction 4.

\[
\hat{R}_{w,DI} = \frac{2k_1c_{O_2}}{1 + \frac{2k_1c_{O_2}}{k_3\sqrt{K_2c_{ethanol}}} + 2\sqrt{K_2c_{ethanol}}} L_1
\] (4.17)

The regression results of models DE and DI can be found in Table 4.10 and 4.11.

<table>
<thead>
<tr>
<th>parameter</th>
<th>estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta S^o_1 [J , \text{mol}^{-1} , \text{K}^{-1}])</td>
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<tr>
<td>(\Delta S^o_2 [J , \text{mol}^{-1} , \text{K}^{-1}])</td>
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</tr>
<tr>
<td>(\Delta S^o_3 [J , \text{mol}^{-1} , \text{K}^{-1}])</td>
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</tr>
<tr>
<td>(\Delta H^o_1 [kJ , \text{mol}^{-1}])</td>
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</tr>
<tr>
<td>(\Delta H^o_2 [kJ , \text{mol}^{-1}])</td>
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</tr>
<tr>
<td>(\Delta H^o_3 [kJ , \text{mol}^{-1}])</td>
<td>61±25</td>
</tr>
<tr>
<td>F-ratio</td>
<td>725</td>
</tr>
</tbody>
</table>

Table 4.10 Parameter estimates with 95\% confidence limits for the model with dissociative adsorption of ethanol, adsorbed oxygen in the rate-determining step and equilibrated dissociative adsorption of oxygen; model DE (rate equation 4.16).

<table>
<thead>
<tr>
<th>parameter</th>
<th>estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta S^o_1 [J , \text{mol}^{-1} , \text{K}^{-1}])</td>
<td>-203±29</td>
</tr>
<tr>
<td>(\Delta S^o_2 [J , \text{mol}^{-1} , \text{K}^{-1}])</td>
<td>-320±60</td>
</tr>
<tr>
<td>(\Delta S^o_3 [J , \text{mol}^{-1} , \text{K}^{-1}])</td>
<td>-80±22</td>
</tr>
<tr>
<td>(\Delta H^o_1 [kJ , \text{mol}^{-1}])</td>
<td>2.1±1.0</td>
</tr>
<tr>
<td>(\Delta H^o_2 [kJ , \text{mol}^{-1}])</td>
<td>-99±30</td>
</tr>
<tr>
<td>(\Delta H^o_3 [kJ , \text{mol}^{-1}])</td>
<td>55±6.9</td>
</tr>
<tr>
<td>F-ratio</td>
<td>1893</td>
</tr>
</tbody>
</table>

Table 4.11 Parameter estimates with 95\% confidence limits for the model with dissociative adsorption of ethanol, adsorbed oxygen in the rate-determining step and irreversible dissociative adsorption of oxygen; model DI (rate equation 4.17).

The regression results of models DE and DI can be found in Table 4.10 and 4.11.

Kinetics of ethanol oxidation
It can be seen from the relative high F-ratio in Table 4.11 that model DI describes much better the experimental data than any other of the proposed models. Also all parameter estimates are significant, as can be viewed from the 95% confidence limits. Figure 4.8 illustrates the capability of equation 4.17 to describe the experimental data. The residual vs. reaction condition diagrams and the calculated rate vs. observed rate diagram can be found in Figure 4.9. These diagrams show that the residuals are evenly distributed and that thus a systematic deviation of the experimental data from the regression equation is absent. The sequence of elementary steps of model DI can thus adequately describe the kinetics of the ethanol oxidation in the investigated range of conditions.

Regression of sequences with adsorbed hydroxyl, OH*, in the irreversible surface reaction step rather than with adsorbed oxygen, O*, step 3 Table 4.9, was not successful.

![Figure 4.9 Parity and residual diagrams for the regression with model DI (equation 4.17 and Table 4.11).](image)

4.3.5. **Assessment of the kinetic parameter estimates**

The absolute value of the estimated standard adsorption enthalpy of ethanol on platinum, $\Delta H^\circ_2$, indicates a strong chemisorption of ethanol as would be expected for a dissociative adsorption (see Table 4.11).
A strict rule for the value of the standard adsorption entropy for adsorption from the gas phase has been put forward by Boudart et al. (1967) and Vannice et al. (1979) for both associative and dissociative adsorption. This rule can be directly translated to the aqueous phase as:

\[ 0 < -\Delta S^0_{ads} < S^0_{aq} \]  \hspace{1cm} (4.18)

Equation 4.18 expresses the necessary loss of standard entropy upon adsorption and the fact that a molecule cannot lose more entropy than it possesses. The estimated standard entropy loss upon adsorption of ethanol, \( \Delta S^0 \), is larger than the standard entropy of aqueous ethanol, \( S^0_{aq} \), of 158 J mol\(^{-1}\) K\(^{-1}\) and even larger than the standard entropy of gaseous ethanol at 324 K which amounts to 288 J mol\(^{-1}\) K\(^{-1}\) (Weast, 1988). This would mean that ethanol loses more entropy than it possesses. However, if the interaction between ethanol and the platinum surface is very strong, platinum surface atoms would also lose some entropy upon ethanol adsorption. The standard entropy of crystalline platinum amounts to 44 J mol\(^{-1}\) K\(^{-1}\) and the standard entropy of gaseous platinum amounts to 194 J mol\(^{-1}\) K\(^{-1}\) at 324 K (Weast, 1988). The standard entropy of a surface platinum atom in a small particle would thus be somewhere in between these two limits. As at least two platinum surface atoms are involved bonding one ethanol molecule dissociatively, the total entropy content of one ethanol molecule and two platinum surface atoms is much higher than the entropy content of one ethanol molecule only. Another possible explanation could be that the adsorption of ethanol induces also changes in the hydration of the surface and the hydration of ethanol. Moreover, as ethanol adsorbs dissociatively two surface species will have to be hydrated instead of one. Hydration will obviously contribute to a more negative adsorption entropy.

The estimated standard activation enthalpy for the adsorption of oxygen on platinum, \( \Delta^aH^0 \), is low. The activation enthalpy for the surface reaction, \( \Delta^sH^0 \), is also low. One has to keep in mind however that the steps reported here are not necessarily elementary steps. If an equilibrium is preceding an elementary reaction step the apparent rate coefficient equals the product of the equilibrium coefficient and the real rate coefficient and, hence (Barrow, 1973):

\[ \Delta^{\text{app}}H^0 = \Delta^aH^0 + RT + \Delta H^0 \]  \hspace{1cm} (4.19)

If this preceding equilibrium is exothermic the apparent activation enthalpy will be lower than the activation enthalpy expected for an elementary reaction step. As the
dissociative adsorption of oxygen on platinum is known to be a strongly exothermic process, with typical values for the standard enthalpy change of -200 to -300 kJ mol\(^{-1}\) for adsorption from the gas phase (Somorjai, 1981; Sen and Vannice, 1991), part of this enthalpy change could be attributed to a preceding adsorption equilibrium of molecular oxygen.

