Platinum catalysed alcohol oxidation: 
Kinetics, reaction engineering, 
and process design

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Summary

Traditionally, due to fast production demands and one pot operation, synthesis routes of fine chemical and pharmaceutical compounds have been based, amongst others, on alcohol oxidation with stoichiometric quantities of inorganic oxidants. This oxidation process suffers from low atom efficiency and high toxic waste production. Alcohol oxidation by enzymes is practiced as an environmentally friendlier alternative, however product separation and waste production remain a problem. Homogeneous catalysis is an efficient alternative, however catalyst recovery, reactant recycling, and reactor corrosion limits its industrial scale utilization. Heterogeneous catalytic alcohol oxidation has been known for a long time. However, in the past 20 years there has been a growing demand for clean and efficient solid catalysts, for the production of fine and speciality chemicals. Noble metal catalyzed alcohol oxidation with cheap oxidants such as air or molecular oxygen, is a clean and elegant alternative with mild reaction conditions and high selectivities that can be obtained.

In this PhD research work, the Pt catalysed selective oxidation of methyl α-D-glucopyranoside and D-glucose in a continuous or semi-batch reaction mode, with oxygen as an oxidant, was investigated. It is generally accepted that the reaction takes place via a dehydrogenation mechanism followed by the oxidation of the adsorbed hydrogen atoms with dissociatively adsorbed oxygen. The nature of catalyst deactivation is largely influenced by the amount of oxygen present at the catalytic surface. Several types of catalyst deactivation mechanisms have been identified, viz. over-oxidation, the formation of carbonaceous deposits, metal particle-growth, metal leaching, and chemical poisoning. These deactivation mechanisms lead to a decrease of the active metal surface area and hence to a decrease of the reaction rate. It has been found that over-oxidation was the major cause of catalyst deactivation in this study and care has been taken to avoid other types of deactivations.

A dynamic transport model is derived to describe the platinum catalysed aqueous alcohol oxidation, considering a single spherical catalyst particle surrounded by a stagnant liquid film. The transport model is based on a heterogeneous kinetic model with mass transfer and intra particle diffusion resistances. The developed model uses formerly developed kinetic model and is validated with the formerly obtained experimental kinetic data of methyl α-D-glucopyranoside
(MGP) oxidation. The model is used to investigate the effect of process conditions, catalyst and particle properties, and transport parameters on the performance of the catalyst for alcohol oxidation. It is found that the electron conductivity of the catalyst support affects the rate of MGP oxidation especially at low bulk liquid oxygen concentrations. At high bulk liquid oxygen concentrations, the catalyst support conductivity does not play a role.

A major cause of catalyst deactivation is over-oxidation under oxygen rich conditions. This can be reversed by applying redox-cycle operation, an alternating exposure of the catalyst to oxidative and reductive environments. The advantages of redox-cycle operation are demonstrated using the developed model. For reactions of negative order, such as MGP oxidation, at high bulk oxygen concentrations ($C_{O_2,L} > 0.3 \text{ mol/m}^3$), concentrating the active catalytic material in a layer buried some distance from the surface (core) gives considerable better performance than the conventional ”egg shell” design of shallow deposition near the surface or uniform distribution. However, at low bulk oxygen concentrations ($C_{O_2,L} \leq 0.3 \text{ mol/m}^3$), the performance of the uniform or egg shell catalyst distribution is superior to the core catalyst, which suffers with strong diffusion limitations.

The model predicts very high oxidation rates, at low bulk liquid oxygen concentrations or oxygen mass transport limited conditions. However, experiments at mass transport limited conditions did not verify these high rates. It is diagnosed that for negative order kinetics, such as the reaction under investigation, kinetic parameters were erroneously estimated, which resulted in inadequate model description for the observed reaction rates at mass transport limited conditions. Kinetic parameters of a reaction rate model are usually estimated using reaction rate measurements obtained at intrinsic kinetic conditions, viz., without limitation of the reaction rate by mass transport, irrespective of the order of the reaction kinetics. For positive order kinetics, this is good practice and the kinetic rate parameters can be safely applied both at intrinsic and mass transport limited conditions. However, for negative order kinetics, erroneous results are obtained because the kinetic rate parameters estimated at intrinsic kinetic conditions fail to predict the reaction rate when mass transport limitation also plays a role. This is demonstrated for the simple case of Langmuir-Hinshelwood negative-order kinetics and for the, more complex, kinetics of the oxidation of methyl $\alpha$-D-glucopyranoside on noble metal catalysts. It is concluded that for a negative-order reaction rate model, which is valid for a wide range of reaction conditions, the kinetic rate parameters need to be estimated both at intrinsic and mass transport limited conditions.

The electrochemical kinetic model with proper kinetic parameters is then used to design the catalyst activity profile for alcohol oxidation. This was done by comparing experimental data obtained in a semi-batch reactor with reactor modelling results, for catalysts of different ac-
tivity distributions viz., egg shell and uniform. Experimental results show that for methyl α-D-glucopyranoside oxidation at oxygen partial pressures below 40 kPa, the egg shell catalytic activity distribution gives a higher rate of oxidation than a uniform distribution. It was also observed that with increase in the oxygen partial pressure from 10 to 40 kPa, the rate of deactivation due to catalyst over-oxidation increased dramatically. For glucose oxidation, both catalyst activity distributions give the same oxidation rate for all investigated oxygen partial pressures (5 kPa-100 kPa). The developed model adequately describes the observed experimental results of both reactions. It was found that the active metal particle size has a significant influence on the catalyst deactivation for MGP oxidation; the uniform catalyst with higher dispersion shows a higher deactivation rate than the egg shell catalyst. For modelling glucose oxidation, the effect of catalyst particle-to-bubble adhesion and higher diffusivity or partition coefficient for oxygen have to be taken into account. Measuring the in-situ open circuit electrochemical catalyst potential has been used as a tool to understand and model alcohol oxidation.

Based on a detailed investigation of the mechanistic steps of alcohol oxidation, the kinetic model is further modified to describe the observed influence of pH. Experiments are performed at pH values between 6 and 10, using carbon and graphite supported Pt catalyst. The kinetic model adequately describes the observed pH effect by considering the alcohol dehydrogenation occurring in two parallel reaction steps, one playing a role at acidic conditions, which is independent of the hydroxyl ion concentration, and a second one playing a role at alkaline conditions, which is linearly dependent on the hydroxyl ion concentration. The intermediate aldehyde dehydrogenation and the catalyst deactivation due to over-oxidation are also described by alkaline and non-alkaline reaction steps.

The developed model is further used in describing the influence of the reaction start-up procedure on the oxidation of methyl α-D-glucopyranoside. Results are obtained using semi-batch experiments in a stirred slurry reactor with a Pt on carbon catalyst and molecular oxygen as oxidant. Three types of reaction start-up procedures are applied with respect to the pretreatment of the catalyst slurry, viz. reduced, oxidised, and inert. The reduced start-up resulted in the highest initial catalyst activity, compared to the other start-up procedures. It is found that the catalyst needs pretreatment before starting the reaction, as the inert start-up results in no catalytic activity at all. Additionally, independent of the start-up procedure, under oxygen rich conditions, for a weak reducing compound, over-oxidation is found to be the main cause of catalyst deactivation. The rate of over-oxidation is lower in the absence of the dehydrogenation reaction, which is modelled by considering that over-oxidation (Pt corrosion) needs free sites in order to take place. The mechanism of catalyst deactivation is experimentally verified through intermediate catalyst reactivation. The model adequately describes this reactivation step.
An industrially viable process design is presented for the platinum catalysed oxidation of methyl $\alpha$-D-glucopyranoside to 1-O-methyl $\alpha$-D-glucuronic acid. In order to overcome catalyst deactivation due to over-oxidation, the process is operated periodically by exposing the catalyst to oxidative and reductive cycles. The selectivity is improved by continuous removal of the main product, avoiding secondary reactions. In this way a high average production rate and high catalyst life span can be maintained.
Samenvatting

Omdat snelle produktie en eenvoudige procesvoering vereist zijn, zijn de gebruikelijke syntheseroutes voor fijnchemicalin en pharmaceutica, veelal, onder andere, gebaseerd op alcoholoxidatie met stoechiometrische hoeveelheden anorganische oxidantia. Dit type oxidatieproces is behept met een lage atomefficiëntie en een hoge produktie van giftig afval. Alcoholoxidatie met behulp van enzymen wordt gebruikt als een milieuvriendelijker alternatief, maar produktafscheiding en afvalproductie blijven daarbij een probleem. Homogene katalyse is een efficiënt alternatief, echter katalysatorterugwinning, reactantenrecycle, en reactorcorrosie, beperken toepassing op industriële schaal. Heterogeen-katalytische alcoholoxidatie is reeds lange tijd bekend. In de laatste 20 jaar is er echter een toenemende vraag naar schone en efficiënte, vaste katalysatoren voor de produktie van fijnchemicalin en specialties. Edelmetaalgekatalyserte alcoholoxidatie met goedkope oxidantia, zoals lucht of moleculaire zuurstof, vormt een schoon en elegant alternatief met milde reaktiecondities en hoge bereikbare selectiviteiten.

In dit promotieonderzoek, werd de Pt-gekatalyseerde, selectieve oxidatie van methyl α-D-glucopyranoside en D-glucose met zuurstof als oxidans, in continue of semi-batch procesvoering, onderzocht. Er wordt in het algemeen aangenomen dat de reaktie plaatsvindt via een dehydrogeneringsmechanisme, gevolgd door oxidatie van de geadsorbeerde waterstofatomen met dissociatief geadsorbeerd zuurstof. De aard van de katalysatordeactivering wordt sterk beïnvloed door de hoeveelheid zuurstof die aanwezig is op het katalysatoroppervlak. Diverse types mechanismen voor katalysatordeactivering zijn geïdentificeerd, te weten over-oxidatie, de vorming van koolafzettingen, groei van metaaldeeltjes, uitlogen van metaal, en chemische vergiftiging. Deze deactiveringsmechanismen leiden tot een afname van het aktieve metaaloppervlak, en dientengevolge een daling van de reaktiesnelheid. Er is gevonden dat overoxidatie de hoofdoorzaak van katalysatordeactivering was in deze studie, en er is zorg gedragen de andere deactiveringstypes te vermijden. Er wordt een dynamisch transportmodel afgeleid, welke een enkel bolvormig katalysatordeeltje, omringd door een stagnante vloeistoffilm, beschouwd.

Het transportmodel wordt gebaseerd op een heterogeen kinetisch model met stofoverdrachts- en inwendige diffusieweerstanden. Het ontwikkelde model maakt gebruik van een eerder on-
Samenvatting
twikkeld kinetisch model, en wordt op waarde getoetst met eerder verkregen experimentele
kinetische gegevens voor methyl-α-D-glucopyranoside (MGP) oxidatie. Het model wordt ge-
bruikt om het effekt van procesomstandigheden, katalysator- en deeltjeseigenschappen, en de
transportparameters te onderzoeken, op de prestatie van de katalysator voor alcoholoxidatie. Er
wordt gevonden dat de electronengeleidbaarheid van de katalysatordrager de snelheid van de
MGP-oxidatie beïnvloedt, vooral bij lage bulk-zuurstofconcentraties. Bij hoge bulk-zuurstofco-
ncentraties, speelt de electronengeleidbaarheid van de katalysatordrager geen rol.

Een belangrijke oorzaak van katalysatordeactivering is over-oxidatie onder zuurstofrijke om-
standigheden. Dit kan worden teniet gedaan door het toepassen van een redox-cyclus, een
wisselende blootstelling van de katalysator aan oxidatieve en reductieve milieus. Gebruikmak-
ende van het ontwikkelde model, worden de voordelen van het uitvoeren van een redox-cyclus
gedemonstreerd. Voor reakties van negatieve orde, zoals de MGP-oxidatie, voldoen, bij hoge
bulk-zuurstofconcentraties \( C_{o2,L} > 0.3 \text{mol/m}^3 \), katalysatoren waarbij het aktief katalytisch ma-
teriaal is begraven op enige afstand van het oppervlak (in de kern), aanzienlijk beter dan con-
vensionele katalysatoren met "eierschaal" ontwerp, ondiepe afzetting nabij het oppervlak, of
met homogene verdeling. Bij lage bulk-zuurstofconcentraties \( C_{o2,L} < 0.3 \text{mol/m}^3 \), is echter de
prestatie van de homogene of eierschaalkatalysator, superieur aan die van de kernkatalysator,
die te lijden heeft onder sterke diffusielimiteringen.

Bij lage vloeistofbulk-zuurstofconcentraties of onder zuurstof-stoftransportlimiterende omstan-
digheden, voorspelt het model zeer hoge oxidatiesnelheden. Experimenten onder stoftrans-
portlimiterende omstandigheden, konden deze hoge snelheden echter niet bevestigen. Er wordt
vastgesteld dat voor negatieve-orde kinetiek, zoals voor de onderzochte reaktie, kinetische pa-
rameters foutief werden geschat, hetgeen een ondeugdelijke modelbeschrijving van de waargen-
omen reaktiesnelheden onder stoftransportlimiterende omstandigheden, tot gevolg had. Kinetis-
che parameters van een reaktiesnelheidsmodel worden gewoonlijk geschat door gebruik te maken
van reaktiesnelheidsmetingen, verkregen onder intrinsiek-kinetische omstandigheden, dwz.
zonder beperking van de reaktiesnelheid door stoftransport, zonder rekening te houden met de
orde van de reaktiekinetiek. Voor reakties van positieve orde is dit de juiste handelwijze, en
canén de kinetische parameters op betrouwbare wijze worden toegepast, onder zowel intrin-
sieke als stoftransportlimiterende omstandigheden. Voor kinetiek van negatieve orde worden
echter foutieve resultaten verkregen, want de kinetische parameters, geschat onder intrinsiek-
kinetische omstandigheden, falen in het voorspellen van de reaktiesnelheid, wanneer ook stof-
transportlimitering een rol speelt. Dit wordt aangetoond voor het eenvoudige geval van Langmuir-
Hinshelwood-negatieve-orde kinetiek, en voor de meer ingewikkelde kinetiek van de oxidatie
van methyl-α-D-glucopyranoside over edelmetaalkatalysatoren. Er wordt tot de slotsom geko-
men dat, voor een reaktiesnelheidsmodel van negatieve orde, geldig voor een breed gebied
Samenvatting

van reaktieomstandigheden, de kinetische parameters geschat dienen te worden onder zowel intrinsieke- als stofoverdrachtslimiterende omstandigheden.

Het electrochemisch-kinetisch model met de juiste kinetische parameters, wordt vervolgens gebruikt om het activiteitsprofiel van de katalysator voor alcoholoxidatie te ontwerpen. De experimentele resultaten laten zien dat, voor de oxidatie van methyl-α-D-glucopyranoside bij zuurstof-partiaaldrukken onder 40 kPa, de eierschaalverdeling van katalytische activiteit een hogere oxidatiesnelheid oplevert dan de homogene verdeling. Ook werd waargenomen dat bij toename van de zuurstof-partiaaldruk van 10 tot 40 kPa, de deactiveringssnelheid van de katalysator ten gevolge van over-oxidatie, sterk steeg. Voor glucose oxidatie geven beide katalysator-aktiviteitsverdelingen dezelfde oxidatiesnelheid, voor alle onderzochte zuurstof-partiaaldrukken (5 -100 kPa). Het ontwikkelde model geeft een passende beschrijving van de experimentele resultaten voor beide reakties.

Voor MGP-oxidatie werd gevonden dat de deeltjesgrootte van het aktieve metaal een belangrijke invloed heeft op de katalysatordeactivering; de homogene katalysator met hogere dispersie vertoont een hogere deactiveringssnelheid dan de eierschaal-katalysator. Bij het modelleren van de glucose-oxidatie moet rekening worden gehouden met het effect van hechting van katalysatordeeltjes aan gasbellen, en met een hogere diffusiesnelheid of een hogere verdelingscoefficient voor zuurstof. Het in-situ meten van de open-circuit electrochemische katalysator-potentiaal, is gebruikt als middel om de alcoholoxidatie te begrijpen en te modelleren.

Gebaseerd op een gedetailleerd onderzoek van de mechanistische stappen van de alcoholoxidatie, wordt het kinetisch model verder aangepast om de waargenomen invloed van de pH te beschrijven. Experimenten worden uitgevoerd bij pH-waarden tussen 6 en 10, gebruikmakende van kool- en grafietgedragen Pt-katalysatoren. Het kinetisch model kan het waargenomen pH-effect goed beschrijven door te veronderstellen dat de alcoholdehydrogenering langs twee parallele reaktiepaden verloopt, waarbij n een rol speelt bij zure omstandigheden en onafhankelijk is van de hydroxylionenconcentratie, en de tweede een rol speelt bij alkalische omstandigheden en lineair afhankelijk is van de hydroxylionenconcentratie. De dehydrogenering van het aldehydetussenproduct en de katalysatordeactivering door over-oxidatie, worden eveneens beschreven met alkalische en niet-alkalische reaktiestappen.

Het ontwikkelde model wordt verder gebruikt om de invloed van de opstartprocedure van de reaktie, op de oxidatie van methyl-α-D-glucopyranoside, te beschrijven. Resultaten worden verkregen door gebruik te maken van semi-batch experimenten in een geroerde slurryreactor met een Pt-op-kool katalysator en moleculaire zuurstof als oxidans. Er worden drie manieren van de opstartprocedure toegepast, welke betrekking hebben op de voorbehandeling van de
katalysatorslurry, te weten gereduceerd, geoxideerd, en inert. De gereduceerde opstart gaf, vergeleken met de andere opstartprocedures, de hoogste initiele katalysatoraktiviteit. Er wordt gevonden dat de katalysator een voorbehandeling nodig heeft, alvorens de reaktie op te starten, want de inerte opstart resulteerde in geheel geen katalytische aktiviteit. Bovendien wordt, onafhankelijk van de opstartprocedure, gevonden dat over-oxidatie de hoofdoorzaak is van katalysatordeactivering voor een zwak-reducerende verbinding onder zuurstofrijke omstandigheden. De snelheid van over-oxidatie is lager in de afwezigheid van de dehydrogeneringsreactie, hetgeen wordt gemodelleerd door te veronderstellen dat over-oxidatie (Pt corrosie) vrije plaatsen nodig heeft om zich te kunnen voltrekken. Het mechanisme van katalysatordeactivering wordt experimenteel vastgesteld door tussentijdse katalysator-ractivering. Het model kan deze reactiveringsstap goed beschrijven.

Voor de platina gekatalyseerde oxidatie van methyl-α-D-glucopyranoside tot 1-O-methyl-α-D-glucuronzuur, wordt een levensvatbaar industrieel ontwerp gepresenteerd. Om katalysatordeactivering door over-oxidatie te overwinnen, wordt het proces periodiek uitgevoerd door de katalysator bloot te stellen aan oxidatieve en reductieve cycli. De selectiviteit wordt verbe- terd door het hoofdprodukt continu te verwijderen, waarmee nevenreakties worden vermeden. Op deze manier kan een hoge gemiddelde produktiesnelheid en een lange levensduur van de katalysator, worden gehandhaafd.
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Chapter 1

Introduction

1.1 Background

Platinum group metals (particularly Pt, Pd and Au) are active catalysts in the liquid phase oxidation of alcohols, diols, and carbohydrates [1–5]. Noble metal catalyzed liquid phase oxidation is an attractive process because besides the use of clean oxidants, such as molecular oxygen or air, high selectivities can be obtained [1, 2, 6]. The reaction is carried out typically at temperatures below 90°C and at atmospheric pressure, in neutral or slightly alkaline media. The process has been extensively studied for a long time; review papers of Mallat and Baiker, Gallezot, and Kluytmans et al. [2, 3, 5–7] offer a useful survey of the subject.

1.1.1 Kinetic studies

The kinetics of liquid phase alcohol oxidation are very complex and not well understood. A correct kinetic analysis of the process is a highly demanding task due to the numerous possible elementary steps and side reactions. It was suggested at early stage, that liquid phase alcohol oxidation on metal surfaces proceeds via a dehydrogenation mechanism followed by the oxidation of the adsorbed hydrogen atom with dissociatively adsorbed oxygen [8]. This was supported by kinetic modelling of oxidation experiments [9], and by direct observation of hydrogen evolving from aldose aqueous solutions at strong basic pH (> 11) [10]. Measurements of electrode potential for the 2-propanol oxidation demonstrated that the Pt-surface was predominantly covered with adsorbed hydrogen even though the oxidation reaction was carried out at 1 bar of oxygen [11].

Although this mechanism has been generally accepted, there are still different opinions and dispute, within the area of heterogeneous chemical catalysis and electro-catalysis, over several steps through which this mechanism takes place. Electro-catalysis is the 'interfacing science' between liquid phase heterogeneous catalysis and electrochemistry. According to Bockris and
Srinivasan [12], electro-catalysis may be defined as the acceleration of an electrochemical reaction by a substance (mostly electrode), which is not consumed in the overall reaction. A liquid phase heterogeneous catalytic system, where an electrified interphase is formed between the solid and liquid phases can also be considered as an electrochemical system [13]. The thermodynamic description of an electrified solid-liquid interphase similar to that of non-ionic systems, requires the introduction of electrochemical parameters: the thermodynamic charge and the electric potential difference between the solid phase considered and a reference electrode. This means that almost all liquid phase heterogeneous catalytic processes can be considered as reduction (cathodic) or oxidation (anodic) processes, if at least one component of the system is involved in at least a single charge transfer process [14]. This concept is supported in the liquid phase catalytic alcohol oxidation literature, e.g. by Mallat and Baiker [15, 16] through demonstration of monitoring on line oxidation state of the catalyst with electrochemical catalyst potential measurements, by Gootzen et al. [17], for electrochemical oxidation of ethanol and MGP, and by Markusse et al. [18], using an electrochemical kinetic model.

In general, the goal of kinetic studies and reaction engineering is to understand the periodic progress of a reacting system under investigation. The information acquired from these studies is mainly used for the interpretation of reaction mechanisms, molecular behaviour, and catalytic phenomena. The data can be subsequently applied in catalyst design, reactor modelling, or process design and optimisation [19]. Several kinetic models have been proposed for the oxidation of different alcohol compounds. Most of them are results of the previous work of our group [9, 18, 20–26]. Almost all of the models are based on heterogeneous catalysis, mostly Langmuir-Hinshelwood kinetics, except the model of Markusse et al. [18]. This model is based on a combination of heterogeneous catalysis and electrochemistry and is essentially a modification of the model proposed by Vleeming et al. [26]. The main feature of this model is that it can describe catalyst deactivation and reactivation as a function of the electrochemical catalyst potential, which is according to Mallat and Baiker [15] a key for monitoring alcohol oxidation. The model is based on intrinsic kinetic data. For process design purposes, the study of the effect of mass transport on the chemical reaction has to be accounted for, explicitly when scaling up from laboratory to industrial scale where high reaction rates are desired. This effect can have a pronounced influence on the rates and selectivities obtained in industrial reactors. It is crucial to have the rate expression that gives the best description of a full range of kinetic data, and allows confident extrapolation beyond the regions in which the experimental data were available for parameter estimation.

Depending on the rate of transfer of molecular oxygen to the catalyst surface, two operating regimes can be distinguished: the so-called mass transport limited regime and the intrinsic kinetic regime. Both regimes have an influence on the catalyst behavior and especially on the
catalyst deactivation, which is one of the major obstacles for large-scale operation of this process [5]. The effect of the rate of oxygen mass transfer on the rate of alcohol dehydrogenation can be illustrated by the bell shaped curve in Fig 1.1.

![Figure 1.1: The effect of oxygen mass transfer rate on alcohol dehydrogenation.](image)

In the oxygen mass transport limited regime, the catalyst surface is reduced, i.e. shows a low electrochemical potential (0.2 - 0.7 V vs reversible hydrogen electrode (RHE)). The rate of dehydrogenation is low and the catalyst may deactivate by adsorption of carbonaceous deposits and CO [27, 28]. This phenomenon is more pronounced when the catalyst is prereduced by the organic reactant [29, 30]. With an increase in the oxygen mass transfer rate, the rate of dehydrogenation increases with increase in the electrochemical catalyst potential and an optimum alcohol dehydrogenation rate can be obtained. However, it is rather difficult to maintain an optimum dehydrogenation rate because the rate of oxygen supply easily exceeds the rate of oxygen consumption, due to low reactivity of the alcohol compound, etc. In the intrinsic kinetic regime, the catalyst surface is oxidised, i.e. high catalyst potential (∼ 1 V vs RHE), and the catalyst deactivates due to over-oxidation [21, 22, 26, 31]. Depending on the type of reaction and conditions applied, other types of catalyst deactivation may exist, such as aldol condensation (polymerisation or coking), crystallite growth (Ostwald ripening), and metal dissolution (leaching) [5, 6], as presented in Figure 1.2.