The estimated standard activation entropies of both reactions are negative which is usually an indication of a strong steric requirement for the reaction step. But if an equilibrium is preceding the reaction step the apparent standard activation entropy can be written as:

\[
\Delta^{\text{app}}S^0 = \Delta^{\text{eq}}S^0 + \Delta S^0
\]  

(4.20)

Thus when the standard entropy change of the equilibrium reaction is negative the apparent activation entropy is lowered with respect to the real activation entropy of the elementary step and can even become negative. If the preceding equilibrium for the oxygen adsorption consists of an oxygen adsorption, the entropy change would surely be negative as adsorption can be regarded as transfer from a three dimensional phase to a two dimensional phase. This would explain the very negative activation entropy reported here for this step.

When the results of the kinetic analysis of the steady-state rate of ethanol oxidation are compared with the results of the kinetic analysis of the initial rate of methyl α-D-glucoside oxidation as reported by Schuurman et al. (1992a, 1992b) the most striking difference is the difference in reaction sequence. Where the ethanol oxidation seems to proceed by a mechanism involving a dissociatively adsorbed ethanol species and irreversible dissociatively adsorbed oxygen the oxidation of methyl α-D-glucoside was reported to proceed by a mechanism involving an associatively adsorbed glucoside species and reversible dissociatively adsorbed oxygen. However, the activation enthalpy for the surface reaction step, the abstraction of a hydrogen atom, of 55 kJ mol\(^{-1}\) for the ethanol oxidation and of 51 kJ mol\(^{-1}\) for the methyl α-D-glucoside oxidation are quite comparable. Moreover, the value of 62 kJ mol\(^{-1}\) found for the adsorption enthalpy of oxygen by regression of model DE (Table 4.9, equation 4.16 and Table 4.10) compares quite well with the value of 60 kJ mol\(^{-1}\) found by Schuurman et al. (1992a, 1992b). These facts indicate that both oxidation reactions are probably proceeding by the same mechanism.

The fractional surface coverages calculated with Equation 4.17 at typical conditions at which the oxidation of ethanol was investigated, i.e. a temperature of 324 K, an ethanol concentration of 500 mol m\(^{-3}\) and an oxygen partial pressure of 50 kPa, amount to a fractional coverage of 0.25 of oxygen, a coverage of 0.11 for both ethanol and hydrogen and a fraction free surface sites of 0.52. When the temperature is
Kinetics of ethanol oxidation

decreased to 303 K the fractional coverages amount to 0.20 for oxygen, 0.26 for both ethanol and hydrogen and 0.28 for the vacant sites. Schuurman et al. (1992a, 1992b) found, at a pH of 8, fractional surface coverages changing from 0.8 to 0.6 for oxygen and changing from 0.08 to 0.13 for methyl α-D-glucoside when the temperature was increased from 303 to 333 K. As the adsorption of methyl α-D-glucoside could be better described by an associative adsorption rather than a dissociative adsorption no significant amount of hydrogen is expected on the surface during the oxidation of methyl α-D-glucoside.

At a pH of 8, a concentration of 200 mol m⁻³, a partial oxygen pressure of 26 kPa and a temperature of 303 K, the initial specific disappearance rate of methyl α-D-glucoside amounts to 2.0 mmol kg⁻¹ s⁻¹ (TOF=13 10⁻¹ s⁻¹), while the steady state specific disappearance rate of ethanol amounts to 3.0 mmol kg⁻¹ s⁻¹ (TOF=20 10⁻³ s⁻¹). In a dual-site reaction the rate of the surface reaction is proportional to the product of the coverages of the two surface species involved in the reaction and the rate coefficient for the surface reaction. The maximum rate occurs for a dual-site reaction when the coverage of both surface species involved in the surface reaction is equal to 0.5. The rate coefficients for the surface reaction, at 303 K amounts for the ethanol oxidation to 0.47 s⁻¹ and for the oxidation of methyl α-D-glucoside to 0.16 s⁻¹. It seems that the higher reactivity of ethanol and the presence of adsorbed hydrogen are keeping the surface relatively free of oxygen. If the oxygen coverage is far from the equilibrium coverage the oxygen adsorption can be described very well by an irreversible reaction step, whereas close to equilibrium the adsorption of oxygen can of course be better described by an equilibrium. This could be an explanation for the different description of the oxygen adsorption during the ethanol and the methyl α-D-glucoside oxidation.

As the fractional surface coverage of oxygen is low and some hydrogen is present on the surface, oxidation of the platinum surface and formation of ionic platinum will not easily occur. This also explains the absence of catalyst deactivation.

4.4. Conclusions

The platinum catalyzed oxidation of ethanol to ethanal and ethanoate with oxygen dissolved in water proceeds by a reaction sequence in which ethanal and ethanoate are formed successively.

No effect of the pH on the disappearance rate of ethanol could be observed as could be expected from the low acidity of ethanol.

The reaction kinetics of the platinum catalyzed oxidation of ethanol to ethanal in water can be described adequately over a broad range of reaction conditions by a relative simple rate equation. This equation is based on irreversible dissociative adsorption of oxygen and reversible dissociative adsorption of ethanol on the same type of sites and
a rate determining surface reaction between these two adsorbed species: a dual-site mechanism.
The dissociative adsorption of ethanol proceeds by abstraction of the hydroxyl hydrogen. The kinetic analysis itself however cannot distinguish between abstraction of the \( \alpha \)-carbon hydrogen or the hydroxyl hydrogen due to the ambiguity of the steady state kinetics. The kinetic analysis shows that the adsorption of ethanol is not rate-determining, however.

An assessment of the estimates of the kinetic parameters reveals that some of the steps in the reaction sequences are not true elementary reaction steps but are probably consisting of a reaction step preceded by an equilibrium reaction.
The absence of catalyst deactivation during most of the ethanol oxidation experiments results from the absence of poisoning or sequestering side products and from the relatively low fractional surface coverage of oxygen, which prevents oxidation of the platinum surface and formation of ionic platinum.

4.5. References

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Kinetics of ethanol oxidation

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Müller E. and Schwabe K., *Z. Electrochem.*, 34 (1928), 170
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5. PLATINUM PARTICLE SIZE EFFECTS

5.1. Introduction

As noble metals are quite expensive, optimal use of the active phase is important. This requires the maximization of the reaction rate per unit mass of noble metal. Another important factor is the resistance of the catalyst against deactivation. Maximization of the reaction rate per unit mass of noble metal cannot always be achieved simply by maximization of the surface area per unit mass of noble metal, i.e., minimization of the particle size of the noble metal or maximization of the fraction exposed atoms, FE. Studies on many reactions show that the reaction rate per unit catalyst surface area can depend on the particle size, hence minimization of the particle size will not automatically yield maximization of the rate per unit mass. Reaction rates are often expressed as turnover frequencies, TOF, i.e. as rates per surface atom of the active phase. Boudart called reactions with a clear dependence of this TOF on the particle size "demanding" or "structure-sensitive" (Boudart et al., 1966; Boudart, 1969). Reactions which do not exhibit such dependency were called "facile" or "structure-insensitive".

Che and Bennet (1989) reviewed recently the effect of particle size of supported metals on the rate of catalytic reactions with omission of the work in the field of electrocatalysis. Possible explanations for the particle size effect of metals can be mainly divided in electronic effects and geometric effects.