### 1.1.2 Remedies for catalyst deactivation

Catalyst deactivation is the major problem in making the alcohol oxidation process industrially competitive. In literature, for specific oxidations, catalyst deactivation was reduced or prevented
Metals with a higher redox potential are less prone to over-oxidation. Promoters are actually heavy metals; if used alone, they are inactive but as promoters to noble metal catalysts they can be very effective. They have led noble metal catalyzed alcohol oxidation to a very competitive stage, for instance in Pd catalyzed glucose oxidation, 95% conversion with 100% selectivity can be achieved at a

![Diagram of catalyst deactivation](image)

*Figure 1.2: Catalyst deactivation in metal catalysed liquid phase alcohol oxidation.*

by the following precautions or methods:

1. **Selection of active metal.** Metals with a higher redox potential are less prone to over-oxidation. Platinum group metals have the highest redox potential compared to other metals. Van Dam et al. [32] have found that for liquid phase alcohol oxidation, Pt offers most resistance against over-oxidation. According to them, the resistivity can be generalized as Pt > Ir > Pd > Rh > Ru. In addition, small metal crystallites (smaller than 2 nm) over-oxidise more rapidly than larger ones [22, 33] and give lower catalytic activity [34, 35].

2. **Selection of catalyst support.** The catalyst support plays an important role. Carbon (active carbon and graphite) supports are most widely used for alcohol oxidation because of their higher stability to withstand severe reaction conditions (acidic and basic media, high temperatures), while the active metal can easily be impregnated in different ways. Carbon also offers cost effective regeneration of spent catalyst. However, for certain alcohol compounds (e.g. 1-methoxy-2-propanol, secondary alcohol), alumina (Pt/Al₂O₃) was considered to be the most suitable support [27]. However, it was observed that for strong chelating agents (carbohydrates), leaching of active metal is possible with alumina as support [36].

3. **Use of promoters.** Promoters are actually heavy metals; if used alone, they are inactive but as promoters to noble metal catalysts they can be very effective. They have led noble metal catalyzed alcohol oxidation to a very competitive stage, for instance in Pd catalyzed glucose oxidation, 95% conversion with 100% selectivity can be achieved at a
catalyst TOF (turn over frequency) of $1 \, \text{s}^{-1}$ [5]. According to Mallat and Baiker [27], the general sequence of promoter efficiency is: $\text{Bi} > \text{Pb} > \text{Sn} \approx \text{Au} \approx \text{Ru}$. In general, addition of bismuth increases the overall catalytic performance of the platinum group catalyst. However, there is no general agreement about the origin of the promoting role of bismuth. According to Gallezot [3], bismuth ad-atoms prevent oxygen poisoning of the palladium surface by acting as co-catalyst in the oxidative dehydrogenation mechanism. Mallat and Baiker [2] found that bismuth ad-atoms decrease the size of Pt ensembles and thus decrease the formation and irreversible adsorption of the substrate and by-products.

4. Oxygen mass transfer regime. The nature of catalyst deactivation is largely influenced by the amount of oxygen present at the catalyst surface, as illustrated in Figure 1.1. In the oxygen mass transfer limited regime, the catalyst surface is reduced, i.e. the catalyst potential is low (0.2 - 0.7 V vs reversible hydrogen electrode (RHE)); the catalyst may deactivate by absorption of carbonaceous deposits. In the intrinsic kinetic regime, the catalyst surface is oxidised, i.e. the catalyst potential is high ($\sim 1$ V RHE); the catalyst deactivates due to over-oxidation. The amount of oxygen present at the catalyst surface is determined by the oxygen mass transfer. The optimum reaction rate can be achieved by controlling the oxygen mass transfer.

5. Monitoring open-circuit catalyst potential. According to Mallat and Baiker [15], monitoring the open-circuit potential of the catalyst can be a key to adjust the rate of oxygen supply to the rate of alcohol oxidation. The catalyst potential is an indicator of the balance between oxidation and reduction processes taking place on the catalyst active sites, as presented in Figure 1.3. However, this technique has its own limitation of precise measurement of the catalyst potential. Nevertheless, it can be helpful for qualitative analysis of the oxidation process.

6. Use of diffusion-stabilized catalysts. Van Dam et al. [31] have demonstrated an interesting solution to over-oxidation, by deliberately introducing oxygen mass transfer limitation in the catalyst pores. This has been achieved by preparing catalysts as porous extrudates where the metal particles are uniformly distributed in the pores. The oxygen concentration decreases continuously from the edge to the core of the extrudates.

7. Redox-cycle operation. In redox-cycle operation, the catalyst is alternatingly exposed to an oxidative and a reductive environment. Vleeming et al. [26] and Markusse et al. [18] demonstrated that through redox-cycle operation the average oxidation rate can be improved dramatically and it is proposed to be the most suitable technique in preventing catalyst deactivation due to over-oxidation.

In summarizing this section, the use of Pt or Pd metal with large crystallite size ($> 2 \, \text{nm}$) on carbon/graphite support and monitoring the electrochemical catalyst potential can be the most...
Figure 1.3: Electrochemical catalyst potential scheme for the coverage of the platinum surface during alcohol oxidation. The surface coverage shown in the figure represents: H (hydrogen species), OH/O (hydroxyl or oxygen species), and O\textsubscript{inact} (inactive oxygen species).

suitable way to carry out alcohol oxidations. Depending on the nature of the catalyst deactivation and the type of alcohol compound (weakly or strongly reducing), the use of promoters can be beneficial. The use of diffusion stabilized catalyst, looks promising against over-oxidation and needs to be explored. Redox-cycle operation is a useful technique to identify the dominating type of catalyst deactivation and improving the productivity of the process.

1.2 Scope of this thesis

Sofar the developed kinetic models are inadequate in describing the effects of pH associated with catalyst deactivation due to over-oxidation. Also research so far lacks a detailed quantitative analysis of the cause of catalyst deactivation and its reactivation. The objective of this thesis is to develop a detailed kinetic model, which can accurately describe the effect of the process conditions, catalyst and alcohol properties on the oxidation rate, and catalyst deactivation and reactivation. In addition, the goal is to demonstrate that with a proper selection of the distribution of active noble metal within the catalyst support, and with proper reactor operating conditions, the performance of precious metal catalysts and hence of the process can be improved significantly.

Emphasis is given on the reaction kinetics, reaction-engineering modelling, and process design aspects of alcohol oxidation. The platinum catalyzed oxidation of methyl $\alpha$-D-glucopyranoside
(MGP), a polyol, to 1-O-methyl α-D-glucuronic acid (MG), is considered as a model reaction. This oxidation is part of an alternative catalytic route for the manufacturing of L-ascorbic acid (vitamin C) [22]. Furthermore, the oxidation product can be hydrolyzed to D-glucuronic acid, which is a potential precursor for several fine chemicals, polymers, and anionic detergents [37].

Figure 1.4: The stoichiometry of the Pt catalysed aqueous MGP oxidation with molecular oxygen as oxidant.

The stoichiometry of the reaction is shown in Figure 1.4. The reaction, MGP to MG, proceeds with the formation of the intermediate aldehyde, methyl aldehydo-glucoside (MAGP). The primary hydroxyl function of MGP is the most reactive, because the methyl group protects the hemi-acetal function. According to Heyns [8], primary hydroxyl groups are most reactive after hemi-acetal groups:
Hemi-acetal > Primary hydroxyl > Axial hydroxyl > Equatorial hydroxyl.

MGP does not contain axial hydroxyl groups, which has been found to activate side reactions for methyl galactoside oxidation. Industrially, methyl α-D-glucopyranoside is obtained in large quantities upon acid catalysed methanolysis of starch [38, 39] or methylation of glucose [40].

1.3 Thesis outline

- In Chapter 2, a model-based investigation of process conditions, catalyst and particle properties, and mass transport parameters on the performance of the catalyst for alcohol oxidation is presented. A dynamic transport model is derived to describe the platinum catalysed aqueous alcohol oxidation, considering a single spherical catalyst particle surrounded by a stagnant liquid film. The transport model is based on a heterogeneous kinetic model with mass transfer and intra particle diffusion resistances. The developed model uses the kinetic model of Markusse et al. [18] and is validated with the experimental kinetic data of methyl α-D-glucopyranoside (MGP) oxidation obtained by Vleeming et al. [26].

- Chapter 3 presents a strategy for proper estimation of kinetic parameters for negative order reactions. To demonstrate that, two types of reaction kinetics are considered, viz. a gen-
eral Langmuir-Hinshelwood (LH) type and the more complex methyl α-D-glucopyranoside oxidation. It is shown that the kinetic parameters are erroneously estimated using intrinsic kinetic data, and the kinetic model fails to predict observed reaction rates at mass transport limited conditions. For accurate parameter estimation, experimental reaction rate data obtained not only at intrinsic conditions but also at mass transport limited conditions, have to be taken into account for an accurate kinetic parameter estimation.

- Chapter 4 deals with the influence of the catalyst activity profile on the catalyst performance. A reaction-engineering model is developed, which describes catalyst performance as a function of the catalyst activity profile, the reaction kinetics, and the degree of catalyst deactivation. Pt catalysed methyl α-D-glucopyranoside (low reactivity) and glucose (high reactivity) oxidations, in a stirred semi-batch reactor, are used as test reactions for validation of the model results.

- Chapter 5 describes the influence of varying pH conditions on the Pt catalysed alcohol oxidation. A dynamic pH dependent electrochemical kinetic model is developed, which combines knowledge of heterogeneous catalysis and electrochemistry. For model development, a detailed regression analysis of experimental data, obtained in a CSTR and semi-batch reactor for MGP oxidation in the absence and presence of deactivation due to over-oxidation, is performed.

- Chapter 6 demonstrates that over-oxidation is the main cause of catalyst deactivation, under oxygen rich and mild reaction conditions. Three types of reaction start-up procedures are applied with respect to the pretreatment of the catalyst slurry, viz. reduced, oxidised, and inert. Results are obtained in a three phase stirred slurry semi-batch reactor using Pt catalysed oxidation of methyl α-D-glucopyranoside. The experimental results are described by the previously developed dynamic, pH dependent, electrochemical kinetic model.

- In Chapter 7 an outline of a process for the selective oxidation of MGP on industrial scale is presented. It is demonstrated through lab scale operation and process design, based on periodic operation and continuous product removal, that high productivity and long catalyst life span can be obtained.

Note. The chapters that are presented in this thesis are presented in the form as they are published or intended to be published in scientific journals (see page 173 for a full list). This may cause some overlaps or repetitions in some of the sections of the chapters, e.g. in the general introduction, the modelling section, and the experimental part.
Bibliography

Chapter 2

Model based investigation of reaction conditions

This chapter has been published as:

Abstract

A dynamic transport model is derived to describe the platinum catalysed aqueous alcohol oxidation, considering a single spherical catalyst particle surrounded by a stagnant liquid film. The transport model is based on a heterogeneous kinetic model with mass transfer and intraparticle diffusion resistances. The developed model uses the kinetic model of Markusse et al. [1] and is validated with the experimental kinetic data of methyl α-D-glucopyranoside (MGP) oxidation obtained by Vleeming et al. [2]. The model is used to investigate the effect of process conditions, catalyst and particle properties, and transport parameters on the performance of the catalyst for alcohol oxidation. It is found that the electron conductivity of the catalyst support affects the rate of MGP oxidation especially at low bulk liquid oxygen concentrations, while at high bulk liquid oxygen concentrations, the catalyst support conductivity does not play a role. A major cause of catalyst deactivation is over-oxidation under oxygen rich conditions. This can be reversed by applying redox-cycle operation, an alternating exposure of the catalyst to oxidative and reductive environments. The advantages of redox-cycle application are demonstrated using the developed model. For reactions of negative order, such as MGP oxidation, at high bulk oxygen concentrations ($C_{O_2,L} > 0.3\, mol/m^3$), concentrating the active catalytic material in a layer buried some distance from the surface (core) gives considerable better performance than the conventional ”egg shell” design of shallow deposition near the surface or uniform distribu-
tion. However, at low bulk oxygen concentrations \(C_{o_{2,L}} \leq 0.3 \text{mol/m}^3\), the performance of the uniform or egg shell distribution catalyst is superior to the core catalyst.

# 2.1 Introduction

The noble metal catalysed oxidation of alcohols, especially polyols, in aqueous phase is attractive because of the mild reaction conditions and the high selectivity that can be obtained. It is an environmentally friendly process compared to classical oxidation methods, as water is the secondary product next to the oxidised alcohol. It provides useful carbonyl compounds and carboxylic acids for various applications in fine chemistry. A promising field of application is the selective oxidation of carbohydrates towards valuable sugar acids.

The platinum catalysed oxidation of methyl α-D-glucopyranoside (MGP), which is a subject of the present study, opens a route to D-glucuronic acid, which has pharmaceutical applications and is a component of energy drinks. Also the electro-oxidation of small alcohol molecules, especially \(C_1\) to \(C_3\) molecules, has shown strong prospects for application in direct fuel cells [3].

The kinetics of these alcohol oxidation reactions are very complex and not well understood. Kinetic models developed so far are applicable at intrinsic kinetic conditions only. Therefore kinetic rate expressions and diffusion-reaction models are needed, which are reliable over a wider range of operating conditions. Extensive work has been done concerning the kinetics of alcohol oxidation over carbon/graphite supported noble metal catalyst, and the review papers of Mallat and Baiker [4] and of Kluytmans et al. [5] offer a useful survey of the subject.

According to Horanyi [6] and Mallat and Baiker [4], noble metal catalysed oxidations can be considered as electrochemical reactions. For example, alcohol oxidation takes place in two half reactions: alcohol dehydrogenation (producing electrons and protons) and oxygen reduction (consuming electrons and protons). In order to give a proper treatment of the kinetics of these reactions, it is useful to distinguish between two different operation regimes: a) the intrinsic kinetic regime, where only chemical kinetics play a role in the process and mass transfer and transport resistances for oxygen are neglected, and b) the oxygen transport regime, where the reaction rate is limited by the physical transport and mass transfer of oxygen along with the chemical kinetics. Both regimes affect not only the amount of oxygen present at the catalyst surface but also the behaviour of the platinum catalyst, especially concerning deactivation. A study on platinum catalysed carbohydrate oxidation by Vleeming et al. [2] showed that platinum over-oxidation is the major cause of deactivation under oxygen rich conditions. It was also shown that deactivation due to over-oxidation can be overcome by applying redox-cycle
2.1. Introduction

Several kinetic models have been proposed to explain alcohol oxidation and catalyst reactivation. Among all the kinetic models proposed so far, the model developed by Markusse et al. [1], which is based on an electrochemical description of the methyl \(\alpha\)-D-glucopyranoside (MGP) oxidation, gives a full account of the catalyst deactivation and reactivation phenomena. This model however is designed for intrinsic kinetic conditions only and does not take into account possible mass transfer and diffusion limitations, such as liquid-to-solid mass transfer in a stirred slurry reactor and intra particle diffusion.

It is well known that catalyst particles in which the catalyst activity is not uniform throughout the particle may offer better performance than the particle wherein the activity is uniformly distributed [7–10]. Under isothermal conditions and in the absence of poisoning, for reactions of positive order (reaction rate increases with reactant concentration), it is best to concentrate the active catalyst near the external surface of the particle. However, for the range of reactant concentrations at which the reaction rate decreases as the reactant concentration increases, it is proper to locate the active catalyst in the interior of the particle. This latter reaction rate behaviour has been observed in CO oxidation [11] and also in glucose oxidation [12] over noble metal catalysts. Becker and Wei [9] have confirmed this result by numerically computing the effectiveness of slab catalyst particles for the case of CO oxidation over platinum. They showed that, except in cases of severe diffusion limitations, catalyst particle activity is increased by distributing the active catalyst in the inner core of the particle.

The purpose of the present chapter is threefold, first to provide a dynamic model for the platinum catalysed aqueous alcohol oxidation, which takes into account the intrinsic kinetics as well as possible external mass transfer and intra particle diffusion limitations. The model considers a single catalyst particle, surrounded by a stagnant liquid film, i.e. suspended in a gas-liquid slurry phase, as for example in a stirred slurry reactor or a slurry bubble column. The validation of the intrinsic kinetic model of methyl \(\alpha\)-D-glucopyranoside (MGP) oxidation is done by comparing simulated behaviour of the developed model with experimental data obtained by Vleeming et al. [2].

Secondly, a detailed investigation of the effect of various parameters, for instance the bulk liquid oxygen concentration, liquid-to-solid mass transfer coefficient, effective intra particle oxygen diffusivity, and catalyst particle size, on the rate of MGP oxidation for different types of catalysts (viz., egg shell, core, and homogeneous) is performed. Thirdly, the advantages of redox-cycle operation for alcohol oxidation are demonstrated, amongst others by addressing the
issue of distribution of the catalyst activity over the particle. Optimum reaction conditions and best distributions of catalytic activity are identified and implications for reactor operation and catalyst design are discussed.

It is to be noted that, due to lack of experimental kinetic data, the developed model is inadequate in describing possible catalyst deactivation due to alcohol degradation products or decarbonylation, which might be possible, if operated for a long time in the oxygen transport limited regime or during the reduction period in the redox cycle. However, care has been taken to avoid the effects of such deactivation, by operating or performing simulations in a safe catalyst potential range and at a proper time scale.

2.2 Modelling

2.2.1 Kinetic model

The reaction mechanism used in this chapter is the one developed by Markusse et al. [1] with the reaction rate equations given in Table 2.1. Figure 2.1 shows the selective oxidation pathway of the MGP on graphite supported platinum catalyst, which can be obtained, without side reactions, by maintaining low conversions (below 10%). The two electrochemical reactions determining the alcohol (MGP) oxidation are: alcohol dehydrogenation (Equations V and VI) and oxygen reduction (Equation VIII). The oxygen adsorption is described by Equation (I), whereas the adsorption of organic reactants and products is described by Equations (II) and (III). The formation of inactive species, platinum surface oxide, is described by Equation (IV) and its reduction by Equation (VII). It is assumed that oxygen and MGP can adsorb independently. Therefore, two site balances are used: one for MGP adsorption and one for oxygen adsorption. The degree of coverage by MGP, \( \Theta_{\text{MGP}} \), and the degree of coverage by oxygen adatoms, \( \Theta_o \), appear in the site balances shown in Equations 2.1 and 2.2.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 + 2* \rightarrow 2\text{O}^* )</td>
<td>( R_1 = k_1 c_{\text{O}_2} \Theta*^2 ) (I)</td>
</tr>
<tr>
<td>( \text{MGP} + <em>_p \rightarrow \text{MGP}^</em>_{p} )</td>
<td>( \Theta_{\text{MGP}} = K_2 c_{\text{MGP}} \Theta*_{p} ) (II)</td>
</tr>
<tr>
<td>( \text{MG} + <em>_{p} \Rightarrow \text{MG}^</em>_{p} )</td>
<td>( \Theta_{\text{MG}} = K_3 c_{\text{MG}} \Theta*_{p} ) (III)</td>
</tr>
<tr>
<td>( \text{O}^* + <em>_{s} \rightarrow \text{O}^</em>_{s} + * )</td>
<td>( R_4 = k_4 \Theta_o (1 - \Theta_{\text{ox}}) ) (IV)</td>
</tr>
<tr>
<td>( \text{MGP}^<em><em>{p} + *</em>{s} \rightarrow \text{MAGP}^</em>_{p} + 2\text{H}^+ + 2e^- + * )</td>
<td>( R_5 = k_5 \Theta_{\text{MGP}} \Theta* \exp \left( \frac{E_F}{RT} \right) ) (V)</td>
</tr>
<tr>
<td>( \text{MAGP}^<em>_{p} + \text{H}<em>2\text{O} + *</em>{s} \rightarrow \text{MG}^</em>_{p} + 2\text{H}^+ + 2e^- + * ) fast</td>
<td>( R_6 = k_6 c_{\text{H}<em>2\text{O}} \Theta</em>{\text{ox}} \Theta* \exp \left( \frac{-E_F}{RT} \right) ) (VII)</td>
</tr>
<tr>
<td>( \text{O}^<em><em>{s} + \text{H}^+ + 2e^- + *</em>{s} \rightarrow \text{OH}^- + 2</em> )</td>
<td>( R_7 = k_7 c_{\text{H}^+} \Theta_o \exp \left( \frac{-E_F}{RT} \right) ) (VIII)</td>
</tr>
</tbody>
</table>
The site balance for the degree of coverage by inactive platinum surface oxide, so-called subsurface oxygen adatoms, $\Theta_{ox}$, is given by Equation 2.3. The site balances, applied in the model are:

\[
\begin{align*}
\text{MGP adsorption,} & \quad \Theta^*_p + \Theta_{MGP} + \Theta_{MG} = 1 \quad (2.1) \\
\text{oxygen adsorption,} & \quad \Theta^* + \Theta_o + \Theta_{ox} = 1 \quad (2.2) \\
\text{subsurface oxygen,} & \quad \Theta^*_s + \Theta_{ox} = 1 \quad (2.3)
\end{align*}
\]

where $\Theta^*_p$ is the coverage of the free alcohol adsorption sites, and $\Theta^*_s$ is the coverage of the free oxide sites. Using Equation 2.1, and the equilibrium Equations. (II) and (III) in Table 2.1, the MGP coverage is determined as:

\[
\Theta_{MGP} = \frac{K_2 C_{MGP}}{1 + K_2 C_{MGP} + K_3 C_{MG}} \quad (2.4)
\]

The surface specific MGP dehydrogenation rate $R_5$ increases with increasing free site coverage, $\Theta^*$, and consequently decreases with increasing oxygen coverage, $\Theta_o$. Based upon the non-steady state site balances and the rate equations given in Table 2.1, the rates of change of oxygen coverage and subsurface oxygen adatoms, are determined by the following differential equations:

\[
\begin{align*}
\frac{d\Theta_o(r,t)}{dt} & = 2k_1C_{o2}\Theta^*_o^2 - k_4\Theta_o(1 - \Theta_{ox}) - k_7\Theta_o C_{H^+} \exp \left(\frac{-EF}{RT}\right) \quad (2.5) \\
\frac{d\Theta_{ox}(r,t)}{dt} & = k_4\Theta_o(1 - \Theta_{ox}) - k_6\Theta_{ox}\Theta^* C_{H^+} \exp \left(\frac{-EF}{RT}\right). \quad (2.6)
\end{align*}
\]

where $(r,t)$ means that all surface coverages are space as well as time dependent.

Depending on the type of support used, the catalyst potential can be described in two ways. First, if the catalyst support is conductive, i.e. electrons can move freely, then we have a uniform potential for the whole particle, which is determined by balancing the rate of electrons produced ($4R_5$) per volume of the catalyst and the rate of electrons consumed ($2R_6 + 2R_7$) per volume of the catalyst as:

\[
E(t) = \frac{RT}{2F} \ln \left( \frac{<k_7\rho_p L_t \Theta_o> + <k_6\rho_p L_t \Theta_{ox} \Theta^*>}{2<k_5\rho_p \Theta_{MGP} L_t \Theta^*>} \right) \quad (2.7)
\]
where $<>$ denotes the volumetric averaged values, i.e. for any function $f(r)$, volumetric averaging is done as:

$$< f > = \frac{3}{R_p^3} \int_0^{R_p} r^2 f(r) dr$$  \hspace{1cm} (2.8)

Secondly, if the support is non-conductive, i.e. the electrons produced are consumed locally, then we have a local potential, which is a function of distance in the particle:

$$E(r, t) = \frac{RT}{2F} \ln \left( C_{H^+} \frac{k_7 \Theta_o + k_6 \Theta_{ox} \Theta^*}{2k_5 \Theta_{MGP} \Theta^*} \right)$$  \hspace{1cm} (2.9)

where the surface coverages $\Theta_o$, $\Theta_{ox}$, and $\Theta^*$ are space and time dependent. It should be noted that two important phenomena limit the range of the catalyst potential, i.e. below a potential of 0 V vs the standard hydrogen electrode (SHE) or 0.4 V vs the reversible hydrogen electrode (RHE), evolution of hydrogen gas, due to water reduction and decarbonylation takes place, while above a potential of 1.05 V vs SHE or 1.5 V vs RHE, oxygen gas is evolved due to water oxidation. Since these reactions are not taken into account in the kinetic model presented in Table 2.1, Equations. 2.7 and 2.9 can be applied only if:

$$0 V < E < 1.05 V$$  \hspace{1cm} (2.10)

and, consequently, the range of $\Theta$’s is numerically limited to:

$$10^{-10} < \Theta_o < 1, \quad 10^{-14} < \Theta_{ox} < 1, \quad 10^{-14} < \Theta^* < 1$$  \hspace{1cm} (2.11)

Throughout the chapter a uniform catalyst potential vs SHE is used, as the case we are considering is MGP oxidation by Pt on graphite support, which is a conductive support. For high oxygen concentrations, resulting in the intrinsic kinetic regime where no oxygen gradients are present, the model gives the same outcomes, both for conducting and non-conducting catalyst supports. However, catalyst conductivity appears to be an important phenomenon at low oxygen concentrations, which is discussed later on.

The kinetic rate expressions presented in Table 2.1 have been derived assuming absence of potential (high electric conductivity of the graphite support) and pH (fast proton diffusion) gradients inside the catalyst particle. These assumptions were verified and it was found that the magnitudes of the potential and pH (proton concentration) differences between the inner of the particle and the particle surface were very small compared to the particle average potential and the proton concentration, respectively, and hence can be neglected. Also the effects of these gradients on the corresponding reaction rates were negligible. Hence, in this chapter potential and pH gradients in the particle are considered to be absent.
2.2.2 Transport model

The transport model considers a single spherical particle of radius \( R_p \), surrounded by a stagnant liquid film of thickness \( \delta \), through which oxygen is transferred to the catalyst surface and from the surface to the active catalytic sites by pore diffusion, as shown in Figure 2.2. The conservation equation is based on the dynamic mass balance in the liquid-filled pores and at the catalyst site. The assumptions used for deriving the model are:

1. Catalyst particles are spherical with constant shape and porosity.
2. Mass transfer across the liquid-solid film is described by molecular diffusion and the film theory.
3. The system is isothermal and heat effects are negligible.

We then write the dynamic conservation equation for the oxygen transport in the pores within the particles with constant diffusivity \( D_e \). The conservation equation for oxygen takes the following form:

\[
\frac{\partial C_{O_2}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_e r^2 \frac{\partial C_{O_2}}{\partial r} \right) - R_{v,O_2}
\]  

(2.12)

with the following initial and boundary conditions:

- \( C_{O_2} \) at the liquid-solid film boundary.
- \( C_{ss} = R_p \) at the surface of the catalyst.
- \( m = C_{ls} / C_{ss} \)
- \( \frac{dC_{ls}}{dr} = 0 \)

Figure 2.2: Oxygen concentration profile.
at \( t = 0 \):
\[
C_{o_2} = 0 \quad (0 \leq r \leq R_p)
\]  
(2.13)

at \( t > 0 \):
\[
\frac{\partial C_{o_2}}{\partial r} = 0 \quad \text{at } r = 0
\]  
(2.14)
\[
V_f \frac{\partial C_{o_2,f}}{\partial t} = A_f k_{ls}(C_{o_2,L} - \frac{C_{o_2}}{m}) - (-AD_e \frac{\partial C_{o_2}}{\partial r}) \quad \text{at } r = R_p
\]  
(2.15)

where \( k_{ls} \) is the liquid-to-solid mass transfer coefficient. The volume of the liquid film is assumed to be \( V_f = \frac{4}{3} \pi ((\delta + R_p)^3 - R_p^3) \). The partition coefficient \( m \) is used to take into account the possibility that the oxygen concentration just within the surface of the solid, \( C_{o_2}\big|_{r=R_p} \), may be sometimes higher than the oxygen concentration in the liquid just adjacent to the solid. Throughout the chapter, it is assumed that the partition coefficient equals 1, viz. \( C_{ss}/C_{ls} = 1 \).

The boundary condition at \( r = R_p \), Equation 2.15, is obtained from the unsteady state balance over the stagnant liquid film and a linear dependency is assumed for the oxygen concentration in the film,
\[
C_{o_2,f} = \frac{C_{o_2,L} + C_{o_2}\big|_{r=R_p}}{2}
\]  
(2.16)

Mass transfer from the bulk liquid to the catalyst particle is determined by a Sherwood relation for a spherical particle in a stagnant medium, i.e.
\[
k_{ls} = \frac{2D}{d} = \frac{D}{\delta}
\]  
(2.17)

The rate of reaction of oxygen, \( R_{v,o_2} \), is dependent on the amount of oxygen present at the catalyst surface as well as on the activity of the catalyst. Therefore, from Equation (I) of Table 2.1,
\[
R_{v,o_2} = L_t \rho p_1 k_{1} \Theta^2 C_{o_2}
\]  
(2.18)

The rate of reaction can also be expressed in terms of the consumption of reactant MGP from Equation (V) in Table 2.1 as:
\[
R_{v,MGP} = L_t \rho p k_5 \Theta_{MGP} \Theta^* \exp \left( \frac{EF}{RT} \right)
\]  
(2.19)

From the reaction stoichiometry, it follows that \( R_{v,o_2} = R_{v,MGP} \). \( L_t \) is the specific number of platinum surface atoms, i.e. \( \text{mol Pt}/\text{kg catalyst} \), based on the assumption that one Pt surface atom equals one catalytic site.

### 2.2.3 Numerical solution

A second order Crank Nicholson finite difference scheme with non-equidistant grid spacing is employed to solve Equation 2.12. In the interior of the catalyst particle, central finite difference
is used and for the surface boundary condition a three-point forward finite difference approximation is used. The speed and accuracy of calculations are ensured through proper selection of the number of grid points (50) and the time step (0.01 sec). The differential equations of the kinetic model discussed earlier (Equations 2.5 and 2.6) are also solved using the finite difference method with a sufficient small time step. The resulting algebraic equations based on Equations 2.5, 2.6, and 2.12 are solved simultaneously. The catalyst potential of Equation 2.7 is based on volumetric averaged quantities and the initial potential of the reduced catalyst is calculated by using the bisection method. For volumetric averaging, a trapezoidal integration method is used. The computer program is equipped with the facility of adopting the time step for a better accuracy during the reduction period of the redox-cycle operation.

2.3 Results and discussion

2.3.1 Intrinsic kinetic model validation

The kinetic data of methyl α-D-glucopyranoside (MGP) oxidation was determined in previous work by reaction rate measurements in a continuous three-phase slurry reactor (CSTR), using graphite supported platinum catalyst. The setup and procedures are described by Vleeming et al. [13]. The catalyst used in the kinetic studies of Vleeming et al. [2] and Markusse et al. [1] has been classically tailored to minimise internal transport effects. The length of the diffusion path is minimised by concentrating the active catalytic material in a thin region (outer 50% volume of the particle) at the liquid-solid interface, a so-called ”egg shell” distribution.

For modelling purpose, it is assumed that the thin region of active sites is represented by the outer 50 percent of the volume of the particle. Figures 2.3a and 2.3b show the effect of MGP concentration and oxygen concentration on the experimental and calculated MGP oxidation rates. It is clear that with an increase in oxygen concentration, the rate of oxidation decreases whereas with an increase in the MGP concentration, the oxidation rate increases fast in the range of MGP concentration less than 200 mol/m$^3$, and thereafter it becomes independent of MGP concentration. Both the transport model and the intrinsic model give a good description of the dependence of MGP oxidation rate on MGP concentration and oxygen concentration as observed in the experiments. However, the intrinsic kinetic model does not include oxygen transport limitation. In the case of the transport model, the initial period is 30 s at which steady rates are obtained, whereas the intrinsic model is a steady state model. Also in the experiments the initial rates can only be measured after 30 s. For convenience of comparison, only experimental and simulated data of the transport model and the intrinsic model at initial period, 1000 s and 10,000 s after start-up are shown.
It is clear that the transport model as well as the intrinsic kinetic model can well describe the experimental data. Using the transport model, the validity of the intrinsic kinetic data can be illustrated, by assessing the oxygen transport limitation in the liquid film as well as in the catalyst particle. For this purpose the effects of external mass transfer and pore diffusion are considered. The particle average initial MGP oxidation rate is calculated using the transport model, first with the actual values of the mass transfer and the effective diffusion coefficients and then with 100 times higher values.

It is assumed that the latter case represents the situation of intrinsic kinetic conditions. From the results shown in Table 2.4, it is concluded that the calculated values with the actual transport coefficients are within 10% difference from the intrinsic results for all experiments except the first one. This might be due to the negative order in oxygen, due to which a sudden shift in the oxidation rate at low oxygen concentration is observed, depending on the value of the liquid-to-solid mass transfer coefficient, effective diffusivity, and uniform potential. Figure 2.4 shows the effect of different liquid-to-solid mass transfer coefficients (obtained from Sherwood number) on the calculated oxygen concentration profiles in the particle.

It is clear that there is no significant concentration gradient in the stagnant liquid film nor in the particle except for Sh = 2 at $C_{o_{2,L}} = 0.1$ mol/m$^3$. This confirms that the kinetic data of Vleeming et al. [2] is obtained under intrinsic conditions. The values of the model parameters used for the simulations are shown in Tables 2.2 and 2.3.
2.3. Results and discussion

Figure 2.4: Effect of liquid-to-solid mass transfer coefficient on oxygen concentration inside the particle, after 60 s. Data used: \( C_{MGP} = 90 \text{ mol/m}^3 \), \( C_{MG} = 10 \text{ mol/m}^3 \), and \( L_t = 0.073 \text{ mol/kgcat} \).

Table 2.2: List of values of model parameters used in the simulations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Comment or reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_p ) [kg m(^{-3})]</td>
<td>particle density</td>
<td>1350</td>
<td>graphite particle</td>
</tr>
<tr>
<td>( R ) [( \mu )m]</td>
<td>radius of the particle</td>
<td>7.5</td>
<td>Markusse et al. [1]</td>
</tr>
<tr>
<td>( D ) [m(^2) s(^{-1})]</td>
<td>oxygen diffusivity</td>
<td>( 3 \times 10^{-9} )</td>
<td>Perry et al. [14]</td>
</tr>
<tr>
<td>( \varepsilon ) [-]</td>
<td>porosity</td>
<td>0.4</td>
<td>Vleeming et al. [13]</td>
</tr>
<tr>
<td>( \tau ) [-]</td>
<td>tortuosity</td>
<td>4</td>
<td>Vleeming et al. [13]</td>
</tr>
<tr>
<td>( D_e ) [m(^2) s(^{-1})]</td>
<td>effective oxygen diffusivity</td>
<td>( 3 \times 10^{-10} )</td>
<td>( \varepsilon D ) / ( \tau )</td>
</tr>
<tr>
<td>( k_{fs} ) [m s(^{-1})]</td>
<td>mass transfer coefficient</td>
<td>( 4 \times 10^{-4} )</td>
<td>( Sh = 2 )</td>
</tr>
<tr>
<td>( C_{H^+} ) [mol m(^{-3})]</td>
<td>proton concentration</td>
<td>( 1 \times 10^{-5} )</td>
<td>( pH ) value of 8</td>
</tr>
<tr>
<td>( \Delta x ) [m]</td>
<td>spatial step</td>
<td>( 1.5 \times 10^{-7} )</td>
<td>spatial discretisation</td>
</tr>
<tr>
<td>( T ) [K]</td>
<td>temperature</td>
<td>323</td>
<td>isothermal condition</td>
</tr>
<tr>
<td>( \Delta t ) [s]</td>
<td>time step</td>
<td>0.01</td>
<td>discretisation in time</td>
</tr>
</tbody>
</table>
Table 2.3: List of values of kinetic parameters and experimental conditions, (Markusse et al. [1]).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ $[m^3/mol^{-1}s^{-1}]$</td>
<td>oxygen adsorption rate constant</td>
<td>$6.5 \times 10^3$</td>
</tr>
<tr>
<td>$K_2$ $[m^3/mol^{-1}]$</td>
<td>MGP adsorption constant</td>
<td>$1.26 \times 10^{-2}$</td>
</tr>
<tr>
<td>$K_3$ $[m^3/mol^{-1}]$</td>
<td>MG adsorption constant</td>
<td>$1.77 \times 10^{-1}$</td>
</tr>
<tr>
<td>$k_4$ $[s^{-1}]$</td>
<td>oxide formation rate constant</td>
<td>$1.20 \times 10^{-3}$</td>
</tr>
<tr>
<td>$k_5$ $[s^{-1}]$</td>
<td>MGP dehydrogenation rate constant</td>
<td>$3.93 \times 10^{-6}$</td>
</tr>
<tr>
<td>$k_6$ $[m^3/mol^{-1}s^{-1}]$</td>
<td>oxide reduction rate constant</td>
<td>$1.61 \times 10^9$</td>
</tr>
<tr>
<td>$k_7$ $[m^3/mol^{-1}s^{-1}]$</td>
<td>oxygen reduction rate constant</td>
<td>$3.53 \times 10^{10}$</td>
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<table>
<thead>
<tr>
<th>condition</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration MGP $[mol/m^3]$</td>
<td>5.6-420</td>
</tr>
<tr>
<td>oxygen partial pressure [kPa]</td>
<td>20-100</td>
</tr>
<tr>
<td>total pressure[kPa]</td>
<td>100</td>
</tr>
<tr>
<td>$pH$[-]</td>
<td>8-10</td>
</tr>
<tr>
<td>degree of conversion of MGP i.e. $\frac{C_{MG}}{C_{MG_{init}}}$ [-]</td>
<td>0.028-0.85</td>
</tr>
<tr>
<td>conversion of oxygen [-]</td>
<td>0.02-0.2</td>
</tr>
<tr>
<td>temperature [K]</td>
<td>303 – 333</td>
</tr>
<tr>
<td>catalyst particle diameter [$\mu m$]</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 2.4: List of values of intrinsic experimental kinetic data (Vleeming et al. [2]) and calculated rates using the transport model.

<table>
<thead>
<tr>
<th>$C_{MGP}$ $mol/m^3$</th>
<th>$P_{02}$ kPa</th>
<th>Initial experimental reaction rate, $mmol/kg.s$</th>
<th>Transport model with actual $(k_{ls}, D_e)$</th>
<th>Transport model with $100 \times (k_{ls}, D_e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>10</td>
<td>2.22</td>
<td>14.65</td>
<td>2.62</td>
</tr>
<tr>
<td>90.3</td>
<td>20</td>
<td>2.31</td>
<td>2.41</td>
<td>2.26</td>
</tr>
<tr>
<td>82</td>
<td>40</td>
<td>2.05</td>
<td>1.75</td>
<td>1.64</td>
</tr>
<tr>
<td>90</td>
<td>100</td>
<td>1.44</td>
<td>1.27</td>
<td>1.14</td>
</tr>
<tr>
<td>17.5</td>
<td>40</td>
<td>1.09</td>
<td>1.05</td>
<td>0.96</td>
</tr>
<tr>
<td>43.2</td>
<td>40</td>
<td>1.27</td>
<td>1.45</td>
<td>1.35</td>
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<td>181</td>
<td>40</td>
<td>1.90</td>
<td>2.00</td>
<td>1.89</td>
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<tr>
<td>388</td>
<td>40</td>
<td>2.04</td>
<td>2.08</td>
<td>1.94</td>
</tr>
<tr>
<td>10.8</td>
<td>40</td>
<td>0.55</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>417</td>
<td>40</td>
<td>2.94</td>
<td>3.07</td>
<td>2.91</td>
</tr>
<tr>
<td>92.8</td>
<td>40</td>
<td>2.23</td>
<td>2.36</td>
<td>2.22</td>
</tr>
<tr>
<td>70</td>
<td>40</td>
<td>1.45</td>
<td>1.09</td>
<td>1.01</td>
</tr>
</tbody>
</table>
2.3. Results and discussion

2.3.2 Effect of process conditions and catalyst properties

Most of the alcohol oxidation kinetic studies have been done with the "egg shell" type catalyst. It is also well known that for reactions of positive order this type of catalyst gives optimum performance. However, the Pt catalysed MGP oxidation reaction shows a negative order dependence on oxygen concentration (Figure 2.3b). Furthermore, some researchers have shown that the deep deposition of the catalyst in the interior of the support (core catalyst) can lead to better performance than the conventional "egg shell" design of shallow deposition near the surface [15, 16].

Therefore, in order to have an optimum catalyst performance it is necessary to see the effects of various important parameters on the performance of these catalysts. A detailed parametric study is carried out with three types of catalyst: egg shell, core, and homogeneous types depending on active site distribution as shown in Figure 2.5. It is assumed that in the egg shell catalyst the active sites are present only in the outer 50% volume of the catalyst particle whereas in core catalyst the active sites are present only in the inner 50% volume of the catalyst particle. In the homogeneous catalyst the active sites are uniformly distributed. The simulations are carried out with the MGP concentration of 90 mol/m³, MG (1-O-methyl α-D-glucuronic acid) concentration of 10 mol/m³, number of surface Pt atoms (Lt) equal to 0.073 mol/kgcat, and model and kinetic parameters as given in Tables 2.2 and 2.3.

![Figure 2.5: Active site distribution of catalysts.](image)

The amount of oxygen present in the bulk liquid has a large influence on the behaviour of the catalyst. Figure 2.6a shows the effect of the bulk liquid oxygen concentration on the MGP oxidation rate. It is clear that the egg shell catalyst shows higher activities at low bulk liquid oxygen concentrations (Co2_L ≤ 0.1 mol/m³) than other catalysts. A sharp transition from the oxygen transport limited regime to the intrinsic kinetic regime, at oxygen concentration of 0.12 mol/m³, is observed for the egg shell catalyst as shown in Figure 2.6a. This transition coincides with a sudden increase of the catalyst potential. Figure 2.6b shows the catalyst potential...
of the conducting catalyst support at different bulk liquid oxygen concentrations.

Effect of transport parameters \((k_{ls}, D_e)\) and particle size \((d_p)\)

Effect of liquid-to-solid mass transfer coefficient \((k_{ls})\), diffusivity \((D_e)\), and particle size \((d_p)\) on the MGP oxidation rate, at different bulk liquid oxygen concentration was evaluated. It was
observed that with increase or decrease in $k_{ls}$ or $D_e$ or $d_p$, the maximum oxidation rate remains unchanged but rather shifts to the another bulk oxygen concentration. E.g. Figure 2.8a shows the effect of $k_{ls}$ on the MGP oxidation rate of the egg shell catalyst, at different bulk liquid oxygen concentrations. It can be seen that the mass transfer coefficient has a large influence at low bulk oxygen concentration, where with increase in the mass transfer coefficient, from $4 \times 10^{-4} \text{ m/s} (Sh = 2)$ to $2 \times 10^{-3} \text{ m/s} (Sh = 10)$, the maximum oxidation rate shifts from

Figure 2.7: Oxygen concentration gradients inside the catalyst particle at different bulk liquid oxygen concentrations. Labels shown in figure are $e1$, $c1$, and $h1$ at $0.1 \text{ mol/m}^3$; $e2$, $c2$, and $h2$ at $0.4 \text{ mol/m}^3$; $e3$, $c3$, and $h3$ at $0.9 \text{ mol/m}^3$, after 60 s.

Figure 2.8: Effect of liquid-to-solid mass transfer coefficient on (a) the particle average MGP oxidation rate: egg shell catalyst and (b) egg shell catalyst potential, at different bulk liquid oxygen concentrations, after 60 s.
relatively higher bulk oxygen concentration $0.1 \text{ mol}/\text{m}^3$ to lower bulk oxygen concentration $0.04 \text{ mol}/\text{m}^3$ respectively, while it has negligible influence at high oxygen concentrations. This behaviour of the egg shell catalyst is due to the shift of the critical potential at the corresponding oxygen concentration, as can be seen in Figure 2.8b, which shows effect of the catalyst potential on the MGP oxidation rate at different bulk liquid oxygen concentrations. For core and homogeneous catalyst particles, it was observed that with increasing mass transfer coefficient, the oxidation rate increases slowly at bulk liquid oxygen concentrations of less than $0.7 \text{ mol}/\text{m}^3$ for the core catalyst and less than $0.2 \text{ mol}/\text{m}^3$ for the homogeneous catalyst. Also in case of the core and homogeneous catalysts, a shift in the maximum oxidation rate with change in the mass transfer coefficient was observed with corresponding shift in the critical potential. It was noted that in case of the core and homogeneous catalysts, the effect of the mass transfer coefficient becomes significant at higher oxygen concentrations, where the catalyst potential was different at different mass transfer coefficients, whereas at lower oxygen concentrations the effect was marginal.

It was found that effective diffusivity has a large effect on the MGP oxidation rate of the core catalyst. When the diffusivity increased, from $3 \times 10^{-10} \text{ m}^2/\text{s}$ to $3 \times 10^{-9} \text{ m}^2/\text{s}$, the maximum oxidation rate shifts from a bulk oxygen concentration of $0.8 \text{ mol}/\text{m}^3$ to lower oxygen concentration of $0.3 \text{ mol}/\text{m}^3$, respectively. This may be due to the fact that with an increase of the diffusivity, the core catalyst potential increases and the critical potential shifts to lower bulk oxygen concentration. Diffusivity has only a very small effect on the performance of the egg shell catalyst. A shift in the maximum oxidation rate of the egg shell catalyst from bulk oxygen concentration of $0.1 \text{ mol}/\text{m}^3$ to lower bulk oxygen concentration of $0.08 \text{ mol}/\text{m}^3$ was observed with increase in the effective diffusivity, from $3 \times 10^{-10} \text{ m}^2/\text{s}$ to $3 \times 10^{-9} \text{ m}^2/\text{s}$ respectively.

The effect of increasing particle size is similar to the decreasing $k_{ls}$ or $D_e$. When the particle size was increased, the catalyst potential decreased along with the increase in the oxygen transport resistance. This resulted in higher activity for the egg shell and homogeneous catalysts relative to the core catalyst. It was noted that with increase in the particle size, from $10 \mu\text{m}$ to $30 \mu\text{m}$, the maximum reaction rate shifts from lower bulk oxygen concentration to higher oxygen concentration, e.g. in case of the egg shell catalyst, the shift was from a bulk oxygen concentration of $0.06 \text{ mol}/\text{m}^3$ to $0.4 \text{ mol}/\text{m}^3$, respectively. This coincided with the shift in the critical potential of the catalyst at the corresponding bulk oxygen concentrations.

### 2.3.3 Catalyst support conductivity

It is observed that for the egg shell catalyst, the reaction is oxygen transport limited at low oxygen concentrations and high initial rates of oxidation are obtained in this regime. This is the case when the catalyst support is highly conductive and the catalyst potential is uniform
for the whole particle. An interesting phenomena is observed if the support is considered to be non-conductive, i.e. electrons produced are consumed only locally (local potential). Figure 2.9 shows the effect of the support conductivity on the MGP oxidation rate at different bulk liquid oxygen concentrations.

![Figure 2.9: Effect of conducting and non-conducting supports on egg shell catalyst performance. Data used: $C_{MGP} = 90 \text{ mol/m}^3$, $C_{MG} = 10 \text{ mol/m}^3$, $L_t = 0.073 \text{ mol/kgcat}$, and simulation period = 60 s.](image)

It is clear that at low oxygen concentrations ($C_{O_2,L} \leq 0.1 \text{ mol/m}^3$), the support conductivity has a large influence on the rate of oxidation, catalysts with conductive support show higher activity over catalysts with non-conductive support, while at higher oxygen concentrations ($C_{O_2,L} > 0.1 \text{ mol/m}^3$) both type of catalyst give the same performance.

### 2.3.4 Reactivation time

It has been seen in previous sections that working at oxygen transport limited conditions results in higher reaction rates than at intrinsic conditions. Also under intrinsic conditions a serious problem is the fast deactivation of the egg shell catalyst due to over-oxidation [2]. Figure 2.10 shows the MGP oxidation rate and surface coverages up to a period of 10,000 s at different oxygen concentrations. It is clear that at low oxygen concentration (transport limited condition) oxide formation is negligible and the reaction rate is high, whereas at high oxygen concentration (intrinsic condition) oxide formation is very high and the reaction rate is very low. Catalyst deactivation due to over-oxidation might be overcome by stopping the flow of oxygen for certain time. Catalyst deactivation due to poisoning might be overcome by subjecting the catalyst to a short surplus of oxygen after certain time [5]. In this section, we limit ourselves to simulating the time required in overcoming the catalyst deactivation due to over-oxidation. The time
assumed for complete reactivation is the time at which oxygen present in the system is completely consumed by the reactant alcohol. It is observed that with increasing bulk liquid oxygen concentration from 0.2 \( \text{mol/m}^3 \) to 0.9 \( \text{mol/m}^3 \), the reactivation time only slightly increases, from 52 s to 59 s. This is because, even though the bulk oxygen concentration is increased, the amount of oxygen present at the catalyst surface is very low compared to the alcohol, so the oxygen gets consumed very fast in the reduction period.