Electronic effects arise from the fact that when metal particles become smaller the electronic character will change from typical for a bulk metal to typical for a single metal atom. The electronic character of a metal cluster influences physical and chemical properties such as electrical conductivity, ionization potential, polarizability, binding energy, Gibbs energy, entropy and so on (Muller et al., 1989).

In a large metal particle the energy levels of the electrons are so close together that these levels form bands. The Fermi level, $E_f$, is the energy of the highest occupied level at T=0. As there are many energy levels in the bands just above the Fermi level, electrons can easily shift to these higher unoccupied levels resulting in a high electrical conductivity. The ratio of the Fermi level of the bulk metal to the number of atoms in the cluster, N, is often taken as an estimate of the difference between two subsequent energy levels:

$$\Delta E = \frac{E_f}{N}$$  \hspace{1cm} (5.1)
Electronic effects will start to occur at a particle size at which the difference between two subsequent energy levels will become appreciable with respect to the thermal energy $kT$:

\[ \frac{E_i}{N} > kT \] (5.2)

For platinum particles this amounts to a particle size of about 2 nm or a fraction of exposed atoms, FE, of 0.6 (Bond, 1985). Such a particle consists of approximately 200 atoms. Some measurements on platinum clusters with X-ray Photoelectron Spectroscopy, XPS, support this calculation as the binding energy of the electrons at the core level changes at this particular particle size (Che and Bennet, 1989).

Geometric effects arise from the fact that the active site for the reaction consists of special surface atoms or groups of surface atoms (Bennet and Che, 1989). Van Hardeveld and Hartog (1969, 1972) calculated for various shapes of particles the ratio of different types of sites with respect to the total amount of surface atoms. The ratio for the face atoms on fcc octahedrons for instance decreases sharply at a FE of 0.6. The ratio of so-called B5 sites on fcc octahedrons with the maximum possible number of B5 sites goes through a maximum at a FE of 0.5. Che and Bennet (1989) concluded from these calculations that when the active site for a certain reaction consists of an ensemble of several atoms the structure sensitivity of the reaction should extend to particles considerably larger than 5 nm. Hence, they call this kind of behavior extended structure sensitivity. When the reaction takes place on a certain type of surface atom rather than on an ensemble, the structure sensitivity is limited to particles smaller than 5 nm. This is therefore called limited structure sensitivity.

The main conclusions of Che and Bennet (1989), based on their review of the experimental data, are that for all reactions the TOF tends to zero as the number of atoms in a particle tends to one. This means that for all reactions very small particles will show a so-called antipathetic behavior. Observations of a constant TOF at a FE close to one could be due to difficulties in particle size determination or due to formation of raft like structures. Probably no real structure insensitive reactions are existing as electronic effects clearly exist when metal particles contain less than approxi-

![Figure 5.1 Schematic curves of different types of idealized structure sensitivity according to Che and Bennet (1989). A) Structure insensitive, B) antipathetic structure sensitivity, and C) sympathetic structure sensitivity.](image)
Platinum particle size effects

...mately 200 atoms, i.e., from a FE higher than 0.6 on. Hence the expected behavior for the TOF of "structure insensitive" reactions as function of the FE is depicted by curve A) of Figure 5.1. As some reactions require ensembles of atoms as active site, which become rarer as particle size decreases, real antipathetic behavior is expected as is depicted by curve B) of Figure 5.1. The larger the ensemble required the lower the FE to which sensitivity persists. When special multi-atom sites or coordinated atoms, which become less rare on smaller particles, are required for the reaction the curve of TOF versus FE could show a maximum as is depicted by curve C) of Figure 5.1. This is a sympathetic structure sensitivity.

Peuckert et al. (1986) showed that turnover frequency of the electrochemical dioxygen reduction over platinum on carbon catalysts in 0.5 M H₂SO₄ at 298 K decreased sharply at particle sizes smaller than 2 to 4 nm. A constant turnover frequency was observed on particles larger than 4 nm. It was also shown by cyclovoltammetry that the oxide reduction was shifted to lower potentials as the particle size decreased. This was ascribed to an increased heat of chemisorption of oxygen on smaller particles.

The latter is in agreement with the gas phase work of Briot et al. (1990), who found for a platinum on alumina catalyst that the turnover frequency of the methane oxidation was much higher for aged catalysts, with platinum particles of approximately 12 nm, than for fresh catalysts with a particle size of approximately 2 nm. Microcalorimetric measurements of the oxygen chemisorption showed a decrease in the heat of chemisorption of oxygen with increasing particle size from 280 kJ mol⁻¹, for the particles of 2 nm, to 250 kJ mol⁻¹, for the particles of 12 nm. This explains the increased reactivity of the adsorbed oxygen with increasing particle size.

Schuurman et al. (1992) explained the particle size effect on the oxidation of methyl α-D-glucoside over Pt/C as a result of the stronger oxygen platinum bond on small particles. This would lead to a higher coverage of oxygen at the surface at the same reaction conditions. As the coverage of oxygen is already larger than 0.5 this would decrease the rate of reaction. The alternative explanation that the oxygen platinum bond would be involved in some way in the rate-determining step was found to be less likely.

Experimental difficulties in determining the particle size effect on the turnover frequency for metal catalysts could arise from various causes (Che and Bennet, 1989). Changes in metal support interaction (Strong Metal Support Interaction, SMSI), incomplete reduction of the metal, particle structure, deactivation and metal reconstruction upon adsorption with the particle size can obscure the real particle size effect on the TOF for a certain reaction. To obtain good data on the effect of the particle size, or the fraction exposed atoms on the turnover frequency for a certain reaction the metal particles should thus be approximately monodisperse, fully reduced, unpoisoned and show little interaction with the support.
The EXAFS analysis discussed in chapter 3 reveals that the particle retains a fcc structure in particles as small as 1.48 nm. There is also no indication for a change in particle morphology. The reduction of small platinum particles is easily accomplished by reduction at 363 K with hydrogen dissolved in water.

5.2. Experimental

The reactor setup and working procedure as described in chapter 4 were used to determine the steady state specific disappearance rate of ethanol for catalyst samples D0 to D5 (see chapter 2). These samples cover a platinum particle size range from 1.46 nm to approximately 3.2 nm and contain 3.9 wt% platinum. Catalyst D6 was also used for these experiments but the uncertainty in the particle size and the reaction rate were too large for a statistically meaningful interpretation of the results. The reaction conditions used for the measurements are given in Table 5.1. The amount of catalyst was varied depending on the catalyst activity from 180 to 350 mg. Most of the experiments were duplicated several times to obtain an estimate of the experimental error in the reaction rate.