Figure 2.10: (a) Calculated MGP oxidation rate and (b) fractional coverage of oxygen, \( \Theta_{\text{ox}} \) and coverage of oxide, \( \Theta_{\text{ox}} \), for egg shell catalyst. Data used: \( C_{\text{O}_2 L} = 0.4 \text{ mol/m}^3 \), \( C_{\text{MGP}} = 90 \text{ mol/m}^3 \), \( C_{\text{MG}} = 10 \text{ mol/m}^3 \), and \( L_t = 0.073 \text{ mol/kg}_{\text{cat}} \).

Figure 2.11: Catalyst (egg shell) reactivation simulation. Data used: \( C_{\text{O}_2 L} = 0.4 \text{ mol/m}^3 \), \( C_{\text{MGP}} = 90 \text{ mol/m}^3 \), \( C_{\text{MG}} = 10 \text{ mol/m}^3 \), and \( L_t = 0.073 \text{ mol/kg}_{\text{cat}} \).

The catalyst reactivation simulations are carried out by making the oxygen concentration zero
in the bulk liquid and allowing oxygen present in the catalyst particle to be consumed by the alcohol. Reactivation is monitored by setting an operational window on the catalyst potential and the fractional coverages. This window works in the range of values shown in Equations 2.10 and 2.11. If the values of the catalyst potential or the fractional coverages exceed the operational window then the oxygen flow is started again and this completes the reactivation procedure. It can be seen from Figure 2.11 that there is a temporary increase in the oxidation rate in the initial stage of reactivation and then it immediately drops.

This increase in oxidation rate with decrease in oxygen concentration indicates the negative reaction order in oxygen. High rates are seen at the beginning of the oxidation period and at the end of the reactivation period, this is due to the fact that a low oxygen concentration is present inside the catalyst particle resulting in a large number of free sites.

### 2.3.5 Redox-cycle operation

In the previous section the problem of catalyst deactivation due to over-oxidation under intrinsic conditions (egg shell catalyst) is seen, against no deactivation due to over-oxidation under oxygen transport limited conditions. In practice the reactivation of the catalyst can be done by applying a so-called redox-cycle operation. In view of rapid deactivation of the egg shell catalyst, under intrinsic kinetic conditions, which exceeds 80% after 5000 s as can be seen in Figure 2.10. The egg shell catalyst performance can be improved substantially by applying redox-cycle operation [1].

A typical particle redox-cycle simulation is demonstrated in Figure 2.12, which shows that by alternating exposure of the catalyst to oxidative and reductive environments, the catalyst activity can be prolonged. From the last section it is clear that the catalyst potential drops significantly upon reactivation (Figure 2.11). As during the reduction period the catalyst surface is largely unoccupied and reduced, there is a possibility of catalyst poisoning due to the blocking of active sites by alcohol reactant degradation products. So to avoid catalyst poisoning during reactivation and to maximise the overall production rate, the reduction time as well as the oxidation time of the redox-cycle have to be optimised.

It is noted that advantages of redox-cycle operation, to improve the overall productivity of the catalyst has been experimentally verified for intrinsic kinetic conditions only. From our modelling results, it is clear that for the transport limited conditions, where deactivation due to over-oxidation is negligible, redox-cycle operation is not necessary. From a practical point of view it is better to avoid catalyst deactivation than to regenerate the catalyst repeatedly. Keeping this view in mind, the performance in terms of productivity of three types of catalyst activity distributions are compared for \( C_{o_2,L} > 0.4 \text{ mol/m}^3 \). Figure 2.13 shows MGP oxidation rate per
Figure 2.12: Redox-cycle operation for the egg shell catalyst. Using parameters in Tables 2 and 3. Data used: $C_{O_2,L} = 0.4 \text{ mol/m}^3$, $C_{MGP} = 90 \text{ mol/m}^3$, $C_{MG} = 10 \text{ mol/m}^3$, $L_t = 0.073 \text{ mol/kgcat}$, $C_{O_2,L} = 0 \text{ mol/m}^3$, after every 7200 s.

It is clear that core and homogeneous catalysts give higher productivity rates than the egg shell catalyst and regeneration is also not necessary. Although, this is very much dependent on the bulk liquid oxygen concentration. For the egg shell catalyst the highest attainable productivity is $20 \text{ mol/kg h}$, at very short oxidation period of 20 s compared to $50 \text{ mol/kg h}$, for the core catalyst.
catalyst, at oxidation period of 400 s. Figure 2.14 shows the oxide coverage at different bulk oxygen concentration. It is clear that oxide coverage for the core catalyst is quite less than for the egg shell and homogeneous catalyst. This means that the core catalyst is less prone to catalyst over-oxidation, unless pressurised oxygen is used ($C_{O_2,L} > 1.5 \text{mol/m}^3$). On the other hand, at low bulk oxygen concentrations ($C_{O_2,L} \leq 0.3 \text{mol/m}^3$), where the transport limitations are strong, the core catalyst gives the worst performance in comparison to the egg shell and homogeneous catalysts (Figure 2.5).

2.4 Conclusions

1. A dynamic transport model is developed and verified for the Pt catalysed MGP oxidation, which can handle liquid to solid mass transfer limitation along with intra particle diffusion limitation. The model exhibits a maximum in the alcohol oxidation rate as a function of oxygen concentration, which shifts from high bulk oxygen concentration to the relatively low bulk oxygen concentration with increasing transport rate. Although this maximum rate is always obtained in the transport limited regime, it is fully determined by the catalytic kinetic constants, and is independent of oxygen mass transfer coefficient, diffusivity, particle size and geometry, as well as active site distribution profile. For the oxidation process this means that, working with an egg shell catalyst, one has to operate at low bulk liquid oxygen concentration, resulting in a high oxygen gradient over the gas-liquid boundary layer, enabling high volumetric rates. However, this way of operation is critical, because a small increase in oxygen concentration can shift the catalyst into the low activity, intrinsic kinetic regime. On the other hand, working with a core catalyst...
needs a high bulk liquid oxygen concentration, and pressurised pure oxygen to obtain the 
same high rates. However, from a process control viewpoint, the operation will be rather 
stable.

2. The catalyst support’s electrical conductivity appears to play a key role in the simulation 
results of this modelling study. Non conducting supports, while resulting in the same reaction 
rates in the low activity, kinetic regime, exhibit much lower rates in the mass transfer 
limited region. This phenomenon reflects the electrochemical nature of the alcohol oxidation 
reaction. For conductive supports, the catalytic steps of alcohol dehydrogenation and oxygen 
reduction, do not need to occur at the same site. Dehydrogenation takes place mainly far inside the catalytic particle, and oxygen reduction in the outer layers, i.e. the 
catalyst particle operates as a short circuited fuel cell.

3. Redox cycle operation appears to be only useful, when operating in the low activity, 
kinetic regime. Redox cycle operation is an experimentally proven technique to improve 
the average performance of the catalyst in the kinetic regime, while working with oxygen 
mass transfer limitation might result in catalyst poisoning (Vleeming et al. [2], Markusse 
et al. [1]). However, data on this long term catalyst deactivation are not available, and 
consequently, have not been incorporated in the model.

**Future work**

The modelling results obtained so far, urge for further exploration of this type of kinetic model, 
as well as for experimental verification of catalyst behaviour in the oxygen mass transfer lim-
ited regime. Modelling studies have to be extended to other dehydrogenating reactants, i.e. 
to simulate the effect of different constants for adsorption and dehydrogenation rates. Experi-
ments must be performed so as to verify that the same maximum, specific reaction rate will be 
obtained, independent of catalyst particle size or active site distribution, just by searching for 
the suitable oxygen concentration. The effect of support electrical conductivity also has to be 
addressed experimentally.

**Notation**

\[ A \] \hspace{1cm} surface area of the catalyst particle, \( m^2 \)

\[ A_f \] \hspace{1cm} surface area of the liquid film, \( m^2 \)

\[ C_{H^+} \] \hspace{1cm} proton concentration, \( mol \, m^{-3} \)

\[ C_{ls} \] \hspace{1cm} oxygen concentration at the liquid-solid interface, \( mol \, m^{-3} \)

\[ C_{MG} \] \hspace{1cm} MG, product concentration, \( mol \, m^{-3} \)

\[ C_{MGP} \] \hspace{1cm} MGP concentration, \( mol \, m^{-3} \)
2.4. Conclusions

\[ C_{o_2} \] oxygen concentration in the particle, \( mol \cdot m^{-3} \)
\[ C_{o_2,f} \] oxygen concentration in the liquid film, \( mol \cdot m^{-3} \)
\[ C_{o_2,L} \] oxygen concentration in the bulk liquid, \( mol \cdot m^{-3} \)
\[ C_{ss} \] oxygen concentration at the catalyst surface, \( mol \cdot m^{-3} \)
\[ D_e \] effective diffusivity, \( m^2 \cdot s^{-1} \)
\[ d_p \] diameter of the catalyst particle, \( m \)
\[ E \] catalyst potential, \( V \)
\[ F \] Faraday’s constant, \( C \cdot mol^{-1} \)
\[ k_i \] defined in Table 3
\[ K_i \] equilibrium rate constants, in Table 3
\[ k_{ls} \] liquid to solid mass transfer coefficient, \( m \cdot s^{-1} \)
\[ L_t \] weight specific catalyst surface, \( mol \cdot kg_{cat}^{-1} \)
\[ m \] distribution/partition coefficient
\[ r \] radial distance, \( m \)
\[ R \] gas constant, \( J \cdot mol^{-1} \cdot K^{-1} \)
\[ R_i \] reaction rate of species i (Table 1), \( mol \cdot m^{-3} \cdot s^{-1} \)
\[ R_p \] radius of the catalyst particle, \( m \)
\[ Sh \] Sherwood number
\[ T \] temperature, \( K \)
\[ V_f \] volume of the liquid film, \( m^3 \)
\[ \ast \] free adsorption site for oxygen
\[ \ast_s \] free site for oxide formation
\[ \ast_{\rho} \] free adsorption site for organic compounds

Greek letters
\[ \delta \] film thickness, \( m \)
\[ \Delta \] change
\[ \epsilon \] porosity
\[ \rho \] density, \( kg \cdot m^{-3} \)
\[ \tau \] tortuosity
\[ \Theta \] surface coverage

Subscripts
\[ cat \] catalyst
\[ f \] liquid film
\[ L \] bulk liquid
\[ ls \] liquid-solid
Bibliography

Chapter 3

The estimation of kinetic parameters

This chapter has been published as:

Abstract

The kinetic rate parameters of a reaction rate model are usually estimated using reaction rate measurements obtained at intrinsic kinetic conditions, viz., without limitation of the reaction rate by mass transport, irrespective of the order of the reaction kinetics. For positive order kinetics, this is good practice and the kinetic rate parameters can be safely applied both at intrinsic and mass transport limited conditions. However, for negative order kinetics, erroneous results are obtained because the kinetic rate parameters estimated at intrinsic kinetic conditions fail to predict the reaction rate when mass transport limitation also plays a role. This is demonstrated for the simple case of Langmuir-Hinshelwood negative-order kinetics and for the, more complex, kinetics of the oxidation of methyl α-D-glucopyranoside on noble metal catalysts. It is concluded that for a negative-order reaction rate model, which is valid for a wide range of reaction conditions, the kinetic rate parameters need to be estimated both at intrinsic and mass transport limited conditions.

3.1 Introduction

The goal of kinetic measurement and reaction engineering is to understand the periodic progress of a reacting system under investigation. The information acquired from these studies is mainly used for the interpretation of reaction mechanisms, molecular behaviour, and catalytic phenomena. The data can be subsequently applied in catalyst design, reactor modelling, or process
design and optimisation [1]. There are two aspects in constructing a reaction kinetic model. The first aspect concerns the structure of the model that specifies the chemical species and reactions in the model. The second aspect concerns the kinetic parameters that are estimated from observed rate data obtained at a specific window of reaction conditions [2].

In catalytic reaction engineering, the rate expressions used in the reaction kinetics are most often derived from the elementary reaction steps and the rate-determining step. The reaction rate expression then allows a quantitative description of the effect of the reaction conditions on the reaction rates, the reactant concentration, and the selectivities for the desired products. In general, the basis of catalytic reaction engineering is the study of the intrinsic reaction kinetics, i.e. those determined solely by chemical events. In addition to that, the study of the effect of physical transport on the chemical reaction has to be accounted for, explicitly when scaling up from laboratory to industrial scale where high reaction rates are desired. These interactions can have a pronounced effect on the rates and selectivities obtained in industrial reactors. It is crucial to have the rate expression that gives the best description of a full range of kinetic data, and allows confident extrapolation beyond the regions in which the experimental data were available for parameter estimation.

Generally, kinetic parameters are estimated from reaction rate data measured under intrinsic conditions. In principle, mass transport limitation, i.e. the reaction rate is limited by the physical transport of the reactants and/or products, can exist at the gas-liquid interface, at the liquid-solid (catalyst particle) interface, at the gas-solid interface, or within the porous catalyst particle due to intra-particle pore diffusion. If any kinetic data are measured at mass transport limited conditions, these data are most often ignored, in order to avoid complexity in the estimation of the intrinsic kinetic parameters. For process design, the reaction rate at mass transport limited conditions is computed from a combination of the mass transport equations and the intrinsic kinetic model. This type of extrapolation works well for positive order kinetics. However, in case of negative order kinetics, the situation is different. For example, in previous work we found very high oxidation rates for a negative order reaction, by extrapolating the intrinsic kinetic model to mass transport limited conditions [3]. Experiments at mass transport limited conditions did not verify these high rates [4].

In this chapter, it is shown that, in general, for negative order kinetics, the kinetic parameters are inaccurately estimated at the intrinsic kinetic condition and the kinetic model fails to predict observed reaction rate data at mass transport limited conditions adequately. Moreover, for negative order reactions, it is not good practice to extrapolate the intrinsic kinetic data to mass transport limited conditions. Experimental reaction rate data obtained not only at intrinsic conditions but also at mass transport limited conditions, have to be taken into account for
an accurate kinetic parameter estimation. To demonstrate this, two types of reaction kinetics are considered, viz. a general Langmuir-Hinshelwood (LH) type and the more complex methyl α-D-glucopyranoside (MGP) oxidation.

### 3.2 Catalytic reaction engineering

In a heterogeneous catalytic reaction between a fluid (gas and/or liquid) and a porous solid catalyst, the reactants in the bulk fluid are first transported to the outer surface of the catalyst. Then they diffuse through the pores of the catalyst to the catalytically active sites. At least one of the reactant species chemisorbes onto the surface of the catalyst. Subsequently, reaction occurs among the chemisorbed species or between a chemisorbed species and another species that is either physically adsorbed or that collides with the chemisorbed species directly from the fluid phase. After reaction, the reaction products are desorbed and diffuse out through the pores of the catalyst particle to the bulk fluid. One or more of these steps may be rate-limiting in the sense that it consumes the major portion of the chemical potential available for carrying out the reaction. In many cases it appears that the rate of reaction of one or more chemisorbed species is the rate-limiting step, rather than the rate of adsorption or desorption as such. A well known kinetic formulation based on this assumption is the Langmuir-Hinshelwood (LH) kinetics, which is further discussed in the following section.

### 3.3 Langmuir-Hinshelwood kinetics

Langmuir-Hinshelwood kinetics is one of the simplest and most frequently used in heterogeneous catalysis. The chemical reaction is assumed to occur between the adsorbed species on the catalyst. If two or more species are present, they compete with each other for adsorption on a fixed number of active sites. Let's consider the following reaction mechanism:

\[
A + * \rightleftharpoons A^* \\
B + * \rightleftharpoons B^* \\
A^* + B^* \rightarrow C + 2^*
\]

where * represents the active site. The reaction rate is taken to be proportional to the product of the concentrations of the adsorbed species, A* and B*. The steady state rate expression is given as follows:

\[
\text{rate} = k \theta_A \theta_B
\]  \hspace{1cm} (3.1)

where k is the reaction rate constant, and \( \theta_A \) and \( \theta_B \) are the surface concentrations of reactants A and B, respectively. Using the Langmuir isotherm, Equation 3.1 leads to:

\[
\text{rate} = k \frac{K_A C_A K_B C_B}{(1 + K_A C_A + K_B C_B + K_C C_C)^2}
\]  \hspace{1cm} (3.2)
where $K_A$, $K_B$, and $K_C$ are the equilibrium adsorption constants of A, B, and C, respectively; $C_A$, $C_B$, and $C_C$ are the concentrations of A, B, and C, respectively. This rate equation can be simplified for the case that A is the limiting reactant, B and C are weakly adsorbed, and the concentration of B is constant. This is a common case in a gas-liquid reaction at the catalyst surface, where the liquid reactant and the reaction products are weakly adsorbed. In that case, Equation 3.2 becomes:

$$\text{rate} = k' \frac{K_A C_A}{(1 + K_A C_A)^2} \quad (3.3)$$

where $k' = k K_B C_B$. The Langmuir-Hinshelwood rate expression, Equation 3.3, represents any reaction order between +1 and -1. For example, when $K_A C_A << 1$, i.e. A is weakly adsorbed or has a low concentration, then the intrinsic volumetric reaction rate becomes positive first order in the reactant concentration A. When $K_A C_A >> 1$, i.e. A is strongly adsorbed or has a high concentration, then A inhibits the reaction and the reaction rate expression becomes negative first order in the concentration of A.

### 3.3.1 Effect of mass transport limitation

No matter how active a catalyst particle is, it can be effective only if the reactant can reach the catalytic surface. The transport of the reactant from the bulk fluid to the catalyst particle surface requires a driving force, the difference in concentrations of the reactant in the bulk fluid and the adsorbed reactant at the catalytic surface, as schematically shown in Figure 3.1. Whether this difference in concentration is significant or negligible depends on the mass transport coefficient between fluid and catalyst surface and on the intrinsic rate of the chemical reaction. The volumetric mass transport rate and the intrinsic catalytic reaction rate are given in the following steps:

$$R_v = k_{gl} a_{gl} (C^* - C_L) \quad \text{(transport from the gas-liquid interface to the bulk liquid)} \quad (3.4)$$

$$= k_{ls} a_{ls} (C_L - \frac{C_{ss}}{m}) \quad \text{(transport from the bulk liquid to the catalyst surface)} \quad (3.5)$$

$$= \eta k'' \left[ \frac{K_A C_{ss}}{(1 + K_A C_{ss})^2} \right] \quad \text{(reaction at the catalytic sites)} \quad (3.6)$$

where $k_{gl} a_{gl}$ is the volumetric gas-to-liquid mass transport coefficient, $C^*$ is the saturation concentration, $C_L$ is the concentration in the bulk liquid, $k_{ls} a_{ls}$ is the volumetric liquid-to-solid mass transport coefficient, $C_{ss}$ is the concentration at the catalyst surface, and $\eta$ is the effectiveness factor of the catalyst. $m$ is the partition coefficient, which is assumed to be equal to 1. At steady state, these three steps (Equations 3.4, 3.5, and 3.6) have the same rate, which is determined by the rate of the slowest step. For simplicity reasons, here onwards, we will only consider the case that gas-to-liquid mass transport limitation (Equation 3.4) along with chemical kinetics (Equation 3.6), play a role, while other types of transport limitations, viz. liquid-to-solid transport (Equation 3.5) and intra-particle pore diffusion are absent, i.e. $C_{ss} = C_L$ and $\eta = 1$. In that
3.3. Langmuir-Hinshelwood kinetics

The following criterion can be used to determine quantitatively which step is rate limiting, viz. the transport from the gas-liquid interface to the bulk liquid or the reaction between the gas and the liquid at the catalytic sites:

\[
\frac{C_L}{C^*} > 0.95
\]  

(3.9)

Figure 3.1: Mass transport of the reactant A from the bulk of gas to the gas-liquid film and through the film to the bulk of liquid, subsequently from the bulk of liquid to the catalyst surface through the liquid-solid film and finally diffused through the pores to the catalytic sites.

The steady state intrinsic volumetric reaction rate is calculated using the Langmuir-Hinshelwood rate expression, Equation 3.8, and simulation parameters in Table 3.1. Figure 3.2a shows the calculated reaction rate against the saturation concentration. In order to incorporate the effect of mass transport limitation, Equations 3.7 and 3.8 are solved simultaneously. The solution method uses a bisection method to search a bulk liquid concentration \(0 < C_L \leq C^*\) such that the mass transport rate, Equation 3.7, and the chemical kinetic rate, Equation 3.8, are equal. Then the overall volumetric reaction rate is calculated by substituting the liquid concentration in any of the rate equations. By applying the criterion of Equation 3.9, the intrinsic rate data and mass transport limited rate data are designated, as shown in Figure 3.2a. It can be seen
that the maximum rate is present in the mass transport limited regime and that the intrinsic kinetic regime represents low reaction rates. Moreover, the plot exhibits typical features where three regions can be identified in any order. Firstly, a high concentration $(C^* > 0.57 \text{ mol/m}^3)$ region is identified with no mass transport influence. Secondly, an intermediate concentration $(0.1 \text{ mol/m}^3 < C^* < 0.58 \text{ mol/m}^3)$ region is observed, where the mass transport limitation is favourable to the reaction, because it lowers the concentration of the inhibiting reactant at the catalyst surface: the result is that the reaction rate is higher than without mass transport limitation. Thirdly, at lower concentration $(C^* < 0.1 \text{ mol/m}^3)$, the mass transport regime predominates and the reaction rate is governed by the maximum mass transport rate. This illustrates that the overall volumetric reaction rate depends on the mass transport coefficient as well as on the kinetic parameters. Hence, in the next section, the effect of mass transport limitation on the kinetic parameter estimation for Langmuir-Hinshelwood kinetics is considered.

### 3.3.2 Kinetic parameter estimation

From the previous section it is clear that the effect of mass transport on the reaction kinetics cannot be ignored. In principle, experimental measurements are usually affected by two types of errors: systematic and random errors. Systematic errors are associated with defective instruments and improper techniques. Random errors arise from uncontrollable and unpredictable conditions that affect the observer, the instruments, and the quantity being measured. It is not possible to eliminate random errors, but they can be reduced by repeating the measurements, thus reducing the statistical significance of the erroneous readings. To imitate the experimental situation, normally distributed random errors, with zero mean, variance of one, and standard deviation of one, are added relatively to the overall reaction rate data obtained in the previous section as follows:

\[ R_{v,\text{real}} = R_v(1 + l_m \varepsilon) \]  

(3.10)

where $R_{v,\text{real}}$ is the volumetric reaction rate with random errors, $\varepsilon$ is a random error, $l_m$ is the magnitude of error. These errors are kept relatively low by selecting a suitable $l_m$ value (Table 3.1). By following the procedure of using alone the intrinsic kinetic data, a regression analysis is carried out with the reaction rate $R_{v,\text{real}}$ data. The set of estimated kinetic parameters, presented as intrinsic parameters in Table 3.1, is obtained. Figure 3.2b shows the overall reaction rate calculated from the estimated intrinsic kinetic parameters. It can be seen that calculated rate data match well with the intrinsic real rate data. However, for the mass transport limited regime it shows significant deviations from the real reaction rate data. This may be because in the intrinsic regime due to strong adsorption of the reactant, inhibition of the catalyst occurs and low reaction rates are obtained, which have been used for the parameter estimation. Moving from the intrinsic to the mass transport limited regime, the reaction passes through an intermediate regime at which both intrinsic kinetics and mass transport limitation play role.
The enhancement in the reaction rate due to decrease in the concentration of the inhibiting reactant at the catalyst surface is observed, which indicates negative order dependency. Subsequently, the rate passes through the maximum and decreases with decrease in the concentration mass transport limitations. The estimated intrinsic kinetic parameters over-predict this enhancement as the estimation procedure does not take into account the effect of the mass transport limitation. Even though this is the most simplest general model with only two parameters, this procedure of parameter estimation has lead the model to predict the maximum reaction rate.
two times higher than the original maximum rate. When the regression analysis is again performed, but this time having a combination of intrinsic as well as mass transport limited rate data, estimated kinetic parameters are presented as intrinsic and mass transport limited kinetic parameters in Table 3.1, calculated overall reaction rates can now well match with not only the intrinsic rate data but also with the mass transport limited rate data. This can be seen in Figure 3.2c.