The turnover frequency for the disappearance of ethanol based on platinum surface atoms is given by:

\[ \text{TOF} = \frac{R \times M_{\text{Pt}}}{w_{\text{Pt}} \times F} \]  (5.3)

5.3. Results and discussion

Table 5.2 summarizes the platinum particle size effect on the ethanol disappearance rate. Figure 5.2 shows the specific disappearance rate of ethanol versus the particle diameter and the fraction of exposed platinum atoms. This figure clearly shows a maximum in the specific disappearance rate of ethanol at a particle size of approximately 2 nm or a fraction of exposed platinum atoms of 0.7. As the particles become larger the specific rate will decrease. Ultimately at a fraction exposed of 0, or at an infinite large particle size, the specific rate will become 0. This trend is clearly visible in Figure 5.2.B.
Platinum particle size effects

<table>
<thead>
<tr>
<th>catalyst</th>
<th>(d_0) [nm]</th>
<th>FE [-]</th>
<th>(R_{W, ethanol}) [mmol kg(^{-1}) s(^{-1})]</th>
<th>TOF ([10^{-3} \text{ s}^{-1}])</th>
<th>no.exp. [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D0</td>
<td>1.46±0.03</td>
<td>0.88</td>
<td>4.7±0.6</td>
<td>27±4</td>
<td>3</td>
</tr>
<tr>
<td>D1</td>
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<td>7.4±1.1</td>
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<tr>
<td>D2</td>
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<td>8.2±2.1</td>
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</tr>
<tr>
<td>D3</td>
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<tr>
<td>D4</td>
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<td>0.59</td>
<td>9.1±2.1</td>
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<tr>
<td>D5</td>
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<td>6.0±1(^*)</td>
<td>75±13(^*)</td>
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</tbody>
</table>

Table 5.2: Experimental results with standard deviation for the particle size effect on the ethanol disappearance rate (\(^*\) = estimated standard deviation). Reaction conditions see Table 5.1.

**Figure 5.2** Specific disappearance rate of ethanol vs.: A) surface area averaged particle diameter; B) fraction of exposed platinum atoms. Reaction conditions see Table 5.1.

**Figure 5.3** Turnover frequency of the ethanol disappearance vs.: A) surface area averaged particle diameter; B) fraction of exposed platinum atoms. Reaction conditions see Table 5.1.
Figure 5.3 shows the turnover frequency of the ethanol disappearance versus particle size and fraction of exposed platinum atoms. It is clear that the turnover frequency is constant on particles larger than 2 nm or with a fraction of exposed platinum atoms less than 0.5. The turnover frequency decreases quickly on particles smaller than 2.5 nm or with a fraction exposed larger than 0.5. Note that the kinetic study reported in chapter 4 was performed on a catalyst batch with a platinum particle size of 1.95 nm, i.e. at a platinum particle size corresponding to the beginning of the "structure insensitive" region and corresponding to the maximum for the specific disappearance rate of ethanol.

The curve clearly indicates a limited structure sensitive reaction as the antipathetic effect becomes only visible at particle sizes smaller than 2 nm. Hence the reaction does not need special atoms or ensembles of several atoms to proceed.

The form of the curve is in good agreement with the results of Peuckert et al. (1986) for the electrochemical reduction of dioxygen over Pt/C and with the results of Schuurman et al. (1992) for the oxidation of methyl α-D-glucoside over Pt/C. Schuurman et al. explained the particle size effect on the oxidation of methyl α-D-glucoside over Pt/C by the stronger oxygen platinum bond on small particles. As the oxygen coverage at the used reaction conditions was larger than 0.5, which is of course the optimal coverage for a dual-site reaction, an increase of this coverage would indeed result in the observed decrease of the turnover frequency.

The kinetic study of the ethanol oxidation, described in chapter 4, indicates that the chemisorption of oxygen is more probably an irreversible reaction than a reversible reaction close to equilibrium, in the investigated range of reaction conditions. Thus the surface coverage of oxygen is not the result of an equilibrium between adsorption and desorption, which is influenced directly by the heat of chemisorption, but is the result of a balance between the adsorption rate of oxygen and the oxygen consumption rate via the surface reaction. The increased heat of chemisorption for oxygen results in a decrease of the activation energy for the adsorption according to the relation of Polanyi (Boudart and Djéga-Mariadassou, 1984), and thus results in an increase of the adsorption rate coefficient. The rate equation selected for the disappearance rate of ethanol in chapter 4, predicts that the oxygen coverage on the catalyst sample with a platinum particle size of 1.95 nm is about 0.34 at the conditions at which the particle size effect has been investigated in the present work. If this coverage would be increased by the increased adsorption rate coefficient, the turnover frequency of the global reaction would increase rather than decrease.

Sabatier formulated a golden rule of catalysis which states that on a good catalyst the reactive intermediate should be stable enough to be formed easily but not too stable in order to decompose easily towards the reaction product (Boudart and Djéga-
Mariadassou, 1984). This effect is clearly observed in the so-called "volcano curves". The rate of reaction first increases with the binding energy of a key reactant with the catalyst, then reaches a maximum and starts to decrease as the binding energy becomes too high.

It is possible to explain the observed decrease in the TOF with decreasing particle size with a Sabatier type of explanation when the oxygen-platinum bond strength influences the rate of the surface reaction and the binding energy is already higher than the optimal binding energy, i.e. when the oxygen-platinum bond strength is situated on the right-hand side of the "volcano plot". This does, however, not necessarily mean that this bond has to be broken during the surface reaction. It is possible that the stronger bonded oxygen on the smaller platinum particles is less capable of abstracting hydrogen from the adsorbed ethanol species. This effect must of course be countered only partially by the increased degree of oxygen coverage, resulting from the higher adsorption rate of oxygen, to result in the observed decrease of the turnover frequency with decreasing particle size.

Alternatively the particle size effect could of course be attributed to changes in the platinum-ethanol bond strength. At present, however, such an explanation is not supported by experimental data.

A more detailed kinetic study of the ethanol oxidation resulting in kinetic parameters as a function of the platinum particle size could possibly provide better insight in the cause of the particle size effect.

5.4. Conclusions

The oxidation of ethanol with dioxygen over a platinum on graphite catalyst shows a clear particle size effect on the turnover frequency at particle sizes smaller than 2 nm, corresponding to a limited structure sensitivity. This indicates that the oxidation of ethanol on platinum does not need active sites consisting of special surface atoms or ensembles of surface atoms. Most probably only a few surface atoms are needed for this reaction.

The particle size effect can be explained by the increased strength of the oxygen platinum bond. The stronger bonded oxygen is less capable of abstracting a hydrogen atom from the adsorbed ethanol species thereby decreasing the rate of reaction.

5.5. References


A.1. Calculation of saturation time for catalyst wafer in XAS-cell

To estimate the time necessary to saturate all of the active sites in a catalyst wafer with oxygen or hydrogen the following calculation was made.

For this situation transport in a flat plate with an irreversible infinite fast adsorption is assumed. The concentration profile for the component dissolved in water at a certain time, $t$, is then given by $C(x,t)$. Because of the symmetry only one half of the pellet of thickness $d$ has to be regarded. We define $C_0$ as the bulk concentration of the component at the outside of the pellet, $C_*$ as the concentration of adsorption sites for the relevant component, and a front position $\bar{x}(t)$ which moves in time and gives the penetration depth of the component (see Figure A.1). This is also the boundary of the region where all sites are already covered and the region were the sites have not yet been covered. For this situation the following partial differential equation can be derived for the concentration profile:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (A.1)$$

with boundary conditions:

$$x = 0, \quad C = C_0$$
$$x = \bar{x}(t), \quad C = 0 \quad (A.2)$$

By introduction of the more appropriate variable $p = \frac{x}{2\sqrt{Dt}}$, equation (A.1) can be rewritten to:

$$\frac{d^2 C}{dp^2} + 2p \frac{dC}{dp} = 0 \quad (A.3)$$

with the boundary conditions:

$$p = 0, \quad C = C_0 \quad (A.4)$$
$$p = \bar{p}, \quad C = 0$$
where:

\[ \hat{p} = \frac{\ddot{x}}{2\sqrt{D}t} \]  

(A.5)

which has as physical meaning the penetration depth with adsorption divided by the penetration depth without reaction or adsorption.