Table 3.1: Reaction and transport parameters for Langmuir-Hinshelwood kinetics.

<table>
<thead>
<tr>
<th>LH model</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>simulation parameters:</strong></td>
<td></td>
</tr>
<tr>
<td>reactant A saturation concentration ([mol m^{-3}])</td>
<td>[0.01-1]</td>
</tr>
<tr>
<td>gas-to-liquid mass transfer coefficient, (k_{gl}a, [s^{-1}])</td>
<td>0.5</td>
</tr>
<tr>
<td>error magnitude, (l_m)</td>
<td>0.05</td>
</tr>
<tr>
<td>reaction rate constant, (k'), ([mol m^3 s^{-1}])</td>
<td>0.15</td>
</tr>
<tr>
<td>adsorption constant for A ([m^3 mol^{-1}])</td>
<td>15.0</td>
</tr>
<tr>
<td><strong>LH kinetics: estimated kinetic parameters</strong></td>
<td></td>
</tr>
<tr>
<td>a) Intrinsic conditions:</td>
<td></td>
</tr>
<tr>
<td>reaction rate constant, (k''), ([mol m^3 s^{-1}])</td>
<td>0.3512</td>
</tr>
<tr>
<td>adsorption constant for A ([m^3 mol^{-1}])</td>
<td>40.0</td>
</tr>
<tr>
<td>b) Intrinsic and mass transport limited conditions:</td>
<td></td>
</tr>
<tr>
<td>reaction rate constant, (k''), ([mol m^3 s^{-1}])</td>
<td>0.1505</td>
</tr>
<tr>
<td>adsorption constant for A ([m^3 mol^{-1}])</td>
<td>15.33</td>
</tr>
</tbody>
</table>

In heterogeneous catalytic systems, Langmuir-Hinshelwood kinetics have a limited applicability and are often modified by considering adsorbed molecules to interact with each other through a feedback parameter or an interaction term, which is a function of their surface coverage [7]. This principle has been successfully used in modelling complex reaction kinetics on noble metal catalyst. For example Jelemensky et al. [8] have used interaction parameters for modelling ethanol oxidation and extended this approach using the electrochemical catalyst potential as a feedback parameter. In a similar way, Markusse et al. [9] have modelled methyl α-D-glucopyranoside (MGP) oxidation. To evaluate the effect of mass transport limitation on the kinetic parameter estimation, as observed for the Langmuir-Hinshelwood kinetics, the MGP oxidation kinetics is further considered as a real life example in the following section.

3.4 MGP oxidation kinetics

In this section for the MGP oxidation, which exhibits a negative reaction order in a certain range of oxygen concentrations, an electrochemical kinetic model, developed by Markusse et al. [9]
is considered. The reaction steps and rate equations of this model are presented in Table 3.2, along with the kinetic parameters in Table 3.3.

Table 3.2: Reaction mechanisms for MGP oxidation, Markusse et al [9].

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Rate equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2 + 2* \rightarrow 2O* )</td>
<td>( R_1 = k_1 C_{o_2} \Theta^2 ) (I)</td>
</tr>
<tr>
<td>( \text{RCH}<em>2\text{OH} + *</em>\rho \rightleftharpoons \text{RCH}<em>2\text{OH}*</em>\rho )</td>
<td>( \Theta_{\text{RCH}<em>2\text{OH}} = K_2 C</em>{\text{RCH}<em>2\text{OH}} \Theta*</em>\rho ) (II)</td>
</tr>
<tr>
<td>( \text{RCHO} + <em>_\rho \rightleftharpoons \text{RCHO}</em>_\rho )</td>
<td>( \Theta_{\text{RCHO}} = K_{2a} C_{\text{RCHO}} \Theta*_\rho ) (IIa)</td>
</tr>
<tr>
<td>( \text{RCH}<em>2\text{OH}</em><em><em>\rho + * \rightarrow \text{RCHO}</em></em>_\rho + 2H^+ + 2e^- + * )</td>
<td>( R_3 = k_3 \Theta_{\text{RCH}<em>2\text{OH}*</em>\rho} \Theta* \exp\left( \frac{EF}{RT} \right) ) (III)</td>
</tr>
<tr>
<td>( \text{RCHO}<em>_\rho + * + \text{H}<em>2\text{O} \rightarrow \text{RCOOH}</em></em>_\rho + 2H^+ + 2e^- + * )</td>
<td>( R_4 = k_4 \Theta_{\text{RCHO}<em>_\rho} \Theta</em> \exp\left( \frac{EF}{RT} \right) ) (IV)</td>
</tr>
<tr>
<td>( O* + H^+ + 2e^- \rightarrow \text{OH}^- + * )</td>
<td>( R_5 = k_5 C_{H^+} \Theta_o \exp\left( -\frac{EF}{RT} \right) ) (V)</td>
</tr>
<tr>
<td>( O* + <em>_s \rightarrow O</em>_s + * )</td>
<td>( R_6 = k_6 \Theta_o (1 - \Theta_{ox}) ) (VI)</td>
</tr>
<tr>
<td>( \text{RCOOH} + <em><em>\rho \rightleftharpoons \text{RCOOH}</em></em>_\rho )</td>
<td>( \Theta_{\text{RCOOH}} = K_7 C_{\text{RCOOH}} \Theta*_\rho ) (VII)</td>
</tr>
<tr>
<td>( O*_s + H^+ + 2e^- + * \rightarrow OH^- + * + *_s )</td>
<td>( R_8 = k_8 C_{H^+} \Theta_{ox} \Theta* \exp\left( -\frac{EF}{RT} \right) ) (VIII)</td>
</tr>
</tbody>
</table>

Table 3.3: Kinetic parameter estimates (“mixed parameters”) with their individual 95% confidence intervals by regression of the data at pH = 8 and T = 323 K, for MGP oxidation.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Intrinsic parameters Pt/Gr [3, 9]</th>
<th>Mixed parameters Pt/Gr</th>
<th>Adopted parameters Pt/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) [( m^3\text{mol}^{-1}\text{s}^{-1} )]</td>
<td>oxygen adsorption</td>
<td>( 6.5 \times 10^3 )</td>
<td>( 9.3 \pm 0.05 ) × (10^{-1} )</td>
<td>( 9.3 \times 10^{-1} )</td>
</tr>
<tr>
<td>( K_2 ) [( m^3\text{mol}^{-1} )]</td>
<td>alcohol adsorption</td>
<td>( 1.3 \times 10^{-2} )</td>
<td>( 2.0 \pm 0.07 ) × (10^{-3} )</td>
<td>( 6.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>( K_{2a} ) [( m^3\text{mol}^{-1} )]</td>
<td>aldehyde adsorption</td>
<td>( 3.9 \times 10^{-6} )</td>
<td>( 4.5 \pm 0.02 ) × (10^{-8} )</td>
<td>( 4.5 \times 10^{-8} )</td>
</tr>
<tr>
<td>( k_3 ) [( s^{-1} )]</td>
<td>alcohol dehydrogenation</td>
<td>( 3.5 \times 10^{10} )</td>
<td>( 1.2 \pm 0.01 ) × (10^{11} )</td>
<td>( 1.2 \times 10^{11} )</td>
</tr>
<tr>
<td>( k_4 ) [( s^{-1} )]</td>
<td>aldehyde oxidation</td>
<td>( 1.2 \times 10^{-3} )</td>
<td>( 1.2 \times 10^{-3} ) (fixed)</td>
<td>( 1.2 \times 10^{-3} )</td>
</tr>
<tr>
<td>( k_5 ) [( m^3\text{mol}^{-1}\text{s}^{-1} )]</td>
<td>oxygen reduction</td>
<td>( 1.8 \times 10^{-1} )</td>
<td>( 5.0 \pm 0.02 ) × (10^{-2} )</td>
<td>( 5.0 \times 10^{-2} )</td>
</tr>
<tr>
<td>( k_6 ) [( s^{-1} )]</td>
<td>oxide formation</td>
<td>( 1.6 \times 10^{9} )</td>
<td>( 1.5 \pm 0.01 ) × (10^{8} )</td>
<td>( 1.5 \times 10^{8} )</td>
</tr>
<tr>
<td>( K_7 ) [( m^3\text{mol}^{-1} )]</td>
<td>acid adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_8 ) [( m^3\text{mol}^{-1}\text{s}^{-1} )]</td>
<td>oxide reduction</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4.1 Experimental

The kinetic data of MGP oxidation was determined in previous work by reaction rate measurements in a continuous three-phase slurry reactor (CSTR), using a graphite supported platinum
In this chapter experiments are carried out in a semi-batch reactor by keeping the aqueous MGP in batch mode and the gaseous oxidant (molecular oxygen) in continuous mode, with a non-uniform (egg shell) Pt on carbon catalyst. The properties of this catalyst are also presented in Table 3.4. As the reaction is carried out in a semi-batch reactor, the liquid reactant is converting to the product with time, i.e. methyl α-D-glucopyranoside (MGP) gives 1-O-methyl α-D-glucuronic acid (MG) with methyl α-D-6-aldehydo-glucopyranoside (MAGP) as an intermediate. It is known that the aldehyde is a highly reactive intermediate, e.g. at low pH ($\leq 6$), the aldehyde concentration in the reactor was never more than 2% [12], and with increase in pH, the aldehyde disappearance rate is even higher than at low pH [13]. However, it is important to consider its formation and disappearance in order to model the initial oxidation rate properly. The reaction rate data is obtained by measuring the acid formation rate, which is equal to the rate of alkali addition to maintain the desired reaction pH. Experiments are performed at a constant set of reaction conditions, as presented in Table 3.4, and by varying oxygen partial pressure alone, such that most of the reaction rate data represent the effect of mass transport limitation.

3.4.2 Equipment and procedure

The oxidation is carried out in a reactor of 1000 ml volume. The glass reactor was equipped with a glass stirrer with internal gas circulation, a pH electrode (Radiometer PHC 2402), an oxygen electrode (Ingold 341003005), and a membrane filter of 0.45 μm (Millipore GVWP09050) to retain the catalyst sample. During the reaction the pH was kept constant automatically using a pH meter (Radiometer-PHM 82), a pH controller (Radiometer-TTT80), and a motor burette (Radiometer-ABU80, 25ml) containing 0.1M sodium hydroxide (NaOH) solution. The inlet gas flow was kept constant using Bronkhorst mass flow controllers. The oxygen concentration in the liquid was monitored using an oxygen electrode. The oxygen electrode displayed the percentage of equivalent saturation pressure of oxygen dissolved in the slurry. The temperature was measured with a Pt-100 probe and controlled by a water bath (Beun de Ronde CS6 and R22). The reactor was operated at atmospheric pressure.

The catalyst and 400 ml of water were introduced into the reactor. The reactor was flushed with 500 ml min$^{-1}$ nitrogen flow and the catalyst slurry was stirred at 1000 r.p.m. until it reached to 323 K. Aqueous reactant solution of 100 ml was then added to the reactor under the constant nitrogen flow of 500 ml min$^{-1}$. For the methyl α-D-glucopyranoside oxidation before adding the reactant solution to the reactor, the catalyst is reduced in a 125 ml min$^{-1}$ hydrogen flow for about 30 min. The reactor content was then stirred until the desired reaction temperature was reached. As soon as the reaction temperature is attained, the pH control system was activated and pH is brought to the desired level. Before starting the reaction, the stirring speed was lowered to 600-700 r.p.m and oxygen was introduced in the reactor at the desired flow rate.
The oxidation is started by setting the stirring speed to the original level of 1000 r.p.m. At the same time recording of all the signals viz, addition of NaOH, liquid oxygen concentration, and electrochemical potential, was activated. The rate of oxidation (acid product formation) is measured through addition of alkali. The reaction was carried out in an aqueous alkaline medium at constant pH and temperature.

3.4.3 Electrochemical measurement

The electrochemical Nernstian potential of the catalyst was measured using a smooth platinum wire, a Ag/AgCl, sat KCl (0.197 V standard potential) reference electrode hosted in a lugin capillary, and a milli volt (mV) meter. The Pt wire electrode was continuously contacted by the catalyst particles in the slurry reactor and thus attained the potential of the catalyst. This method is well established in metal catalyzed hydrogenation reactions and Mallat and Baiker [14, 15] have effectively demonstrated its usefulness in alcohol oxidation. However this method is affected by several factors like support conductivity, catalyst concentration, frequency and duration of collisions of particles, electrolyte resistance, substrate deposition on the electrode, adhering support particles, and electrochemical and geometrical area of the electrode. In spite of all these, with use of a low electrochemical surface area electrode (smooth Pt wire), sufficient catalyst concentration, high stirring speed, and using the reference electrode at close distance, makes this technique unique, in giving in-situ on line information on the oxidation state of the catalyst.

<table>
<thead>
<tr>
<th>Catalyst property</th>
<th>Pt/C, this chapter</th>
<th>Pt/Gr, former work [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>dispersion [%]</td>
<td>42</td>
<td>43</td>
</tr>
<tr>
<td>B.E.T surface area [m^2/gm]</td>
<td>900</td>
<td>102</td>
</tr>
<tr>
<td>Pt content [wt.%]</td>
<td>5</td>
<td>3.3</td>
</tr>
<tr>
<td>particle size, d_p [μm]</td>
<td>40</td>
<td>15</td>
</tr>
</tbody>
</table>

### Table 3.4: List of values of semi-batch reactor experimental conditions.

<table>
<thead>
<tr>
<th>operating condition</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH [-]</td>
<td>8</td>
</tr>
<tr>
<td>oxygen partial pressure [kPa]</td>
<td>5-100</td>
</tr>
<tr>
<td>initial MGP concentration [mol/m^3]</td>
<td>100</td>
</tr>
<tr>
<td>degree of conversion [%]</td>
<td>5-20</td>
</tr>
<tr>
<td>temperature [K]</td>
<td>323</td>
</tr>
<tr>
<td>catalyst concentration [kg/m^3]</td>
<td>2</td>
</tr>
<tr>
<td>stirring speed [r.p.m]</td>
<td>1000</td>
</tr>
</tbody>
</table>
3.4.4 Kinetic parameter estimation

From the previous section, it is clear that for simple negative order LH kinetics, the estimation of the intrinsic kinetic parameters has a great influence on the model performance. For the kinetic parameter estimation, a set of twenty-one experiments performed in a CSTR, each containing 40 reaction rate data, are used from Vleeming et al. [10]. It was verified that nearly all data were obtained at intrinsic kinetic conditions, except data at low oxygen partial pressure (10 kPa), which represents the effect of gas-to-liquid mass transport limitation [3].

3.4.5 Intrinsic kinetic data

The intrinsic kinetic parameters have been estimated by Markusse et al. [9], by fitting the electrochemical model with the observed intrinsic rate data. Here onwards in this chapter these parameters are referred to as the 'intrinsic' parameters, as presented in Table 3.3. Figures 3.3a and 3.3b show the effect of oxygen partial pressure and MGP concentration on the MGP oxidation rate, respectively. The model with the 'intrinsic' parameters gives a good description of the dependence of the MGP oxidation rate on oxygen concentration and MGP concentration, as observed in the intrinsic experiments. In order to predict the experimental data at mass transport limited conditions, the electrochemical kinetic model is implemented in a dynamic CSTR model by considering gas-to-liquid mass transport limitations, while other types of mass transport limitations, viz., liquid-to-solid transport and pore diffusion, are considered to be absent. Figure 3.3c shows that the model extrapolation to the mass transport limited conditions predicts very high oxidation rates and high catalyst activity. However, the observed oxidation rates are much lower and decrease continuously with time due to over-oxidation of the catalyst [11]. That means the model with the 'intrinsic' parameters over-predicts the oxidation rates and fails to describe the observed rates at mass transport limited conditions.

3.4.6 Intrinsic kinetic and mass transport limited data

In this chapter the kinetic parameters are re-estimated, by fitting the electrochemical kinetic model with a combination of the observed intrinsic as well as mass transport limited rate data. The regression is performed using the orthogonal distance regression package (ODRPACK). The kinetic parameters set, giving the best fit for the electrochemical model, with corresponding statistical significance, is presented in Table 3.3. Since all kinetic parameters are more or less correlated, the apparent statistical error is low. Here onwards, in this chapter these estimated parameters are referred as the 'mixed' parameters. From Figures 3.3a and 3.3b, it can be seen that the electrochemical kinetic model with the 'mixed' parameters describes the observed intrinsic rate data equally well compared to the model with the 'intrinsic' parameters. When the model with the 'mixed' parameters is implemented in a CSTR model, Figure 3.3c shows
that model extrapolation to the mass transport limited conditions is able to predict the observed oxidation rate data. Now, the model with the ‘mixed’ parameters can well describe the MGP oxidation rate as well as the catalyst deactivation, at both intrinsic kinetic and mass transport limited conditions.

Figure 3.3: Effect of (a) oxygen partial pressure, (b) MGP concentration, and (c) mass transport limitation, on the experimental (symbols) and the calculated (dashed lines: model with the 'intrinsic' parameters and continuous lines: model with the 'mixed' parameters) MGP oxidation rates, at \( t_1 = \text{initial period} \), \( t_2 = 1000 \text{ s} \), and \( t_3 = 10,000 \text{ s} \). (a1) Enlargement of Figure a, to get detail view on the model predictions. Other data: (a) \( C_{\text{MGP}} = 90 \text{ mol/m}^3 \), \( C_{\text{MG}} = 10 \text{ mol/m}^3 \), \( L_t = 0.073 \text{ mol/kg}_{\text{cat}} \), (b) \( P_{\text{O}_2} = 40 \text{ kPa} \), \( \frac{C_{\text{MG}}}{C_{\text{MGP}}} = 0.1 \), \( L_t = 0.073 \text{ mol/kg}_{\text{cat}} \), and (c) \( C_{\text{MGP}} = 90 \text{ mol/m}^3 \), \( C_{\text{MG}} = 10 \text{ mol/m}^3 \), \( L_t = 0.073 \text{ mol/kg}_{\text{cat}} \), \( P_{\text{O}_2} = 10 \text{ kPa} \).
3.4.7 Modelling semi-batch reaction

To investigate the robust nature of the electrochemical kinetic model with the 'mixed' kinetic parameters, its ability to describe un-steady state mass transport limited experimental data obtained in a semi-batch reactor, has been verified. Figure 3.4 shows the experimental and calculated rate of oxidation at different oxygen partial pressures. It is verified that experiments at 5, 10, and 20 kPa suffer from the gas-liquid, the liquid-solid, and the pore diffusion type of mass transport limitation. The experimental data at 40 and 100 kPa are free from these limitations and represent intrinsic kinetic data. Figure 3.4a shows the initial rate of acid formation against oxygen partial pressure. It can be seen that the rate of oxidation increases with increase in oxygen partial pressure and the highest observed rate of oxidation is 5.2 mmol/kg s.

In order to predict the observed semi-batch data, the electrochemical kinetic model is implemented in a dynamic semi-batch reactor model, details of which are described elsewhere [4]. However, the parameter estimates needed some modification to accommodate the effect of the catalyst support. According to Vleeming et al. [16], the Pt catalyst on a carbon support showed a three to four times higher oxidation rate than the Pt catalyst on a graphite support. To put up this fact, the adsorption constant of the liquid reactant on the catalyst surface, in case of the carbon support, is considered to be approximately three times higher than the adsorption constant obtained for the graphite support. These adopted parameters are also presented in Table 3.3. Simulations are then performed using the 'intrinsic' and the adopted kinetic parameters, Pt/C catalyst properties, and the transport parameters, as presented in Tables 3.3, 3.4, and 3.5, respectively. The simulation results are compared with experimental data in Figure 3.4a. The semi-batch reactor model with the 'intrinsic' kinetic parameters predicts very high acid formation rates, e.g. five times higher than the maximum observed rate. It fails to predict the observed mass transport limited data, whereas the model predictions with the adopted 'mixed' kinetic parameters well describes the observed data. The oxidation rates under mass transport limited conditions and under intrinsic condition are presented as a function of time in Figures 3.4b and 3.4c, respectively. At 5 kPa oxygen partial pressure, the oxidation rate is low and no sign of catalyst deactivation is observed in the experimental data, whereas the model with the 'intrinsic' parameters predicts a very high initial acid formation rate followed by a fast decrease. Only after 5000 s, the model predicts acid formation rates close to the observed rates. However, by this time, considering 100 % selectivity, the model predicts full conversion, against 18% observed conversion in the experiment. For the experiment at 40 kPa oxygen partial pressure, it can be seen that the initial rate of acid formation is higher than at 5 kPa, but also the rate of catalyst deactivation due to over-oxidation. Whereas the model with the 'intrinsic' parameters predicts a very high initial acid formation rate, but as soon as the oxygen concentration increases on the catalyst surface, i.e. intrinsic conditions are reached, the model rates drop to low values and show similar behaviour as seen in the experiment, albeit at two times lower rate. At both conditions, the model with the adopted 'mixed' kinetic parameters is well able to
3.4. MGP oxidation kinetics

Figure 3.4: Semi-batch experimental data validation. (a) Initial acid rate formation data prediction at intrinsic and mass transport limited conditions, (b) effect of mass transport limited conditions, acid formation rate data at low oxygen partial pressure, and (c) modelling intrinsic kinetic conditions, acid formation rate data at high oxygen partial pressure. Symbols: experimental; calculated: continuous lines for adopted kinetic parameters and dashed lines for 'intrinsic' kinetic parameters of Markusse et al. [9]. Conditions: $C_{MGP} = 100\, \text{mol/m}^3, L_t = 0.1077\, \text{mol/kg}_{cat}$ and (b) $P_{O_2} = 5\, \text{kPa}$ (c) $P_{O_2} = 40\, \text{kPa}$.
Table 3.5: List of values of model parameters used in the semi-batch reactor simulations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_p [kgm^{-3}]$</td>
<td>carbon particle density</td>
<td>1050</td>
</tr>
<tr>
<td>$D [m^2s^{-1}]$</td>
<td>oxygen diffusivity in water</td>
<td>$3 \times 10^{-9}$</td>
</tr>
<tr>
<td>$\varepsilon [-]$</td>
<td>porosity</td>
<td>0.8</td>
</tr>
<tr>
<td>$\tau [-]$</td>
<td>tortuosity</td>
<td>2-4</td>
</tr>
<tr>
<td>$D_e [m^2s^{-1}]$</td>
<td>effective oxygen diffusivity</td>
<td>$1.2 \times 10^{-9}$</td>
</tr>
<tr>
<td>$k_g/a [s^{-1}]$</td>
<td>gas-to-liquid mass transfer coefficient</td>
<td>0.4</td>
</tr>
<tr>
<td>$k_{ls} [m s^{-1}]$</td>
<td>liquid-to-solid mass transfer coefficient</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

describe the low and steady rate of acid formation at 5 kPa oxygen pressure, and also the higher acid formation rate with fast deactivation at 40 kPa oxygen partial pressure.

### 3.5 Conclusions

This chapter shows the pitfalls in obtaining proper kinetic parameters for negative order reactions. For negative order reactions, kinetic parameters obtained with intrinsic data only, result in erroneous model predictions. This has been demonstrated for simple Langmuir-Hinshelwood kinetics and for Pt catalysed MGP oxidation kinetics. A new parameter estimation from a combination of intrinsic and mass transport limited data greatly improves the prediction capability of both models. The observed MGP oxidation rate in an unsteady state semi-batch reactor is now well described. Consequently, for negative order reactions, kinetic parameters have to be obtained from a combination of intrinsic data as well mass transport limited data.
Bibliography

Chapter 4

Reaction-engineering modelling and experiments

This chapter has been published as:

Abstract

A reaction-engineering model is presented, which describes catalyst performance as a function of the catalyst activity profile, the reaction kinetics, and the degree of catalyst deactivation. With this model, the catalyst activity profile can be optimised for Pt catalysed methyl α-D-glucopyranoside (slowly-reactive) and glucose (highly-reactive) oxidations. This is done by comparing modelling results with experimentally obtained data for catalysts of different activity distributions. Experiments in a semi-batch stirred reactor showed that for methyl α-D-glucopyranoside (MGP) oxidation at oxygen partial pressures below 40 kPa, egg shell catalytic activity distribution gives a higher rate of oxidation than a uniform distribution. It was also observed that with increase in oxygen concentration from 10 to 40 kPa, the rate of deactivation due to catalyst over-oxidation increased dramatically. For glucose oxidation, both catalyst activity distributions give the same oxidation rate for all investigated oxygen partial pressures (5 kPa-100 kPa). The developed model adequately describes the observed experimental results of both reactions. It was found that the active metal particle size has a significant influence on the catalyst deactivation for MGP oxidation; the uniform catalyst with higher dispersion shows a higher deactivation rate than the egg shell catalyst. For modelling glucose oxidation, the effect of catalyst particle-to-bubble adhesion and higher diffusivity or partition coefficient for oxygen have to be taken into account.
Noble metal catalysed selective oxidation of alcohols with molecular oxygen is an attractive process. It proceeds at rather mild reaction conditions, typically at temperatures below 90°C and at atmospheric pressure, in neutral or slightly alkaline aqueous media. It has a major advantage of using a relatively cheap and environmentally friendly oxidant, as against traditional stoichiometric oxidations, which are based on expensive inorganic oxidants and yield large amount of toxic waste.

The noble metal catalysed alcohol oxidation has been extensively studied for a long time; review papers of Mallat and Baiker [1], Gallezot [2], and Kluytmans et al. [3] offer a useful survey of the subject. It is generally accepted that reaction takes place via a dehydrogenation mechanism followed by the oxidation of the adsorbed hydrogen atom with dissociatively adsorbed oxygen. The nature of catalyst deactivation is largely influenced by the amount of oxygen present at the catalytic surface. Several types of catalyst deactivation mechanisms have been identified, viz. over-oxidation, carbonaceous deposits, metal particle-growth, metal leaching, and chemical poisoning [4]. These deactivation mechanisms lead to a decrease of the active metal surface area and hence to a decrease of the reaction rate. It is known that over-oxidation is the most critical and predominant deactivation of all the types, which is also considered to be a main cause of catalyst deactivation in this study.

Extensive work has also been done in the field of electrochemistry on alcohol oxidation, but it is more focused on fuel cell applications as methanol oxidation. A detailed mechanism through which electro-oxidation of methanol occurs seems to be generally accepted [5]. For higher aliphatic alcohols, the mechanism is more complex due to increased variation in terms of intermediates and products, so different electro-oxidation mechanisms have been proposed [5, 6].

According to Horanyi [7] and Mallat and Baiker [1], noble metal catalysed oxidations can be considered as electrochemical reactions. For example, alcohol oxidation takes place in two half reactions: alcohol dehydrogenation (producing electrons and protons) and oxygen reduction (consuming electrons and protons). Based on this principle Markusse et al. [8] have developed a kinetic model, which uses the electrochemical potential of the catalyst to describe the experimentally observed data in the heterogeneous catalytic system. However, this model was only based on intrinsic kinetic data. Gangwal et al. [9] explored the model rigorously by including oxygen mass transport limitation. It was found that the catalytic active site distribution has a strong influence on the catalyst performance. The present work deals with an experimental study on the effect of active site distributions, viz. egg shell and uniform, on the catalyst performance. The goal is to develop a reaction-engineering model for alcohol oxidation, which describe catalyst performance as a function of the catalyst activity profile, the reaction kinetics,
and the degree of catalyst deactivation. Pt catalysed oxidation of methyl α-D-glucopyranoside (MGP), a low chemical reactivity compound, and of glucose, a high chemical reactivity compound, were used as test reactions. The stoichiometry of the reactions is shown in Figure 4.1.

![Figure 4.1: Reactions under investigation.](image)

**4.2 Reaction-engineering model**

This work uses the electrochemical kinetic model developed by Markusse et al. [8]. According to this model, with increase in oxygen concentration, the electrochemical potential of the catalyst increases, which leads to an increase in the oxidation rate as well as to catalyst deactivation due to over-oxidation. The electrochemical kinetic model is presented in Table 4.1, a detailed description is given elsewhere [9]. It was found that for the methyl α-D-glucopyranoside (MGP) oxidation a new set of kinetic parameters improved the performance of the kinetic model, now being suited for intrinsic kinetic as well as for mass transport limited conditions [10]. The new kinetic parameters are presented in Table 4.2.

For the reaction to take place, oxygen has to be transferred from the gas phase to the liquid phase, through the liquid to the catalyst particle, and finally has to diffuse through the pores to
Table 4.1: Reaction mechanism for the alcohol oxidation, with rate equations (Markusse et al. [8]).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 + 2\ast \rightarrow 2\text{O}^\ast )</td>
<td>( R_1 = k_1\text{O}_2\Theta^2 ) (I)</td>
</tr>
<tr>
<td>( \text{RCH}_2\text{OH} + \ast \rho \rightleftharpoons \text{RCH}_2\text{OH}^\ast \rho )</td>
<td>( \Theta_{\text{RCH}_2\text{OH}} = K_2\text{RCH}_2\text{OH}^\ast \rho ) (II)</td>
</tr>
<tr>
<td>( \text{RCHO} + \ast \rho \rightleftharpoons \text{RCHO}^\ast \rho )</td>
<td>( \Theta_{\text{RCHO}} = K_2\text{aRCHO}^\ast \rho ) (IIa)</td>
</tr>
<tr>
<td>( \text{RCH}_2\text{OH}^\ast \rho + \ast \rightarrow \text{RCHO}^\ast \rho + 2\text{H}^\ast + 2\text{e}^- + \ast )</td>
<td>( R_3 = k_3\Theta_{\text{RCH}_2\text{OH}}\Theta^\ast \exp \left( \frac{\text{EF}}{RT} \right) ) (III)</td>
</tr>
<tr>
<td>( \text{RCHO}^\ast \rho + \ast \rightarrow \text{RCHO}^\ast \rho + 2\text{H}^\ast + 2\text{e}^- + \ast )</td>
<td>( R_4 = k_4\Theta_{\text{RCHO}}\Theta^\ast \exp \left( \frac{\text{EF}}{RT} \right) ) (IV)</td>
</tr>
<tr>
<td>( \text{O}^\ast + \text{H}^\ast + 2\text{e}^- \rightarrow \text{OH}^\ast + \ast )</td>
<td>( R_5 = k_5\text{C}_\ast\Theta \exp \left( -\frac{\text{EF}}{RT} \right) ) (V)</td>
</tr>
<tr>
<td>( \text{O}^\ast + \ast \rightarrow \text{O}^\ast + \ast )</td>
<td>( R_6 = k_6\Theta_{\text{O}}(1 - \Theta_{\text{Ox}}) ) (VI)</td>
</tr>
<tr>
<td>( \text{RCHO}^\ast \rho + \text{NaOH} \rightleftharpoons \text{RCOONa}^\ast \rho + \text{H}_2\text{O} )</td>
<td>( \Theta_{\text{RCOOH}} = K_7\text{RCOOH}^\ast \rho ) (VII)</td>
</tr>
<tr>
<td>( \text{O}^\ast + \ast \rightarrow \text{OH}^\ast + \ast )</td>
<td>( R_8 = k_8\text{C}<em>\ast\Theta</em>{\text{Ox}}\Theta^\ast \exp \left( -\frac{\text{EF}}{RT} \right) ) (VIII)</td>
</tr>
</tbody>
</table>

Table 4.2: List of values of kinetic parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Old parameters</th>
<th>New parameters</th>
<th>Adopted parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) ( [m^3\text{mol}^{-1}\text{s}^{-1}] )</td>
<td>oxygen adsorption</td>
<td>Pt/Gr [8, 9]</td>
<td>Pt/Gr [10]</td>
<td>Pt/Carbon</td>
</tr>
<tr>
<td>( K_2 ) ( [m^3\text{mol}^{-1}] )</td>
<td>alcohol adsorption</td>
<td>( 6.5 \times 10^3 )</td>
<td>( 9.3 \times 10^{-1} )</td>
<td>( 9.3 \times 10^{-1} )</td>
</tr>
<tr>
<td>( K_2\text{a} ) ( [m^3\text{mol}^{-1}] )</td>
<td>aldehyde adsorption</td>
<td>( 1.3 \times 10^{-2} )</td>
<td>( 2.0 \times 10^{-3} )</td>
<td>( 6.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>( k_3 ) ( [\text{s}^{-1}] )</td>
<td>alcohol dehydrogenation</td>
<td>( 3.9 \times 10^{-6} )</td>
<td>( 4.5 \times 10^{-8} )</td>
<td>( 4.5 \times 10^{-8} )</td>
</tr>
<tr>
<td>( k_4 ) ( [\text{s}^{-1}] )</td>
<td>MGP dehydrogenation</td>
<td>( 2.1 \times 10^{-6} )</td>
<td>( 5.6 \times 10^{-6} )</td>
<td>( 2.1 \times 10^{-6} )</td>
</tr>
<tr>
<td>( k_5 ) ( [m^3\text{mol}^{-1}\text{s}^{-1}] )</td>
<td>glucose dehydrogenation</td>
<td>( 3.5 \times 10^{10} )</td>
<td>( 1.2 \times 10^{11} )</td>
<td>( 1.2 \times 10^{11} )</td>
</tr>
<tr>
<td>( k_6 ) ( [\text{s}^{-1}] )</td>
<td>aldehyde oxidation</td>
<td>( 1.2 \times 10^{-3} )</td>
<td>( 1.2 \times 10^{-3} )</td>
<td>( 1.2 \times 10^{-3} )</td>
</tr>
<tr>
<td>( K_7 ) ( [m^3\text{mol}^{-1}] )</td>
<td>oxygen reduction</td>
<td>( 1.8 \times 10^{-1} )</td>
<td>( 5.0 \times 10^{-2} )</td>
<td>( 5.0 \times 10^{-2} )</td>
</tr>
<tr>
<td>( k_8 ) ( [m^3\text{mol}^{-1}\text{s}^{-1}] )</td>
<td>oxide formation</td>
<td>( 1.6 \times 10^9 )</td>
<td>( 1.5 \times 10^8 )</td>
<td>( 1.5 \times 10^8 )</td>
</tr>
</tbody>
</table>

the catalytic site inside the particle, as shown in Figure 4.2. The assumptions used for deriving the model are:

1. The system is isothermal and heat effects are negligible
2. No concentration gradients for the alcohol reactant; at the liquid-solid film and inside the catalyst particle
3. The catalyst particles are flat plate with constant shape and porosity
The transient material balance equations for oxygen, in the gas phase, the liquid phase and the solid phase are discussed consecutively.

Gas phase (G) mass balance. 
Oxygen mass transport from the gas phase to the liquid phase:

\[
\frac{V_G}{RT} \frac{dP}{dt} = F_{V,G}^\text{in} \frac{P^\text{in}}{RT} - F_{V,G}^\text{out} \frac{P}{RT} - k_{GL} a_{GL} V_L (C_{\text{sat}} - C_L)
\]

where \(P\) is the oxygen partial pressure in the reactor, \(k_{GL} a_{GL}\) is the volumetric gas-to-liquid mass transport coefficient, \(C_{\text{sat}}\) is the saturation oxygen concentration, and \(C_L\) is the oxygen concentration in the liquid phase.

Liquid phase (L) mass balance. 
Oxygen mass transport from the liquid phase to the solid phase:

\[
V_L \frac{dC_L}{dt} = k_{GL} a_{GL} V_L (C_{\text{sat}} - C_L) - k_{LS} a_{LS} V_L (C_L - \frac{C_S}{m})
\]

where \(k_{LS} a_{LS}\) is the volumetric liquid-to-solid mass transport coefficient, and \(C_S\) is the oxygen concentration at the solid particle. The partition coefficient \(m\) is used to take into account the possibility that the oxygen concentration just within the surface of the solid, \(C_S\), may be higher than the oxygen concentration in the liquid just adjacent to the solid, \(C_{IS}\). Throughout the chapter, it is assumed that the partition coefficient equals 1.

Solid phase (S). 
It is assumed that active sites are located inside the pores of the catalyst particle. This is also necessary to be able to differentiate between catalyst of different intra particle activity distributions. For a uniformly activated flat plate catalyst particle and constant oxygen diffusivity, the oxygen balance under isothermal conditions leads to:

\[
\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - R_v O_2
\]
with the following initial and boundary conditions:

at \( t = 0 \):

\[
C = 0 \quad (0 \leq x \leq l)
\]  

(4.4)

at \( t > 0 \):

\[
\frac{dC}{dx} = 0 \quad \text{at } x = 0
\]

(4.5)

\[
(-D_e \frac{dC}{dx}) = k_{LS}(C_L - \frac{C_S}{m}) \quad \text{at } x = l
\]

(4.6)

where \( C \) is oxygen concentration inside the catalyst particle, \( l \) is the diffusion path length, and \( D_e \) is the effective diffusivity for oxygen. The volumetric rate of reaction of oxygen, \( R_{v,O_2} \), is dependent on the amount of oxygen present at the catalyst surface as well as on the activity of the catalyst. Therefore, from Equation (1) of Table 4.1,

\[
R_{v,O_2} = L_t \rho_p k_1 \Theta^2 C
\]

(4.7)

The rate of reaction can also be expressed in terms of the specific consumption of reactant alcohol from Equation (III) in Table 4.1 as:

\[
R_{RCH_2OH} = L_t k_3 \Theta RCH_2OH \Theta \exp \left( \frac{EF}{RT} \right)
\]

(4.8)

\( L_t \) is the specific number of platinum surface atoms, i.e. mol Pt/s/kgcatalyst, based on the assumption that one Pt surface atom equals one catalytic site. For the egg shell catalyst the given amount of active metal is distributed in the outer 20 percent of the volume of the flat plate particle.

Material balance for liquid reactant and products.
The liquid reactant alcohol is in a batch mode and continuously converting to the product as reaction progresses; e.g. methyl glucoside (MGP) gives methyl glucuronic acid (MG) with methyl aldehydo-glucoside (MAGP) as an intermediate; whereas glucose, first gives gluconic acid, which further reacts to give glucaric acid, as shown in Figure 4.1.
The rate of disappearance of MGP to aldehyde is:

\[
\frac{dC_{RCH_2OH}}{dt} = -C_{\text{cat}} R_{RCH_2OH}
\]

(4.9)

Aldehyde is a highly reactive intermediate. It was found that at slightly acidic pH, the aldehyde content during MGP oxidation was never more than 2% [11]. Additionally increasing pH (alkaline condition) leads to even higher rate of aldehyde disappearance [12]. The model developed here also shows a low aldehyde concentration of less than 1%. However, it is important to consider its formation and disappearance, in order to model the initial oxidation rate properly. It is
4.2. Reaction-engineering model

given as:

\[
\frac{dC_{RCHO}}{dt} = C_{\text{cat}}(R_{RCH_2OH} - R_{RCHO})
\]  

(4.10)

where \(R_{RCHO}\) is the rate of aldehyde dehydrogenation and is determined from Equation (IV), Table 4.1 as:

\[
R_{RCHO} = L_t k_4 \Theta_{RCHO} \Theta^* \exp \left( \frac{EF}{RT} \right)
\]  

(4.11)

where \(\Theta_{RCHO}\) is aldehyde surface coverage and is calculated from Equation (IIa) of Table 4.1.

The adsorption constant of aldehyde is considered to be equal to that of reactant alcohol. The catalyst potential, \(E\), is determined by balancing the rate of electrons produced \((2R_3 + 2R_4)\) per volume of the catalyst and the rate of electrons consumed \((2R_5 + 2R_8)\) per volume of the catalyst as:

\[
E = \frac{RT}{2F} \ln \left( \frac{< L_t \rho_p C_{H^+} k_5 \Theta_O > + < L_t \rho_p C_{H^+} k_5 \Theta_{Ox} \Theta^* >}{< L_t \rho_p k_3 \Theta_{RCH_2OH} \Theta^* > + < L_t \rho_p k_4 \Theta_{RCHO} \Theta^* >} \right)
\]  

(4.12)

where \(< >\) denotes the averaged values.

The rate of acid formation is calculated from the rate of dehydrogenation of aldehyde as:

\[
\frac{dC_{RCOOH}}{dt} = C_{\text{cat}} R_{RCHO}
\]  

(4.13)

During the reaction, as alkali (NaOH) is used for controlling the pH, the reactor liquid volume is changing with the reactant conversion. This also depends upon the concentration of alkali used. Therefore, the total volume is determined as follows:

\[
V_L = \frac{V_{L, \text{ini}}}{(1 - C_{RCOOH}/C_{\text{NaOH}})}
\]  

(4.14)

where \(V_{L, \text{ini}}\) is the initial liquid volume in the reactor, and \(V_L\) is the new volume of the reactor due to alkali addition.

For D-glucose oxidation, glucose is considered to be in aldehyde form. Therefore, the rate of disappearance of glucose is modelled through the rate of dehydrogenation of aldehyde (Equation 4.11) and the respective kinetic parameter is presented in Table 4.2. At kinetic limited conditions, glucose oxidation on Pt gives rise to a consecutive reaction, in which gluconic acid reacts further to give glucaric acid as shown in Figure 4.1. However, the second reaction is slower than the first one and at low conversion (less than 30%) its influence on kinetics can be neglected. In this chapter, only the first step to gluconic acid is considered.

For modelling purpose, as the catalyst used in this study is Pt on active carbon support, in order to obtain the best fit, the alcohol adsorption constant \((K_2)\) comes out to be three times higher than the one presented in Table 4.2 for the graphite support. Vleeming et al. [13] have thoroughly investigated the effect of catalyst supports and found that in case of methyl glucoside oxidation, the catalyst support has significant influence on the initial activity of the catalyst.
According to Vleeming, the initial activity for the activated carbon support is 3-4 times higher than for the graphite support. This can be due to the interaction of the support groups with the alcohol molecule, which then determines the orientation of the hydroxyl groups of the alcohol compound towards the platinum surface and thus influences the adsorption of the alcohol on a platinum site. This can have a strong effect on turnover frequency [14].

The reactor model equations are solved with Matlab software. The ordinary differential equations 4.1 and 4.2 are solved using ODE23s routine. For solving the partial differential equation (Equation 4.3), a second order finite difference method is used. The speed and accuracy of calculations are ensured through proper selection of the number of grid points (50) and the time step (0.05 sec). The boundary condition (Equation 4.6) is solved using a three point forward finite difference method. The model simulations are performed with the adopted kinetic parameters for Pt on carbon (Pt/C) catalysts presented in Table 4.2 and parameters presented in Table 4.5.

### 4.3 Experimental

The experimental work is performed in a three phase semi-batch stirred slurry reactor. The reaction is carried out by keeping the aqueous alcohol reactant in batch mode and the gaseous oxidant (molecular oxygen) in continuous mode. The partial pressure of oxygen was the main operating variable, while all other operating conditions were remained constant during the experiments. An overview of the reaction conditions for the methyl α-D-glucopyranoside (MGP) and glucose oxidation experiments is given in Table 4.3. The details of the experimental procedure, in case of the MGP oxidation, are described in Chapter 3 (section 3.4.2). In case of the glucose oxidation also same experimental procedure was used, except the glucose solution was directly added to the reactor without reducing the catalyst as it is a stronger reducing agent. It is

<table>
<thead>
<tr>
<th>condition</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial concentration (molm^{-3})</td>
<td>100</td>
</tr>
<tr>
<td>oxygen partial pressure [kPa]</td>
<td>5-100</td>
</tr>
<tr>
<td>total pressure[kPa]</td>
<td>100</td>
</tr>
<tr>
<td>(pH) [-]</td>
<td>8</td>
</tr>
<tr>
<td>degree of conversion [%]</td>
<td>5-40</td>
</tr>
<tr>
<td>temperature [K]</td>
<td>323</td>
</tr>
<tr>
<td>catalyst particle size [(\mu m)]</td>
<td>40</td>
</tr>
<tr>
<td>stirring speed [r.p.m]</td>
<td>1000</td>
</tr>
</tbody>
</table>

*Table 4.3: Experimental conditions used for both the reactions.*
to be noted that all the experimental results presented here are obtained at potentials higher than 0.4 V vs reversible hydrogen electrode (RHE), which supports the fact that the observed data are free from possible catalyst deactivation due to alcohol degradation products or decarbonylation, and that the observed catalyst deactivation is only caused by over-oxidation.

4.3.1 Catalysts

Pt on carbon catalysts with different activity distributions were obtained from Engelhard B.V. The Netherlands.

<table>
<thead>
<tr>
<th>properties</th>
<th>egg shell</th>
<th>uniform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt loading [wt%]</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Dispersion [%]</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>BET surface area [cm$^2$ gm$^{-1}$]</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>Particle size distribution [μm]</td>
<td>7-120</td>
<td>7-120</td>
</tr>
<tr>
<td>Porosity [%]</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>$L_t$ [mol Pt/kg catalyst]</td>
<td>0.5384</td>
<td>0.1487</td>
</tr>
</tbody>
</table>

The different activity distributions were uniform and edge coated (egg shell). The uniform catalyst distribution means that the Pt metal is evenly distributed inside the pores of the carbon particle. The edge coated (egg shell) distribution means that the Pt metal is located mainly at the outer part of the carbon particle. According to the manufacturer, catalysts have the same particle size distribution, Pt loading, and BET surface area, which is verified with our own measurements; the catalyst properties are given in Table 4.4. In order to compare the different catalysts for their total catalytic activity, the Pt loading and the fraction of exposed atoms (dispersion) must be determined. The dispersions for the two types of the catalyst, as measured by CO chemisorption, are presented in Table 4.4. The uniform catalyst has a significantly higher dispersion than the egg shell catalyst.

4.4 Results and discussion

4.4.1 Methyl α-D-glucopyranoside oxidation

Effect of low oxygen partial pressure

Figure 4.3a shows the acid formation rate as a function of time for the egg shell and the uniform catalyst at 10 kPa oxygen partial pressure. From the experimental observation, it can be seen that the egg shell catalyst shows a higher activity than the uniform catalyst. This also can
Table 4.5: List of values of model parameters used in the simulations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Comment or reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_p$ [kgm$^{-3}$]</td>
<td>particle density</td>
<td>1050</td>
<td>carbon particle</td>
</tr>
<tr>
<td>$D$ [m$^2$s$^{-1}$]</td>
<td>oxygen diffusivity</td>
<td>$3 \times 10^{-9}$</td>
<td>Perry et al. [15]</td>
</tr>
<tr>
<td>$\varepsilon$ [-]</td>
<td>porosity</td>
<td>0.8</td>
<td>mercury porosimetry</td>
</tr>
<tr>
<td>$\tau$ [-]</td>
<td>tortuosity</td>
<td>2-4</td>
<td>Vleeming et al. [4]</td>
</tr>
<tr>
<td>$D_e$ [m$^2$s$^{-1}$]</td>
<td>effective oxygen diffusivity</td>
<td>$1.2 \times 10^{-9}$</td>
<td>$\frac{\varepsilon D}{\tau}$</td>
</tr>
<tr>
<td>$k_{GLAGL}$ [s$^{-1}$]</td>
<td>gas-to-liquid coefficient</td>
<td>0.4</td>
<td>dynamic gas absorption [16]</td>
</tr>
<tr>
<td>$k_{LS}$ [ms$^{-1}$]</td>
<td>liquid-to-solid coefficient</td>
<td>$1.2 \times 10^{-3}$</td>
<td>Sano et al. [17]</td>
</tr>
<tr>
<td>$C_{H+}$ [molm$^{-3}$]</td>
<td>proton concentration</td>
<td>$1 \times 10^{-5}$</td>
<td>$pH$ value of 8</td>
</tr>
<tr>
<td>$T$ [K]</td>
<td>temperature</td>
<td>323</td>
<td>isothermal condition</td>
</tr>
</tbody>
</table>

be seen in Figure 4.3b, where the concentration of methyl glucoside against time is presented. Here, the egg shell catalyst gives almost 1.5 times higher conversion than the uniform catalyst.

The simulation results shown in Figure 4.3a, indicate that the model adequately describes the initial observed rates for the egg shell catalyst. However, the model shows slightly faster deactivation than observed in the experiment. The catalyst deactivation can be seen through Figure 4.3c, which shows the simulated oxide coverage against time. For the uniform catalyst, the model is well able to describe the observed rate. The possible explanation for the low performance of the uniform catalyst is that stronger oxygen concentration gradients are present inside the particle as compared to the egg shell catalyst, which lowers the effectiveness of the uniform catalyst.