Solving this differential equation with boundary conditions gives:

\[
\begin{align*}
C &= C_0 \left(1 - \frac{\text{erf}(p)}{\text{erf}(\hat{p})}\right) \quad \text{for} \ 0 \leq p \leq \hat{p} \\
C &= 0 \quad \text{for} \ p > \hat{p}
\end{align*}
\]

(A.6)

The velocity at which the \( \hat{p} \) plane moves through the pellet can be found by realizing that all gas diffusing through this plane is instantaneously adsorbed on the sites in this plane until these are all covered:

\[
\frac{dx}{dt} = -\frac{D}{C_0} \frac{\partial C}{\partial x} \bigg|_{x(t)}
\]

(A.7)

This expression can be rewritten to:

\[
\frac{dx}{dt} = -\frac{D}{C_0} \left( \frac{\partial C}{\partial p} \frac{\partial p}{\partial x} \right) \bigg|_{x(t)}
\]

(A.8)

which becomes after differentiation:

\[
\frac{\sqrt{D}t}{dt} \frac{dx}{dt} = \frac{DC_0}{\sqrt{\pi C_0 \text{ erf}(\hat{p}) \exp(\hat{p}^2)}}
\]

(A.9)

Alternatively from the relation between \( \hat{p} \) and \( \ddot{x} \) given by equation A.5:

\[
\frac{dx}{dt} = 2\dot{p}\sqrt{\frac{D}{t}} + 2\sqrt{Dt} \frac{dp}{dt}
\]

(A.10)

From substitution of equation A.10 into A.9:

\[
2t \frac{dp}{dt} = \frac{C_0}{\sqrt{\pi C_0 \text{ erf}(\hat{p}) \exp(\hat{p}^2)}} - \hat{p}
\]

(A.11)
By assuming $\frac{dp}{dt} = 0$, which is equal to assuming that the penetration depth with adsorption divided by the penetration depth without reaction or adsorption is constant, this can be rewritten to:

$$\tilde{p} \text{erf}(\tilde{p}) \exp(\tilde{p}^2) = \frac{C_0}{C_\star \sqrt{\pi}}$$

(A.12)

The saturation time of the wafer, $\tau$, can now be found from equation A.12 by determining when the $\tilde{p}$ plane is exactly in the middle of the wafer:

$$\tilde{p} = \frac{d}{4\sqrt{D\tau}}$$

(A.13)

Figure A.2 Diagram for penetration time in a pellet with $C' = \frac{C_0}{C_\star \sqrt{\pi}}$ and $t' = \frac{d}{4\sqrt{D\tau}}$. Solid line: numerical solution of equation (A.12). Dashed line: second order approximation of equation (A.12) resulting in equation (A.15) for small values of $C'$.

This implicit equation is solved numerically and depicted in Figure A.2. This equation can also be approximated by a Taylor series:

$$\tilde{p} \text{erf}(\tilde{p}) \exp(\tilde{p}^2) = \frac{2}{\sqrt{\pi}} \tilde{p}^2 + \frac{4}{3\sqrt{\pi}} \tilde{p}^4 + O(\tilde{p}^6)$$

(A.14)
By taking the second order Taylor series expansion equation (A.12) can be rewritten to give explicitly the penetration time for sufficiently small values of \( \frac{C_o}{C \cdot \sqrt{\pi}} \):

\[
\tau = \frac{d^2 C_o}{8 D C_o} \quad (A.15)
\]

for \( \frac{C_o}{C \cdot \sqrt{\pi}} < 0.15 \)

Equation (A.15) is also obtained for shell progressive poisoning as discussed by Froment and Bischoff (1990).

The diffusion coefficient needed in the calculations, described above, is the effective diffusion coefficient, \( D_{\text{eff}} \), which is given by:

\[
D_{\text{eff}} = \frac{D \varepsilon_p}{\tau_p} \quad (A.16)
\]

in which \( \varepsilon_p \) is the porosity and \( \tau_p \) is the tortuosity of the catalyst wafer. For the catalyst pellet used in this work the porosity amounts to 0.5 and the tortuosity is taken as 4. The concentration Pt surface atoms per volume catalyst is calculated, using a catalyst density of 2250 kg m\(^{-3}\), a catalyst porosity of 0.5, and fraction exposed Pt atoms of 0.7, and amounted to 201.5 molPt m\(^{-3}\). To calculate the concentration of adsorption sites for H\(_2\) and O\(_2\), the reaction stoichiometry has to be taken in account. In this case it is assumed that H\(_2\) adsorption takes place on an O\(_2\) covered surface and that O\(_2\) adsorption takes place on a H\(_2\) covered surface:

\[
\begin{align*}
3H_2 + 2O^* &\rightarrow 2H_2O + 2H^* \\
3O_2 + 4H^* &\rightarrow 2H_2O + 4O^*
\end{align*}
\quad (A.17)
\]

The time needed to saturate the wafer of thickness \( d=10^{-3} \) m can now be calculated. The necessary information and the results are given in Table A.1.

<table>
<thead>
<tr>
<th>component</th>
<th>temperature [K]</th>
<th>( D ) [m(^2) s(^{-1})]</th>
<th>( D_{\text{eff}} ) [m(^2) s(^{-1})]</th>
<th>( C_0 ) [mol m(^{-3})]</th>
<th>( C^* ) [mol m(^{-3})]</th>
<th>sat. time [hr.]</th>
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<td>hydrogen</td>
<td>363</td>
<td>4.7 ( \times ) 10(^{-8})</td>
<td>5.9 ( \times ) 10(^{-9})</td>
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<td>302</td>
<td>2.4</td>
</tr>
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<td>oxygen</td>
<td>323</td>
<td>4.0 ( \times ) 10(^{-9})</td>
<td>5.0 ( \times ) 10(^{-10})</td>
<td>0.933</td>
<td>151</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Table A.1 Calculation of the component penetration time into the wafer from equation A.15.
Table A.2 Selected kinetic data used for regression analysis.
A.3. Assessment of absence of transfer limitations on kinetic data

A.3.1. Mass transfer limitations

As the concentration of oxygen in the aqueous phase is much lower than the other concentrations of the other stoichiometrically used and formed components in the ethanol oxidation, mass transfer limitations are expected for oxygen before other mass transfers will become limiting. Therefore only the rate of oxygen consumption will be considered for the assessment of absence of mass transfer limitations.

As oxygen is consumed in both the ethanol oxidation and the ethanal oxidation, the total net consumption rate of oxygen can be calculated according to:

\[ F_{O_2} = \frac{1}{2} (R_{W,\text{ethanol}} + R_{W,\text{ethanoate}}) W \]  \hspace{1cm} (A.18)

in which \( F_{O_2} \) is the net consumption rate of oxygen, \( R_{W,\text{ethanol}} \) and \( R_{W,\text{ethanoate}} \) are respectively the net specific disappearance rate of ethanol and the net specific production rate of ethanoate, and \( W \) is the total mass of catalyst in the reactor, typically \( 3.5 \times 10^{-4} \) kg.

A.3.2. Gas/liquid transfer of oxygen

Oxygen is first transferred from the gas phase to the liquid phase. The transfer rate can be expressed by:

\[ F_{O_2} = k_{gl,O_2} a_{gl} V_L C_{O_2}^{sat} (1 - \Gamma_{L,O_2}) \]  \hspace{1cm} (A.19)

in which \( k_{gl} \) is the gas/liquid mass transfer coefficient, \( a_{gl} \) is the volumetric gas/liquid interface surface area, \( V_L \) is the volume of the liquid phase, typically \( 3.5 \times 10^{-4} \) m\(^3\), \( C_{O_2}^{sat} \) is the oxygen concentration in equilibrium with the gas phase, and finally \( \Gamma_{L,O_2} \) is the degree of oxygen saturation of the liquid phase.

The criterion for absence of any transfer limitation is generally set to allow for a maximum deviation of 5% in the measured reaction rate from the actual reaction rate at the observed reaction conditions. This allows also, assuming a first order reaction, a maximum deviation in the actual oxygen concentration from the saturated oxygen concentration of 5%. Or, differently put, a minimum degree of oxygen saturation of 0.95.

This leads to the following criterion for the absence of oxygen mass transfer limitation:

\[ 1 - \frac{F_{O_2}}{k_{gl,O_2} a_{gl} V_L C_{O_2}^{sat}} > 0.95 \]  \hspace{1cm} (A.20)
The equilibrium oxygen concentration can be calculated for a given temperature and partial oxygen pressure with the correlation of Battino (1981):

$$C_{O_2}^{eq} = 0.5483 \exp(-179.3439 + 8747.547/T + 24.45264 \ln(T))P_{O_2}$$  \hspace{1cm} (A.21)

The product $k_{GL,O_2}a_{GL}$ is more difficult to determine. Correlations as given in literature are only valid for large industrial-scale reactors. Laboratory reactors are in general far more effective in contacting gas with liquid than industrial-scale reactors with their typical $k_{GL,O_2}a_{GL}$ of 0.1 s\(^{-1}\). In a simple laboratory reactor in which gas was contacted with liquid by the vortexing action of the impeller a $k_{GL,O_2}a_{GL}$ of 0.35 s\(^{-1}\) has been observed. The reactor used in this work was equipped with a special gas dispersion impeller which is more efficient than the impeller of the simple laboratory reactor. For this reason a $k_{GL,O_2}a_{GL}$ of 0.5 s\(^{-1}\) was assumed for this reactor.

All the selected data for the regression analysis were subjected to the criterion for gas/liquid mass transfer of oxygen. As depicted in Figure A.3 only three experiments suffered from a slight oxygen mass transfer limitation. These experiments were all at quite low oxygen partial pressures and were not rejected because data at low pressures is scarce and very important for a good regression. As the reaction order in oxygen is lower than first order the error in reaction rates is still estimated to be lower than 5%.

It is possible to lower the catalyst content of the reactor to obtain kinetic data at the conditions which would normally lead to gas/liquid oxygen transfer limitations.

### A.3.3. Liquid/solid transfer of oxygen

Oxygen is subsequently transferred from the liquid phase to the surface of the catalyst particles. The transfer rate can again be expressed by:

$$F_{O_2} = k_{LS,O_2}a_{LS} V_L C_{O_2}^{eq}(1 - \Gamma_{s,O_2})$$  \hspace{1cm} (A.22)
in which \( F_{O_2} \) is the net consumption rate of oxygen calculated with equation A.18, \( k_{LS} \) is the liquid/solid mass transfer coefficient, \( a_{LS} \) is the volumetric liquid/solid interface surface area, and \( \Gamma_{s,O_2} \) is the degree of oxygen saturation at the catalyst particle surface.

In analogy to the gas/liquid transfer, the following criterion can be derived for the absence of oxygen mass transfer limitation from the liquid to the particle surface:

\[
1 - \frac{F_{O_2}}{k_{LS,O_2} a_{LS} V_L C^{O_2}_{L_0}} > 0.95 \quad (A.23)
\]

The liquid/solid mass transfer coefficient, \( k_{LS} \), can be determined from the correlation of Sano et al. (1974):

\[
Sh = \varphi_c (2 + 0.4 R_e^{K} S_c^{K}) \quad (A.24)
\]

in which \( Sh = k_{LS} d_p / D \) is the dimensionless Sherwood number, \( \varphi_c \) is the Carman correction factor for the geometry of the particle (\( \varphi_c = 1 \) for a spherical particle), \( Re \) is the dimensionless Reynolds number based on the Kolmogoroff theory for isotropic turbulence, and \( Sc = \mu_L / \rho_L D \) is the dimensionless Schmidt number.

The dimensionless number of Reynolds based on the Kolmogoroff theory for isotropic turbulence is given by:

\[
Re = \frac{N_p d_i^3 N_i d_p^4 \rho_L^3}{\mu_L^3 V_L} \quad (A.25)
\]

in which \( N_p \) is the impeller power number (=5; Bates et al., 1963), \( d_i \) is the impeller diameter (= 0.032 m), \( N_i \) is the impeller revolution speed (=18.3 s\(^{-1}\)), \( d_p \) is the powder size of the solid, \( \rho_L \) is the volumetric mass of the liquid, and \( \mu_L \) is the dynamic viscosity of the liquid.

The powder size, \( d_p \), is for the catalyst used taken as 15 \( \mu \)m for a conservative evaluation of the criterion. Most of the powder particles are smaller than 10 \( \mu \)m. The volumetric mass of the liquid, water in this case, does not depend much on the temperature in the investigated temperature range and is therefore taken constant as 1000 kg m\(^{-3}\). The dynamic viscosity of water was calculated with the following correlation valid between 293 and 373 K (Weast, 1988):

\[
\mu_{H_2O} = 1.002 \times 10^{-3} \ 10^{-\frac{(13272(293.15 - T) - 0.001053(T - 293.15)^3}{T - 108.15}} \quad (A.26)
\]
The diffusion coefficient of oxygen in water is calculated by the Wilke-Chang correlation (Perry and Green, 1984) which results for oxygen in water using S.I. units in:

\[ D_{O_2,H_2O} = 6.7449 \times 10^{-15} \frac{T}{\mu_{H_2O}} \]  \hspace{1cm} (A.27)

Using the above correlations the value of the liquid/solid mass transfer coefficient for oxygen, \( k_{LS,O_2} \), can be estimated. A typical value for this coefficient at 323 K amounts to \( 10^{-3} \) m s\(^{-1}\).