Figure 4.3d shows measured and calculated potentials as a function of time. It can be seen that starting from a reduced catalyst (0.1 V potential) surface, the catalyst potential instantly increases to 0.8 V, as soon as the oxygen reaches the catalyst surface. The catalyst potential stabilizes at a higher level of around 0.9 V. The developed model predicts the experimentally observed potential well for both catalysts. Although, the trend for the modelling results is opposite than measured in the experiments, it is not considered significant at the moment, in view of the limitations of the potential measurement method.
Figure 4.3: MGP oxidation: the effect of a low oxygen partial pressure on the catalyst performance. (a) Acid formation rate, (b) Concentration of MGP, (c) Fraction of the oxide coverage, and (d) In-situ open-circuit catalyst potential. Symbols represent the experimental and continuous lines represent the modelling results. For the egg shell catalyst, triangles and solid lines are used, whereas for the uniform catalyst circles and dashed lines are used.
Effect of higher oxygen partial pressure

Figure 4.4a shows the acid formation rate as a function of time for the egg shell and the uniform catalyst at 40 kPa oxygen partial pressure. The initial oxidation rate is almost a factor of two times higher for both catalysts than at 10 kPa oxygen partial pressure, but also the rate of deactivation due to over-oxidation is faster. It can also be seen from Figure 4.4a that the egg shell catalyst gives a slightly higher initial rate of oxidation than the uniform catalyst, which is similar as for 10 kPa oxygen partial pressure. The results presented in Figure 4.4a and 4.4b indicate that the model is well able to describe the experimentally observed high initial rate followed by faster deactivation, for both catalysts. However, for the uniform catalyst, the model predicts higher rates and less deactivation than observed in the experiment. This may be due to
the fact that the simulations have been carried out considering similar Pt-oxygen bonding for both catalysts, i.e. the uniform catalyst with higher dispersion, results in higher activity.

In practice it has been found that the dispersion or Pt particle size, has a large influence on the Pt-oxygen bonding. X-ray photoelectron spectroscopy studies performed by Parmigiani et al. [18] revealed that platinum is more easily oxidized with decreasing particle size (higher dispersion). Schuurman et al. [11] have found a similar effect for the methyl glucoside oxidation. In order to verify these facts, simulations are performed using increased Pt-oxygen bonding. This is done simply by taking the oxide formation constant five times higher. The results in Figure 4.4a show that the model performance has improved significantly and that the model describes the observed experimental rates and conversion accurately. Figure 4.4c shows oxide formation as function of time, it can be seen that at 5000 s more than 60% of the active sites are covered with the oxide, which indicates how fast the deactivation is at higher oxygen concentration. Simulations are also performed using increased Pt-oxygen bonding for 10 kPa oxygen partial pressure. It was found that, not shown in Figure 4.3a, the oxide coverage fraction increased by a factor of five, from 0.016 to 0.08, which decreases acid formation rate, less than 10%, i.e., considered to be insignificant. To understand the observed catalyst deactivation, catalyst potential against time is presented in Figure 4.4d. It can be seen that starting from a reduced catalyst (0.1 V potential) surface, the catalyst potential instantly increases to 0.9 V as soon as the oxygen reaches the catalyst surface and stabilizes to a higher level around 0.97 V. This indicates that the catalyst is deactivated very fast, i.e. high oxide coverage, which is very well described by the model for both catalysts. Comparing Figure 4.3d with 4.4d, although the difference of 0.9 V and 0.97 V might seem small, it has a very large effect on the catalyst deactivation, the oxide coverage becomes almost two times higher.

4.4.2 Glucose oxidation

Effect of low oxygen partial pressure

Figure 4.5a shows the acid formation rate as a function of time for the egg shell and the uniform catalyst at 5 kPa oxygen partial pressure. It is clearly seen from the acid formation rate that both catalysts are active, and show no sign of deactivation. Experimental data show that the uniform catalyst gives a slightly higher oxidation rate. The model results presented in Figure 4.5a, show that strong concentration gradients are present inside the particle for both catalysts, corresponding to lower oxidation rates than found experimentally. This deviation of the model might be caused by a fast reaction, like glucose oxidation on Pt/C catalyst, which mainly takes place at the gas-liquid interface [19, 20]. The effect is even more pronounced if there is particle-gas bubble interaction, which has a significant influence on the liquid-to-solid mass transfer [21]. This phenomenon is termed as particle bubble adhesion (PBA).
Figure 4.5: Glucose oxidation: the effect of a low oxygen partial pressure on the catalyst performance. (a) Acid formation rate, (b) Concentration of glucose, (c) Fraction of the oxide coverage, and (d) In-situ open-circuit catalyst potential. Symbols represent the experimental and continuous lines represent the modelling results. For the egg shell catalyst, triangles, dash-dot line (with a values from Table 4.5), and solid lines (with a 10 times higher $D_{eff}, k_{GL,O_2}, a_{GL,O_2}$, and $k_{LS,O_2}$) are used, whereas for the uniform catalyst, circles, dashed line (with a values from Table 4.5) and dotted lines (with a 10 times higher $D_{eff}, k_{GL,O_2}, a_{GL,O_2}$, and $k_{LS,O_2}$) are used.

So, taking above effects into account, simulations were performed with factor of 5-10 times higher gas-to-liquid and liquid-to-solid mass transfer coefficients. The model performance did improve, but still large deviations from the observed experimental data was found. At a low oxygen concentration, egg shell catalysts are expected to perform better than uniform catalysts, which is not seen in the experiments. Possibly, the apparent oxygen diffusivity is higher than what is used so far. Alternatively, the distribution coefficient ($m$) for carbon support may be higher due to a high affinity for oxygen. To investigate the sensitivity to diffusivity and mass transfer coefficients, simulations are performed with a factor of 10 times higher effective dif-
fusivity and mass transfer coefficients than presented in Table 4.5. The results presented in Figure 4.5a indicate a significant improvement in the model performance. The model is now able to describe the trend qualitatively and quantitatively, for both catalysts. Figure 4.5b shows the change in glucose concentration as a function of time. It can be seen that the model with adopted mass transfer and diffusion parameters, describes the observed conversion to gluconic acid. The uniform catalyst gives 7% conversion after 1000s, whereas the egg shell gives a slightly lower of 6%. Figure 4.5c and 4.5d show oxide formation and catalyst potential as a function of time respectively. It can be seen that the oxide coverage is negligible, which is well reflected in the lower potential. However, the model predicts higher potential than the measured potential. This might be due to the fact that the model does not consider presence of adsorbed hydrogen species, which are expected to be present for an easily dehydrogenating agent like glucose [3].

**Effect of higher oxygen partial pressure**

Figure 4.6a shows the acid formation rate as a function of time for the egg shell and the uniform catalyst at 100 kPa oxygen partial pressure. It can be seen that increasing oxygen partial pressure from 5 kPa (Figure 4.5a) to 100 kPa (Figure 4.6a) the initial rate of acid formation for both catalysts becomes almost 8 times higher. However, the rate of catalyst deactivation due to over-oxidation is also fast. It can also be seen that both catalysts show similar behaviour and activity. The simulation results presented in Figure 4.6a, indicate a large influence of the effective diffusivity or distribution coefficient, and possible particle-bubble interaction. Figure 4.6b shows that the model describes the experimental rates till 25 % conversion. For higher conversions the reaction rate is slightly over-estimated for both catalysts. Figure 4.6c and 4.6d show oxide formation and catalyst potential as a function of time respectively. At the beginning, the measured potential is irregular, possibly due to the presence of an easily dehydrogenating agent and pure oxygen gas. Only after some deactivation by over-oxidation the reading becomes stable and agrees with the simulated response.
Figure 4.6: Glucose oxidation: the effect of a high oxygen partial pressure on the catalyst performance. Symbols represent the experimental and continuous lines represent the modelling results. For the egg shell catalyst, triangles, dash-dot line (with a values from Table 4.5), and solid lines (with a 10 times higher $D_{eff}$, $k_{GL,O_2,aGL,O_2}$, and $k_{LS,O_2}$) are used, whereas for the uniform catalyst, circles, dashed line (with a values from Table 4.5) and dotted lines (with a 10 times higher $D_{eff}$, $k_{GL,O_2,aGL,O_2}$, and $k_{LS,O_2}$) are used.
4.5 Concluding remarks

In a semi-batch stirred reactor, the reaction rate of methyl glucoside (MGP) oxidation at oxygen partial pressure below 40 kPa, is found to be higher for the egg shell activity distribution than for the uniform catalyst activity distribution. Also, the deactivation rate due to over-oxidation increased dramatically with increasing oxygen partial pressure from 10 to 40 kPa, for both catalysts. For glucose, which has a higher rate of dehydrogenation, experimentally it is found that both catalysts give the same oxidation rate for all investigated oxygen partial pressures (5-100 kPa). Also, the rate of oxidation was 5-8 times higher than the MGP oxidation rate.

The developed reaction-engineering model is able to describe the observed experimental data for both catalysts. It is found that for the uniform catalyst, which has a small Pt particle size (higher dispersion), increasing the Pt-oxygen bonding, improved the model performance, especially for methyl glucoside oxidation. It is also found that glucose oxidation can only be modelled by considering that the reaction is taking place at the gas-liquid interface and is influenced by particle-bubble adhesion. For proper modelling good estimates for the effective diffusivity ($D_{eff}$) and partition coefficient (m) should be obtained, and the effect of PBA on mass transfer enhancement should be assessed.

The catalyst potential measurement and its subsequent modelling are proven to be accurate for low reducing compounds. However, for high reducing compounds, in the presence of pure oxygen gas, potential measurement is instable and the measuring technique needs to be improved. Also, the electrochemical kinetic model has to be improved by taking into account adsorbed hydrogen species and additional electro active reaction of proton formation.

In this chapter it is shown through modelling, that Pt particle size (dispersion) has a strong effect for a low reducing compound like methyl glucoside (MGP). However, this effect needs to be scrutinized via experiments, using more catalysts with different dispersion. Also, the effect of support needs to be investigated, along with possible limitations for the active sites accessibility for the alcohol molecule. The model can be further improved by taking into consideration of diffusion limitation for the alcohol molecule, which can be crucial at higher conversion.

Notation

- $a$: surface area of the gas-liquid and liquid-solid film, $m^{-1}$
- $C_{cat}$: catalyst concentration, $kgm^{-3}$
- $C_{ls}$: concentration at the liquid side of liquid-solid interface, $mol m^{-3}$
- $C_{MGP}$: MGP concentration, $mol m^{-3}$
$C_{MAGP}$  MAGP concentration, $mol\ m^{-3}$
$C_{MG}$  MG, product concentration, $mol\ m^{-3}$
$C$  oxygen concentration in the particle, $mol\ m^{-3}$
$C_{sat}$  equilibrium oxygen concentration in the liquid, $mol\ m^{-3}$
$C_L$  oxygen concentration in the bulk liquid, $mol\ m^{-3}$
$C_S$  oxygen concentration at the catalyst surface, $mol\ m^{-3}$
$D_e$  effective diffusivity, $m^2\ s^{-1}$
$E$  catalyst potential, $V$
$F$  Faraday’s constant, $C\ mol^{-1}$
$F_{V,G}$  volumetric gas flow rate, $m^3\ s^{-1}$
$k_i$  rate constants of species i, defined in Table 4.2
$K_i$  equilibrium rate constants of species i, defined in Table 4.2
$k_{GL}$  gas-to-liquid mass transfer coefficient, $ms^{-1}$
$k_{LS}$  liquid-to-solid mass transfer coefficient, $ms^{-1}$
l  diffusion path length, $m$
$L_t$  weight specific catalyst surface, $mol\ kg_{cat}^{-1}$
$P$  oxygen partial pressure inside the reactor, $kPa$
$R$  gas constant, $J\ mol^{-1}k^{-1}$
$R_i$  reaction rate of species i, defined in Table 4.1
$R_{RCH_2OH}$  specific reaction rate of alcohol, $mol\ kg^{-1}s^{-1}$
$R_{RCHO}$  specific reaction rate of aldehyde, $mol\ kg^{-1}s^{-1}$
$R_{v,O_2}$  volumetric reaction rate of oxygen, $mol\ m^{-3}s^{-1}$
t  time, $s$
$T$  temperature, $K$
$V$  volume, $m^3$
x  distance inside the catalyst particle, $m$
*  free adsorption site for oxygen
*ρ  free adsorption site for organic compounds
*s  free site for oxide formation

Greek letters
ε  porosity
ρ  density, $kg\ m^{-3}$
τ  tortuosity
Θ  surface coverage

Subscripts
$cat$  catalyst
4.5. Concluding remarks

\[ e \quad \text{effective} \]
\[ G \quad \text{bulk gas} \]
\[ L \quad \text{bulk liquid} \]
\[ GL \quad \text{gas-liquid} \]
\[ LS \quad \text{liquid-solid} \]
\[ Ox \quad \text{surface oxide} \]
\[ p \quad \text{catalyst particle} \]
\[ v \quad \text{volume} \]

Abbreviations

\[ C \quad \text{Carbon} \]
\[ Gr \quad \text{Graphite} \]
\[ MAGP \quad \text{methyl } \alpha\text{-D-6-aldehydo-glucopyranoside} \]
\[ MG \quad \text{1-O-methyl } \alpha\text{-D-glucuronic acid} \]
\[ MGP \quad \text{methyl } \alpha\text{-D-glucopyranoside or methyl glucoside} \]
\[ RCH_2OH \quad \text{alcohol compound} \]
\[ RCHO \quad \text{aldehyde compound} \]
\[ RCOOH \quad \text{acid compound} \]
Bibliography


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Chapter 5

Influence of pH: Reaction kinetics and modelling

This chapter has been published as:

Abstract

The Pt catalysed oxidation of the alcohol methyl α-D-glucopyranoside to 1-O-methyl α-D-glucuronic acid, at different pH conditions, has been studied. Two types of catalysts with different metal dispersion are used, viz., Pt on active carbon support and Pt on graphite support. The pH of the reaction medium is varied between 6 and 10. The initial reaction rate increases with an increase in pH and so does the rate of catalyst deactivation due to over-oxidation, for both catalysts. The carbon supported Pt catalyst gives higher initial reaction rates compared to the graphite supported Pt catalyst.

A dynamic, pH dependent, electrochemical kinetic model, based on a detailed investigation of mechanistic steps of alcohol oxidation, is presented. The model adequately describes the observed pH effect by considering the alcohol dehydrogenation occurring in two parallel reaction steps, one playing a role at acidic conditions, which is independent of the hydroxyl concentration, and a second one playing a role at alkaline conditions, which is linearly dependent on the hydroxyl concentration.

5.1 Introduction

Traditionally, due to fast production demands and one pot operation, synthesis routes of fine chemical and pharmaceutical compounds have been based on alcohol oxidation with stochio-
metric quantities of inorganic oxidants. This oxidation process suffers from low atom efficiency and high toxic waste production [1]. Alcohol oxidation by enzymes is practiced as an environmentally friendlier alternative, however product separation and waste production remain a problem. Homogeneous catalysis is an efficient alternative, however catalyst recovery, reactant recycling, and reactor corrosion limits its industrial scale utilization. A recent review of Mallat and Baiker [2] gives an extensive survey of ”green” methods for heterogeneously catalysed alcohol oxidation. Noble metal catalyzed alcohol oxidation with cheap oxidants such as air or molecular oxygen, is a clean and elegant alternative with mild reaction conditions, where high selectivities can be obtained [3–5].

Generally, aqueous alcohol oxidation is carried out in a weakly acidic or alkaline medium (pH = 6 - 11). The influence of pH on alcohol oxidation is complex and difficult to study as the pH can influence the reaction in several direct and indirect ways [4]. A multiple influence of pH has been reported. Firstly, with an increase in pH, the rate of oxidation increases in an alkaline medium [6–9]. Secondly, the selectivity towards the aldehyde intermediate decreases with increasing pH [10, 11]. Thirdly, at low pH (< 6), product adsorption on the catalyst strongly inhibits the reaction [12]. Finally, at high pH (> 11), the formation of by-products or leaching of the catalyst inhibits the reaction [13, 14]. However, in case of alcohols with low acidity (high pKa value) and strong reducing ability, the pH has no influence on the oxidation rate [14–16]. Vleeming et al. showed that with Pt on graphite catalyst, the rate of initial oxidation decreases with an increase in pH from 8 to 10 [11]. However, in an earlier study with Pt on carbon catalyst, a linear increase of the rate at pH > 8.5 was reported [8]. These seemingly contradictory findings may be due to the multiple influence of pH, on the interaction of the catalyst support with the adsorbed reactant alcohol and/or oxygen species, the concentration of intermediate aldehyde and (side) products, and on the catalyst deactivation due to over-oxidation.

Several types of catalyst deactivation mechanisms have been identified, viz. over-oxidation (corrosion), decarbonylation (CO formation), aldol condensation (polymerisation or coking), crystalline growth (Ostwald ripening), and metal dissolution (leaching) [17]. These deactivation mechanisms lead to a decrease of the active metal surface area and hence to a decrease of the reaction rate.

In electrochemistry research, reactions are carried out without oxidising agents like oxygen but with electrode potentials. At low potential (< 0.4 V RHE) in acidic or neutral medium, CO poisoning is the main cause of the catalyst deactivation [18, 19]. However, most of the experimental evidence on CO poisoning is obtained from methanol oxidation experiments [20, 21]. The extent of formation of adsorbed CO can be reduced or avoided by increasing the pH of the solution or the electrode potential (> 0.7 V RHE), or by promoting electrodes with heavy
metal, such as Bi, Pb, etc. [20, 22].

In gas-solid catalysis, extensive work has been done on the decomposition pathways of alcohols and aldehydes on single crystal metal surfaces [23]. A fundamental surface science study on a Pd metal surface under ultra high vacuum (UHV) conditions, has demonstrated that on a clean or oxygen free Pd surface the deacarbonylation is inevitable, whereas oxygen-covered surfaces suppress decarbonylation reactions [24].

There is hardly any evidence of CO formation under normal conditions of liquid phase heterogeneous alcohol oxidation. Only working at oxygen mass transport limited conditions, for certain compounds like aromatic alcohols and aldehydes, CO formation has been observed [25]. In the absence of oxygen mass transport limitations, the study of Abbadi et al. on the influence of pH on Pt catalysed D-glucose oxidation, revealed that the "free" form of the product, D-gluconic acid, and not CO is the main poisoning species in an acidic medium [12]. In weakly alkaline or acidic medium under kinetic limited conditions, over-oxidation has been observed as the main cause of the catalyst deactivation [26–29].

The present work focuses on the Pt-catalysed oxidation of a primary polyol under oxygen rich conditions (> 0.7 V RHE), at which CO formation or deposition of carbonaceous species is unlikely [30]. Also, for the investigated pH range, the aldol reaction resulting in a high molecular weight by-product is unlikely [8, 28]. Hence, these types of catalyst deactivation are excluded from the present kinetic model. Additionally, long term catalyst deactivation by coking, attrition, crystalline growth, and leaching are not subject of this study and care is taken to avoid these types of deactivation. It was verified through intermediate catalyst reactivation that over-oxidation is the main cause of the catalyst deactivation.

In literature some efforts have been taken to model the possible effects of pH on alcohol oxidation. Schuurman et al. performed initial rate kinetic modelling by considering two reaction paths, the first involved adsorbed alcohol dominating at low pH, and the second involved alcohol anion dominating at high pH [8]. In previous work, another approach was shown in electrochemical kinetic modelling through oxygen and oxide reduction, being proton concentration dependent steps [31, 32]. However, these models are inadequate in describing the effects of pH associated with catalyst deactivation due to over-oxidation.

The goal of this work is to develop a dynamic electrochemical kinetic model that quantitatively describes the observed reaction rates and the catalyst deactivation due to over-oxidation. In addition to that the model provides a better understanding of the effect of catalyst support and active metal dispersion in relation to the catalyst deactivation. Experiments are performed
at pH values between 6 and 10, using carbon and graphite supported Pt catalyst, for methyl α-D-glucopyranoside (MGP) oxidation as a test reaction.

5.2 Mechanistic steps of alcohol oxidation

It is generally accepted, both in heterogeneous catalysis and electrochemistry, that liquid phase alcohol oxidation on noble metal catalysts takes place via a dehydrogenation mechanism followed by the oxidation of the adsorbed hydrogen atom with dissociatively adsorbed oxygen [5–7, 15, 33–36]. Alternative mechanisms such as direct involvement of the oxidising species in the rate determining step of dehydrogenation [8, 16, 17, 26, 37, 38], and more recently, oxygen assisted dehydrogenation mechanisms [25] have also been proposed. However, the exact reaction sequence through which the dehydrogenation mechanism occurs is still under dispute [39], due to the complex nature of the adsorbed species on the metal surface, such as the origin of adsorbed oxygen species, O₂ or OH⁻ or H₂O, type of adsorbed reactant alcohol, RCH₂OH or RCH₂O⁻ or RCH₂O. The nature of the adsorbed species mainly depends on the pH of the reaction medium, the concentration of the oxidising agent, and the acidity of the catalyst.

Several possible reaction sequences describing the global reaction of alcohol oxidation with oxygen on Pt catalysts by different adsorption and surface reaction steps have been considered in the literature. Excluding formation of CO and carbonaceous deposits, three steps (in any order) can be identified as important ones:

1. Oxygen adsorption and reduction.
2. Alcohol/Aldehyde dehydrogenation.
3. Platinum oxide formation, i.e., over-oxidation or corrosion (deactivation) and reduction (reactivation).

5.2.1 Oxygen adsorption and reduction

One of the most essential functions of the catalyst is the activation of oxygen. The way in which oxygen becomes activated is a crucial problem in oxidation catalysis [40]. Generally speaking, oxygen activation is considered to occur by its adsorption. Oxygen may adsorb on metal surfaces as

1. Weakly adsorbed molecular oxygen.
2. Chemisorbed atomic oxygen.
3. Oxygen atoms penetrating into the most external layers of metal crystals, thus forming "subsurface" oxygen.
The kind of metal oxygen bond depends on the purity of the metal surfaces, on temperature, and also on the crystal face being studied. At platinum (111), molecular adsorption of oxygen is predominant below 120 K and exhibits a desorption peak at 150 K,

\begin{align}
O_2 + \ast &\rightleftharpoons O_2\ast, \\
O_2 + e^- + \ast &\rightleftharpoons O_2^-\ast,
\end{align}

where \ast is free adsorption site.

In case of silica supported and presumably finely divided platinum, \(O_2^-\) species were identified by EPR (Electron Spin Resonance technique) measurements at ambient temperature, besides which \(O^-\) species were also present [40]. Electron transfer from the metal to the oxygen results in a positive potential of the metal, up to 1.5 V RHE [41]. Molecularly adsorbed oxygen plays the role of precursor of adsorbed atomic oxygen:

\begin{align}
O_2\ast + \ast &\rightleftharpoons 2O\ast \\
O_2^-\ast + e^- + \ast &\rightleftharpoons 2O^-\ast
\end{align}

Atomic oxygen at the surface of Pt is the predominant form of adsorbed oxygen within the temperature range of 150-500 K. Further heating of platinum in oxygen above 500 K results in the formation of ”subsurface” oxide, which decomposes at 1250 K [42]. A direct proof of the penetration of oxygen into the near-to-surface layer of the solid was obtained for Pt (111) by ion scattering [40].

According to electrochemistry research in corrosion processes, the oxygen reduction reaction is a multi step process involving four electron transfers during which bonds are broken and formed with an important involvement of the surrounding water molecules [43]:

\begin{align}
O_2\ast + 2H_2O + 4e^- &\rightarrow 4OH^- + \ast \text{ alkaline medium} \\
O_2\ast + 4H^+ + 4e^- &\rightarrow H_2O_2\ast + 2H^+ + 2e^- \rightarrow 2H_2O + \ast \text{ acidic medium}
\end{align}

Bockris and coworkers [44] have proposed that the adsorption of oxygen atoms arises from an equilibrium of the water discharge reaction with the Pt surface in acidic medium, which usually occurs at 0.6-0.8 V RHE:

\begin{equation}
H_2O + \ast \rightarrow O\ast + 2H^+ + 2e^- \tag{5.7}
\end{equation}

whereas in alkaline medium adsorption of \(OH^-\) species is taking place,

\begin{equation}
OH^- + \ast \rightarrow O\ast + H^+ + 2e^- \tag{5.8}
\end{equation}

Recently, Harting and Koper [45] have proposed in their theoretical study that the rate determining step in oxygen adsorption is molecular electrosorption, by accepting one electron from
the metal, as shown in Equation 5.2. Depending on the acidity of the solution, this electron transfer is accompanied or followed by a proton transfer to the oxygen leading to a precursor for hydrogen peroxide formation:

\[ O_2 + H^+ + e^- + \rightarrow HO_2^* \] (5.9)

In liquid phase heterogeneous catalysis, which is normally carried out at 293-353 K, it is considered that oxygen adsorption on the Pt occurs via dissociative chemisorption, which may be either reversible [8, 28], Equation 5.3, or irreversible [16, 31], as follows:

\[ O_2 + 2* \rightarrow 2O* \] (5.10)

It can be seen that oxygen adsorption on the metal catalyst can be described through different steps, depending on the temperature, the electrochemical potential, and the pH of the reaction medium.