The volumetric liquid/solid interface surface area, \( a_{LS} \), is given by:

\[ a_{LS} = \frac{6W}{d_p V_L \rho_p} \]  \hspace{1cm} (A.28)

in which \( \rho_p \) is the volumetric mass of the dry particle which can be calculated from the particle porosity, \( \varepsilon_p \), and the volumetric mass of the support, \( \rho_s \), as

\[ \rho_p = (1-\varepsilon_p) \rho_s. \]

The volumetric mass of the particle, with a porosity of 0.68 and a volumetric mass of the support of 2250 kg m\(^{-3}\), then amounts to 720 kg m\(^{-3}\). The volumetric liquid/solid interface surface area amounts to 556 m\(^{-1}\).

Using the above correlations and values all selected data were subjected to the criterion for liquid/solid mass transfer of oxygen. Figure A.4 shows clearly that none of the data points were acquired at liquid/solid oxygen transfer limiting conditions. As the particle size is take to be 15 \( \mu \)m, which is quite larger than the surface area averaged catalyst particle size, the liquid/solid transfer does not seem to be critical for the ethanol oxidation with the used catalyst.

If liquid/solid transfer limitations would occur, grinding the catalyst powder would strongly improve the liquid/solid transfer and probably eliminate these problems.

Figure A.4 Evaluation of the liquid/solid mass transfer criterion of oxygen (A.23) for all the data used in the regression analysis.
A.3.4. Pore diffusion of oxygen

After oxygen is transferred to the external surface of the catalyst powder, the oxygen will diffuse into the pores of the catalyst and react at the small platinum particles located in the pores. The effectiveness factor, \( \eta \), is defined as the ratio of the observed rate to the rate at the same external conditions but without any pore diffusion limitation. This effectiveness factor can be related to the so-called Weisz modulus, \( \Phi \), for a given rate equation (Mears, 1971; Froment and Bischoff, 1990). Assuming that oxygen reacts according to an irreversible first order reaction, which is an overestimation of the real reaction order of oxygen and thus a conservative assumption, the Weisz modulus has to be smaller than 0.24 in order to obtain an effectiveness factor larger than 0.95. The criterion for absence of pore diffusion limitation is thus given by:

\[
\frac{d_p^2 F_{O_2} \rho_p}{36 D_{O_2}^{\text{eff}} C_{O_2} W} < 0.24
\]  

(A.29)

The effective diffusion coefficient, \( D^{\text{eff}} \), can be calculated by:

\[
D^{\text{eff}} = \frac{D \varepsilon_p}{\tau_p}
\]  

(A.30)

The particle tortuosity, \( \tau_p \), is taken to be 4, which is the value which normally is taken when experimental data is absent.

Evaluation of criterion A.29 for all selected data used in the regression analysis is shown in Figure A.5. It is clear that pore diffusion limitation of oxygen is absent at the used conditions.

![Figure A.5 Evaluation of the pore diffusion criterion of oxygen (A.29) for all the data used in the regression analysis.](image-url)
A.3.5. Solid/liquid heat transfer

The heat transfer from solid to liquid can be described by:

\[ Q = \alpha_{LS} a_{LS} V_L (T_s - T_L) \]  \hspace{1cm} (A.31)

in which \( Q \) is the heat transferred, and \( \alpha_{LS} \) is the heat transfer coefficient.

The heat production can be estimated by:

\[ Q = (R_{W,\text{ethanol}} + R_{W,\text{ethanoate}}) \rho W \Delta H^0 \]  \hspace{1cm} (A.32)

in which \( \Delta H^0 \) is the enthalpy change for an oxidation reaction and is conservatively taken to be 500 kJ mol\(^{-1}\) for ethanol and ethanal oxidation.

The heat transfer coefficient, \( \alpha_{LS} \), can be estimated from the mass transfer coefficient, \( k_{LS} \), by the so-called Chilton-Colburn analogy between heat and mass transfer (Satterfield, 1970), which can be rewritten to give:

\[ \alpha_{LS} = 1.37 k_{LS} \rho_L c_{p,L} \left( \frac{Sc}{Pr} \right)^{1/3} \]  \hspace{1cm} (A.33)

in which \( c_{p,L} \) is the specific heat capacity of the liquid, and \( Pr = \mu_L c_{p,L} / \lambda_L \) is the dimensionless Prandtl number. In this calculation the estimation of the heat transfer coefficient was performed for water at 323 K. Taking a specific heat capacity of 4.18 kJ kg\(^{-1}\) K\(^{-1}\) and heat conductivity, \( \lambda_L \), of 0.643 W m\(^{-1}\) K\(^{-1}\) the heat transfer coefficient amounts to 75 kW m\(^{-2}\) K\(^{-1}\). Taking a maximum total oxidation rate of 20 mmol kg\(^{-1}\) s\(^{-1}\), i.e. the sum of the disappearance rate of ethanol and production rate of ethanoate, the heat production amounts to 3.5 W which leads to an temperature difference of 2.5 \( 10^{-4} \) K between the particle surface and the liquid. At 323 K and with an apparent activation energy of 100 kJ mol\(^{-1}\) the maximum temperature difference which could be allowed for a 5% deviation in reaction rate is 0.5 K. From these results it can be concluded that the heat transfer from solid to liquid will not significantly influence the observed rate.
A.3.6. Intra-particle heat transfer
According to Mears (1971) internal heat transfer is fast compared to solid/liquid heat transfer for sufficiently small values of the dimensionless Biot number for the powder particle, Biₚ:

\[ \text{Bi}_p = \frac{\alpha_{ls} d_p}{\lambda_p} < 10 \]  

(A.34)

The heat conductivity of the particle, \( \lambda_p \), can, as an estimation, taken to be equal to the conductivity of the liquid phase of 0.643 W m⁻¹ K⁻¹, especially in the case of carbon supports which have a solid phase heat conductivity of 0.84 W m⁻¹ K⁻¹ (Sehr, 1958). Using the values given above the dimensionless Biot number amounts to 1.75. Hence the internal heat transport will not influence the observed rate significantly.
A.4. Calculation of equilibrium and rate coefficients from kinetic parameters

The equilibrium coefficients for the various reaction steps mentioned in chapter 4 can be calculated from the estimated kinetic parameters by:

\[ K = K^0 \exp\left(-\frac{\Delta H^0}{RT}\right) = 10^{-3} \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(-\frac{\Delta H^0}{RT}\right) \]  \hspace{1cm} (A.35)

The factor 10\(^{-3}\) is necessary to convert from the standard concentration of mol dm\(^{-3}\) to the SI units of mol m\(^{-3}\). The dimension of K calculated according to Equation A.35 amounts for all models and reaction steps mentioned in this work to m\(^{1}\) mol\(^{-1}\).

The rate coefficient can be calculated by:

\[ k = A^0 \exp\left(-\frac{\Delta' H^0}{RT}\right) = \frac{zRT}{2N_e h} \exp\left(\frac{\Delta' S^0}{R}\right) \exp\left(-\frac{\Delta' H^0}{RT}\right) \]  \hspace{1cm} (A.36)

The factor \(\frac{zRT}{2N_e h}\) amounts in this work to 2.028 \(10^{13}\) s\(^{-1}\). The dimension of the surface reaction rate coefficients, \(k_3\), amounts for all discussed models to s\(^{-1}\).

The dimension of the rate coefficients for oxygen adsorption, \(k_1\), amounts for all models to dm\(^3\) mol\(^{-1}\) s\(^{-1}\) as the formula takes implicitly into account the standard concentration of mol dm\(^{-3}\) in the liquid phase. To obtain \(k_1\) in the SI units of m\(^3\) mol\(^{-1}\) s\(^{-1}\) the numerical value obtained from equation A.36 has to be multiplied with 10\(^{-3}\).
A.5. Literature


## NOTATION

**Roman symbols**

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>a</td>
<td>volumetric surface area</td>
<td>(m^2) (m^3)</td>
</tr>
<tr>
<td>A</td>
<td>normalised white-line surface area</td>
<td>eV</td>
</tr>
<tr>
<td>(A^0)</td>
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<td>J K(^{-1})</td>
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<td>J K(^{-1})</td>
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<td>W</td>
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<td>Definition</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>R</td>
<td>gas constant (=8.3144)</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>R(_w)</td>
<td>coordination distance, distance</td>
<td>m</td>
</tr>
<tr>
<td>s</td>
<td>standard deviation</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>entropy</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>(\bar{T})</td>
<td>average temperature for reparametrization</td>
<td>K</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>m(^3)</td>
</tr>
<tr>
<td>w</td>
<td>weight fraction</td>
<td>-</td>
</tr>
<tr>
<td>W</td>
<td>catalyst mass</td>
<td>kg(_{\text{cat}})</td>
</tr>
<tr>
<td>x</td>
<td>mole fraction</td>
<td>-</td>
</tr>
<tr>
<td>x</td>
<td>position</td>
<td>m</td>
</tr>
<tr>
<td>x</td>
<td>vector of independent variables</td>
<td>-</td>
</tr>
<tr>
<td>z</td>
<td>number of neighboring sites</td>
<td>-</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>probability of rejecting correct hypothesis</td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td>heat transfer coefficient</td>
<td>W m(^{-2}) K(^{-1})</td>
</tr>
<tr>
<td>(\beta)</td>
<td>vector of parameters</td>
<td></td>
</tr>
<tr>
<td>(\Delta\sigma^2)</td>
<td>relative mean square displacement</td>
<td>m(^2)</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>porosity</td>
<td>-</td>
</tr>
<tr>
<td>(\varepsilon_v^2)</td>
<td>goodness of fit for EXAFS</td>
<td>-</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>degree of saturation</td>
<td>-</td>
</tr>
<tr>
<td>(\phi_c)</td>
<td>Carmann correction factor</td>
<td></td>
</tr>
<tr>
<td>(\lambda)</td>
<td>heat conductivity</td>
<td>W m(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>(\mu)</td>
<td>normalised absorption coefficient</td>
<td>-</td>
</tr>
<tr>
<td>(\mu)</td>
<td>dynamic viscosity</td>
<td>kg m(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>(\rho)</td>
<td>volumetric mass</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>stoichiometric number</td>
<td>-</td>
</tr>
<tr>
<td>(\tau)</td>
<td>characteristic time, penetration time</td>
<td>s</td>
</tr>
<tr>
<td>(\tau)</td>
<td>tortuosity</td>
<td>-</td>
</tr>
<tr>
<td>(\chi)</td>
<td>normalised modulation of absorption coefficient</td>
<td>-</td>
</tr>
</tbody>
</table>
### Functions

- $\delta(k)$: phase shift function
- $F(k)$: amplitude function
- $\text{SRS}(b)$: sum of squared residuals

### Dimensionless groups

- $\text{Bi}$: Biot number
- $\text{FE}$: Fraction Exposed atoms
- $\text{Pr}$: Prandtl number
- $\text{Re}$: Reynolds number
- $\text{Sc}$: Schmidt number
- $\text{Sh}$: Sherwood number

### Subscripts

- $0$: edge, at boundary
- $1$: oxygen
- $2$: ethanol
- $3$: surface reaction
- $\text{app}$: apparent
- $c$: critical, correction
- $\text{C}$: carbon atoms
- $\text{cat}$: catalyst
- $f$: degrees of freedom
- $\text{GL}$: gas to liquid
- $i$: of $i$th class
- $i$: impeller
- $j$: of $j$th shell
- $\text{L}$: liquid
- $\text{LS}$: liquid to solid
- $\text{obs}$: observations
- $p$: particle, pellet, powder
- $\text{par}$: parameters
- $s$: surface area averaged
- $s$: solid
- $*$: of active sites/adsorption sites
Superscripts

$\text{eff}$ effective
$s$ saturated
$0$ at reactor inlet, standard
$s$ activation
$\wedge$ calculated
$\sim$ at front position
CURRICULUM VITAE


DANKWOORD

Gaarne wil ik bij deze, zonder namen te noemen en bijdragen te vermelden, een ieder bedanken die zich op enigerlei wijze in gezet heeft bij het stand komen van dit proefschrift.

ACKNOWLEDGEMENT

The Dutch Organization for Scientific Research (NWO) supplied the beam time at the Synchrotron Radiation Source in Daresbury (UK) for the X-ray Absorption measurements described in chapter 3.
STELLINGEN

behorende bij het proefschrift

Platinum Catalysis with Oxygen in Water
Catalyst characterization and
kinetics of partial ethanol oxidation

van

Johan Albert Arno van den Tillaart

1. De veel gebruikte bepaling van de "white-line" oppervlakte in een röntgen absorptie spectrum (XAS) door het verschil te nemen ten opzichte van een gekozen referentie is principeel fout indien er een duidelijk verschil is in chemische omgeving tussen deze beiden. Hoofdstuk 3 van dit proefschrift.

2. De relatie tussen de pKₐ van de betreffende alcoholgroep en het karakter van de adsorptie op het platina-oppervlak, associatief of dissociatief, is niet eenvoudig. Hoofdstuk 4 van dit proefschrift.

3. Hoewel voor de oxydatie van verschillende alcoholgroepen de reactiestappen toch gelijk kunnen zijn, kunnen verschillen in de reactiesnelheidscoefficiënten van de elementaire stappen leiden tot belangrijke verschillen in het macroscopische gedrag van de reactie, in het bijzonder in het gedrag van de katalysatordesactivering. Hoofdstuk 4 van dit proefschrift.


6. Het slechts stationair bezien van de reactiekinetiek verbergt grotendeels de meer interessante rijke wereld van achterliggend dynamisch gedrag van een reactie.

7. Het toenemen van het aantal milieuschandalen is zeker voor een deel toe te schrijven aan de verlaging van de detectiegrens met behulp van moderne analysetechnieken.

8. Een gedeelte van de tijdwinst die wordt behaald met het automatiseren van bepaalde taken wordt veelal gebruikt om de eisen die gesteld worden aan het eindresultaat van die taak te verhogen.

9. Om via de media een objectief beeld van de wereld om ons heen te krijgen dient men zich goed te realiseren dat de nieuwswaarde van slecht nieuws vele malen groter is dan die van goed nieuws.