### 5.2.2 Alcohol/Aldehyde dehydrogenation

A number of different ways to describe the surface chemistry of the oxidative dehydrogenation mechanism have been proposed [4]. In a pure dehydrogenation mechanism, the rate determining step is considered to be dehydrogenation of alcohol to the intermediate aldehyde, followed by aldehyde hydration and dehydrogenation to the acid:

\[ RCH_2OH* + 2* \rightleftharpoons RCHO* + 2H* \] (5.11)

\[ RCHO* + H_2O \rightleftharpoons RCH(OH)_2* \] (5.12)

\[ RCH(OH)_2* + 2* \rightleftharpoons RCOOH* + 2H* \] (5.13)

This is in agreement with the observed high rate of aldehyde oxidation in cases where the hydration equilibrium is shifted towards the geminal glycol form and the hydration is catalysed by bases [3, 6]. If the glycol formation is negligible, the aldehyde to acid transformation is an oxidation reaction. It has also been observed that the oxidation rate of aldehyde increases with increase in pH [11]. Due to their higher nucleophilic property, at high pH, hydroxyl ions are involved in aldehyde dehydrogenation rather than water [38]:

\[ RCHO* + OH^- \rightarrow RCOOH* + H^+ + 2e^- \] (5.14)

Dijkgraaf et al. have proposed that the dehydrogenation of alcohol starts with proton abstraction, followed by hydride transfer from the carbon atom towards the noble metal surface [26]:

\[ RCH_2OH* + OH^- \rightleftharpoons RCH_2O^-* + H_2O \] (5.15)

\[ RCH_2O^-* + * \rightarrow RCHO* + H^-* \] (5.16)
The validity of this step has been disputed as deprotonation of a very weak acid, such as sugar alcohols, in weakly alkaline medium is rather difficult [46]. Another possibility of this step is hydrogen abstraction from the adsorbed alcohol molecule in two successive steps assuming that the O-H bond is broken first forming surface alkoxides [8, 15]:

\[
\begin{align*}
RCH_2OH^* + * & \rightleftharpoons RCH_2O^* + H^* \\
RCH_2O^* + * & \rightarrow RCHO^* + H^*
\end{align*}
\]

Recently, Markusse et al. in their kinetic studies, have proposed that at high catalyst potentials, the alcohol and aldehyde dehydrogenation steps can be described as irreversible, and are accompanied by the production of electrons and protons [31], as:

\[
\begin{align*}
RCH_2OH^* & \rightarrow RCHO^* + 2H^+ + 2e^- \\
RCHO^* + H_2O & \rightarrow RCOOH^* + 2H^+ + 2e^-
\end{align*}
\]

In electrochemistry, depending on the pH of the medium, methanol dehydrogenation steps have been proposed [20] as following:

- in acidic medium:

\[
\begin{align*}
CH_3OH^* & \rightarrow CH_3O^* + H^+ + e^- \\
CH_3O^* & \rightarrow CH_2O^* + H^+ + e^-
\end{align*}
\]

- in alkaline medium:

\[
\begin{align*}
CH_3OH^* + OH^- & \rightarrow CH_3O^* + H_2O + e^- \\
CH_3O^* + OH^- & \rightarrow CH_2O^* + H_2O + e^-
\end{align*}
\]

It can be seen that the pH plays a crucial role in the alcohol/aldehyde dehydrogenation step.

### 5.2.3 Platinum oxide formation and reduction

It emerges from the dehydrogenation mechanism of alcohol oxidation that the reaction proceeds on free noble metal sites. There is no significant catalyst deactivation while the reactor is operated in a transport limited regime, i.e. the oxygen supply is the rate determining step and there are free active metal sites present. In batchwise operation, the situation changes after a certain conversion: the surface chemical reaction becomes the rate determining step due to the lower liquid reactant concentration. This means that the rate of oxygen supply to the catalyst surface is higher than its consumption, which causes successive oxidation of the active metal sites, and the catalyst deactivates. This phenomenon is called over-oxidation, which can be seen at oxygen rich conditions. According to Dijkgraaf et al., adsorbed oxygen atoms on the platinum active
metal sites slowly penetrate the skin of the platinum metal (dermasorption) and forms a 'subsurface' atom leading to platinum oxide formation, which finally causes catalyst deactivation [26]. It was considered to be a purely chemical and reversible step [28, 47]:

\[ O* + *s \rightleftharpoons O_{s} + (*) \]  

(5.25)

where \(*_s\) denotes adsorption sites for the formation of inactive platinum oxide \((O_{s})\), and (*) means free sites that are not available for further adsorption. The simplest way for reduction or reactivation of the catalyst is to substitute oxygen with nitrogen (inert gas) and then the alcohol reactant reduces the noble metal surface:

\[ RCH_2OH* + O_{s} \rightarrow RCHO* + H_2O + *s \]  

(5.26)

Markusse et al. have supported the above mechanism, Equation 5.25, but assumed that formation of the inactive oxide is a purely chemical step, being irreversible, as observed through cyclic voltammetry experiments, while reduction of the oxide depends on the catalyst potential, being a electrochemical step [31]:

\[ O_{s} + H^+ + 2e^- + * \rightarrow OH^- + * + *s \]  

(5.27)

In electrochemistry, oxide formation is considered as a corrosion phenomenon, and it has been proposed that the origin of the oxygen species, responsible for the oxide formation, is water and not molecular oxygen, which has only one role, that is increasing the catalyst potential [44]. The corrosion process occurs above 0.8 V RHE potential, e.g. in acidic medium:

\[ H_2O + * \rightarrow OH* + H^+ + e^- \]  

(5.28)

whereas in alkaline medium, adsorption of \(OH^-\) species is taking place:

\[ OH^- + * \rightarrow OH* + e^- \]  

(5.29)

followed by:

\[ OH* \rightarrow O_{s} + H^+ + e^- \]  

(5.30)

It can be seen from this section that in heterogeneous catalysis, the oxide formation step has been considered as pH independent. However, from electrochemistry, it can be concluded that with an increase in pH, the rate of catalyst deactivation due to over-oxidation or corrosion increases.

### 5.3 Kinetic model

From above discussions, it is clear that aqueous alcohol oxidation can be described through several mechanisms, which can lead to various kinetic models. It seems complex and difficult to
5.3 Kinetic model

Arrive at a general mechanism, which can explain all the phenomena. In recent work, Gangwal et al. have demonstrated the versatile nature of the previously developed electrochemical kinetic model of Markusse et al. for alcohol oxidation and catalyst deactivation due to over-oxidation [31, 33]. However, this model is only suitable for modelling alcohol oxidation at pH = 8. It is found that at pH = 6, the model predicts nearly 20 times higher oxidation rates than experimentally observed, whereas at pH = 10, the model predicts nearly 20 times lower oxidation rates, comparative to pH = 8. It is verified with the present experimental work that the Markusse et al. model fails to describe, qualitatively and quantitatively, the observed pH dependent reaction rates. In order to describe the pH effect, the adopted kinetic mechanism along with the reaction rate equations, is presented in Table 5.1. It is assumed that oxygen and the organic compounds (reactant alcohol and the reaction products) adsorb independently. The oxygen adsorption step (I) is considered to be irreversible, as described in Equation 5.10. The alcohol reactant adsorption step (II), the intermediate adsorption step (IIa), and the acid product adsorption step (X) are considered to be associative, as considered by Markusse et al. [31].

The pH effect is considered through parallel reaction steps, occurring through dehydrogenation of the alcohol (III and IV), the oxidation of aldehyde (V and VI), and through platinum oxide formation (VIII and IX). Depending on the pH of the reaction medium, acidic or alkaline, the rate determining or dominating reaction step will switch. At acidic conditions, step III is the rate determining step for alcohol dehydrogenation, in accordance with Equations 5.19 and 5.21, whereas at alkaline conditions, step IV is the dominating step, Equation 5.23. For aldehyde oxidation, at acidic conditions, step V is the dominating step, Equation 5.20, whereas at alkaline conditions, step VI is the dominating step, Equation 5.14. It is assumed that strongly adsorbed oxygen is responsible for platinum oxide formation due to over-oxidation or corrosion, no discrimination is made between adsorbed oxygen and adsorbed hydroxyl species. At acidic conditions, step VIII is the dominating oxide formation step, in accordance with Equation 5.25, whereas at alkaline conditions, step IX is the dominating step, Equations 5.29 and 5.30.

In the present model, the oxygen reduction (VII) and oxide reduction (XI) reaction steps are considered to be independent of pH, in contrast to the Markusse et al. model, which considered proton concentration dependency [31]. The site balances applied in the present kinetic model are similar to the Markusse et al. model, except additional involvement of the aldehyde site coverage, as follows:

\[
alcohol\text{ adsorption, } \Theta_{\rho} + \Theta_{RCH_2OH} + \Theta_{RCHO} + \Theta_{RCOOH} = 1 \quad (5.31)
\]
\[
oxygen\text{ adsorption, } \Theta* + \Theta_o + \Theta_{ax} = 1 \quad (5.32)
\]
\[
\text{subsurface oxygen, } \Theta_{*s} + \Theta_{ax} = 1 \quad (5.33)
\]
Table 5.1: Reaction steps and rate equations for alcohol oxidation mechanism.

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Rate equation</th>
</tr>
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<tbody>
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<td>(I)</td>
<td>$R' = 1$</td>
</tr>
<tr>
<td>(II)</td>
<td>$d*'Θ = 2$</td>
</tr>
<tr>
<td>(III)</td>
<td>$(x0-1)*Θ = \theta$</td>
</tr>
<tr>
<td>(IV)</td>
<td>$(x0-1)*Θ = \theta$</td>
</tr>
<tr>
<td>(V)</td>
<td>$(x0-1)*Θ = \theta$</td>
</tr>
<tr>
<td>(VI)</td>
<td>$(x0-1)*Θ = \theta$</td>
</tr>
<tr>
<td>(VII)</td>
<td>$R' = 0$</td>
</tr>
<tr>
<td>(VIII)</td>
<td>$R' = 0$</td>
</tr>
<tr>
<td>(IX)</td>
<td>$R' = 0$</td>
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<tr>
<td>(X)</td>
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<tr>
<td>(XI)</td>
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<td>(XV)</td>
<td>$R' = 0$</td>
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<td>(XVI)</td>
<td>$R' = 0$</td>
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<tr>
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<td>$R' = 0$</td>
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<td>$R' = 0$</td>
</tr>
<tr>
<td>(L)</td>
<td>$R' = 0$</td>
</tr>
</tbody>
</table>
where \( \Theta_{\ast p} \) is the fraction of the free organic compound adsorption sites, \( \Theta_{\ast} \) is the fraction of the free oxygen adsorption sites, \( \Theta_{ox} \) is the coverage of inactive oxide formation, and \( \Theta_{\ast s} \) is the fraction of the oxide formation sites. Using Equation 5.31, and the equilibrium Equations II, IIa, and X, in Table 5.1, the alcohol coverage fraction is determined as:

\[
\Theta_{RCH_2OH} = \frac{K_2C_{RCH_2OH}}{1 + K_2C_{RCH_2OH} + K_2aC_{RCHO} + K_{10}C_{RCOOH}}
\] (5.34)

where \( K_i \) are the equilibrium adsorption parameters defined in Table 5.1. Similarly, for the intermediate aldehyde and the product acid, the coverage fractions are determined as:

\[
\Theta_{RCHO} = \frac{K_2aC_{RCHO}}{1 + K_2C_{RCH_2OH} + K_2aC_{RCHO} + K_{10}C_{RCOOH}}
\] (5.35)

\[
\Theta_{RCOOH} = \frac{K_2C_{RCH_2OH}}{1 + K_2C_{RCH_2OH} + K_2aC_{RCHO} + K_{10}C_{RCOOH}}
\] (5.36)

The surface specific alcohol dehydrogenation rate \( R_3 \) (step III, Table 5.1) increases with increasing free site fraction, \( \Theta_{\ast} \), and consequently decreases with increasing oxygen coverage, \( \Theta_o \). Based upon the non-steady state site balances and the rate equations given in Table 5.1, the rates of change of oxygen coverage (\( \Theta_o \)) and oxide coverage (\( \Theta_{ox} \)), are determined by the following differential equations:

\[
\frac{d\Theta_o}{dt} = 2k_1C_{O_2}\Theta_{\ast}^2 - k_7\Theta_o\exp\left(-\frac{EF}{RT}\right) - k_8\Theta_o(1 - \Theta_{ox})
\] (5.37)

\[
\frac{d\Theta_{ox}}{dt} = k_8\Theta_o(1 - \Theta_{ox}) + k_9C_{OH}\Theta_{\ast}\exp\left(\frac{EF}{RT}\right) - k_{11}\Theta_{ox}\Theta_{\ast}\exp\left(-\frac{EF}{RT}\right)
\] (5.38)

where \( k_i \) are the reaction rate parameters defined in Table 5.1, \( C_{O_2} [mol m^{-3}] \) is the oxygen concentration at the catalyst surface, \( E [V] \) is the electrochemical catalyst potential, \( F [C mol^{-1}] \) is the Faraday’s constant, \( R [J mol^{-1} K^{-1}] \) is the ideal gas constant, and \( T [K] \) is the reaction temperature. The catalyst potential is determined by balancing the rate of electrons produced (\( R_3 + R_4 + R_5 + R_6 + R_9 \)) per volume of the catalyst and the rate of electrons consumed (\( R_7 + R_{11} \)) per volume of the catalyst as:

\[
E = \frac{RT}{2F} \ln\left(\frac{R_{oxid1} + R_{oxid2}}{R_{red1} + R_{red2} + R_{red3} + R_{red4} + R_{red5}}\right)
\] (5.39)

where \( R_i \) are the reaction rates of species i, defined in Table 5.1, and

\[
R_{red1} = k_3L_1\rho_{p}\Theta_{RCH_2OH}\Theta_{\ast}
\] (5.40)

\[
R_{red2} = k_4L_1\rho_{p}C_{OH}\Theta_{RCH_2OH}\Theta_{\ast}
\] (5.41)

\[
R_{red3} = k_5L_1\rho_{p}\Theta_{RCHO}\Theta_{\ast}
\] (5.42)

\[
R_{red4} = k_6L_1\rho_{p}C_{OH}\Theta_{RCHO}\Theta_{\ast}
\] (5.43)

\[
R_{red5} = k_9L_1\rho_{p}C_{OH}\Theta_{\ast}
\] (5.44)

\[
R_{oxid1} = k_7L_1\rho_{p}\Theta_{o}
\] (5.45)

\[
R_{oxid2} = k_{11}L_1\rho_{p}\Theta_{ox}\Theta_{\ast}
\] (5.46)
where \( k_i \) are the reaction rate parameters defined in Table 5.1, \( L_t \) is the weight specific number platinum surface atoms, i.e. \( mol Pt_s/\text{kg} \) catalyst, based on the assumption that one Pt surface atom equals one catalytic site, and \( \rho_p \) is the catalyst particle density. It should be noted that two important phenomena limit the range of the catalyst potential. Firstly, below a potential of 0.4 V RHE, hydrogen gas evolves, due to water reduction, and CO formation is possible. Secondly, above a potential of 1.5 V RHE, oxygen gas evolves, due to water oxidation. Since these reactions are not taken into account in the kinetic model presented in Table 5.1, Equation 5.39 can only be applied, if:

\[
0.4V_{\text{RHE}} < E < 1.5V_{\text{RHE}}
\] (5.47)

The overall volumetric rate of consumption of oxygen, \( R_{v, O_2} \ [mol \ m^{-3} \ s^{-1}] \), is dependent on the amount of oxygen present at the catalyst surface as well as on the activity of the catalyst. Therefore, from Equation (I) of Table 5.1,

\[
R_{v, O_2} = L_t C_{\text{cat}} k_1 \Theta^2 \Theta^2 C_{O_2}
\] (5.48)

where \( C_{\text{cat}} \) is the catalyst concentration. The weight specific dehydrogenation rate of the reactant alcohol, \( R_{RCH_2OH} \ [mol \ kg^{-1} \ s^{-1}] \), from Equations (III) and (IV) of Table 5.1, can be determined as:

\[
R_{RCH_2OH} = L_t (k_3 + k_4 C_{OH}) \Theta_{RCH_2OH} \Theta^* \exp \left( \frac{EF}{RT} \right)
\] (5.49)

The weight specific acid formation rate, \( R_{RCOOH} \ [mol \ kg^{-1} \ s^{-1}] \), which is measured through the rate of alkali (NaOH) addition, can be calculated from the rate of aldehyde oxidation, Equations (V) and (VI) of Table 5.1, as:

\[
R_{RCOOH} = L_t (k_5 + k_6 C_{OH}) \Theta_{RCOOH} \Theta^* \exp \left( \frac{EF}{RT} \right)
\] (5.50)

### Table 5.2: Catalyst properties.

<table>
<thead>
<tr>
<th>Catalyst property</th>
<th>Pt/Gr (Vleeming et al. [28])</th>
<th>Pt/C (Engelhard, 43545)</th>
<th>Pt/Gr (JM287)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dispersion [%]</td>
<td>43</td>
<td>42</td>
<td>15</td>
</tr>
<tr>
<td>B.E.T. area [m²/gm]</td>
<td>102</td>
<td>900</td>
<td>15</td>
</tr>
<tr>
<td>Pt content [wt.%]</td>
<td>3.3</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>particle size [µm]</td>
<td>15</td>
<td>35-40</td>
<td>15</td>
</tr>
<tr>
<td>moisture content [%]</td>
<td>dry</td>
<td>46.88</td>
<td>dry</td>
</tr>
<tr>
<td>porosity [%]</td>
<td>40</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>density [kg/m³]</td>
<td>1350</td>
<td>1050</td>
<td>1350</td>
</tr>
</tbody>
</table>
5.4 Experimental

In this chapter, experiments are performed in a stirred three-phase semi-batch reactor. The aqueous alcohol, methyl α-D-glucopyranoside (MGP), is added in a batch mode. The gaseous oxidant (molecular oxygen) is supplied continuously by a mass flow controller. The oxygen partial pressure is set by the nitrogen flow, also supplied by a mass flow controller. The pH is monitored and kept at a constant level by controlled addition of a 0.1 M NaOH solution.

During the reaction, the liquid reactant is converting to the product with time, i.e. MGP gives 1-O-methyl α-D-glucuronic acid (MG) with methyl α-D-6-aldehydo-glucopyranoside (MAGP) as the intermediate. The acid formation rate is measured through the rate of addition of alkali. The oxygen concentration in the liquid phase is measured using an oxygen electrode. The open circuit electrochemical catalyst potential is measured with a smooth Pt wire as working electrode and Ag/AgCl, saturated KCl as a reference electrode.

Two commercial non-uniform (egg shell) catalysts, a 5 wt % Pt on carbon (Engelhard, code-43545) and a 5 wt % Pt on graphite (Johnson Matthey, JM287), were used. The properties of the catalysts are presented in Table 5.2. The pH of the reaction medium is the only parameter that is different between the experiments. Experiments were performed at the set of reaction conditions as presented in Table 5.3, and the experimental procedure is described in Chapter 3 (section 3.4.2).

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>CSTR (Vleeming et al. [28])</th>
<th>Semi-batch reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH [-]</td>
<td>8</td>
<td>6-10</td>
</tr>
<tr>
<td>degree of conversion [%]</td>
<td>3 - 47</td>
<td>5 - 40</td>
</tr>
<tr>
<td>temperature, T [K]</td>
<td>323</td>
<td>323</td>
</tr>
<tr>
<td>catalyst concentration, $C_{cat}$ [kg m$^{-3}$]</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>stirring speed [r.p.m]</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>oxygen partial pressure, $P_{o_2}$ [kPa]</td>
<td>10 - 100</td>
<td>40</td>
</tr>
<tr>
<td>initial MGP conc., $C_{MGP}$ [mol m$^{-3}$]</td>
<td>11 - 427</td>
<td>100</td>
</tr>
<tr>
<td>initial MG conc., $C_{MG}$ [mol m$^{-3}$]</td>
<td>1.5 - 41</td>
<td>0</td>
</tr>
<tr>
<td>liquid volume, $V_L$ [m$^3$]</td>
<td>$0.35 \times 10^{-3}$</td>
<td>$0.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>gas volume, $V_G$ [m$^3$]</td>
<td>$0.2 \times 10^{-3}$</td>
<td>$0.35 \times 10^{-3}$</td>
</tr>
<tr>
<td>volumetric gas flow, $F_G$ [m$^3$ s$^{-1}$]</td>
<td>$5 \times 10^{-6}$</td>
<td>$14 \times 10^{-6}$</td>
</tr>
<tr>
<td>gas-to-liquid coefficient, $k_{GLaGL}$ [s$^{-1}$]</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>
5.5 Kinetic parameter estimation

The goal of this work is to obtain a dynamic electrochemical model with a set of kinetic parameters that can adequately describe the observed experimental data, at different pH conditions for the catalyst with different supports and metal dispersion. In order to avoid strong interdependence and mutual correlation of the parameters and to have a reliable parameter estimation, the kinetic parameters of the model described in section 5.3 are obtained in two consecutive steps. Firstly, pH independent parameters \(k_1, K_2, k_3, k_7, k_8, \) and \(K_{10}\) are estimated, which are then further used for the estimation of pH dependent parameters \(k_4, k_5, k_6, \) and \(k_9\).

5.5.1 pH independent kinetic parameters

The pH independent kinetic parameters are estimated using a set of 12 experiments performed in a CSTR with Pt on graphite catalyst (43 \% dispersion). The catalyst properties and experimental conditions are presented in Tables 5.2 and 5.3, respectively. Each experiment is performed at a constant pH of 8 and contains 40 reaction rate data measured by keeping constant conversion level. The details of the experimental procedure are described elsewhere [28]. It was verified that all data were obtained at intrinsic kinetic conditions, except data at 10 kPa oxygen partial pressure, which represent the effect of gas-to-liquid mass transport limitation [32].

The kinetic model presented in Table 5.1 is simplified with the help of the following assumptions to account for the constant pH:

- The intermediate aldehyde disappearance, step V, is very fast, i.e. the rates of the disappearance of the aldehyde, Equation 5.42, and of the alcohol, Equation 5.40, can be considered equal:
  \[ R_{\text{red3}} = R_{\text{red1}}. \]

- The hydroxyl ion concentration dependent steps IV, VI, and IX are considered to be insignificant because experimental data are available at sufficiently low pH (pH = 8). This means:
  \[ R_{\text{red2}} \ll R_{\text{red1}}, R_{\text{red4}} \ll R_{\text{red1}}, \] and \[ R_{\text{red5}} \ll R_{\text{red1}}. \]

Using the above assumptions, the catalyst potential equation (Equation 5.39) can be rewritten as:

\[ E = \frac{RT}{2F} \ln \left( \frac{R_{\text{oxid1}} + R_{\text{oxid2}}}{2R_{\text{red1}}} \right) \] (5.51)

which then leads to:

\[ \exp \left( \frac{EF}{RT} \right) = \left( \frac{k_7 \Theta_o + k_{11} \Theta_{ox} \Theta^*}{2k_3 \Theta_{RCH_2OH} \Theta^*} \right)^{\frac{1}{2}} \] (5.52)

and

\[ \exp \left( \frac{-EF}{RT} \right) = \left( \frac{2k_3 \Theta_{RCH_2OH} \Theta^*}{k_7 \Theta_o + k_{11} \Theta_{ox} \Theta^*} \right)^{\frac{1}{2}} \] (5.53)
By substituting the above Equations 5.52 and 5.53 in Equations 5.37, 5.38, and 5.49 results in:

\[
\frac{d\Theta_o}{dt} = 2k_1C_{o2}\Theta^* - k_7\Theta_o\left(\frac{2k_3\Theta_{RCH2OH}\Theta^*}{k_7\Theta_o + k_{11}\Theta_{ox}\Theta^*}\right)^{\frac{1}{2}} - k_8\Theta_o(1 - \Theta_{ox}) \tag{5.54}
\]

\[
\frac{d\Theta_{ox}}{dt} = k_8\Theta_o(1 - \Theta_{ox}) - k_{11}\Theta_{ox}\Theta^*\left(\frac{2k_3\Theta_{RCH2OH}\Theta^*}{k_7\Theta_o + k_{11}\Theta_{ox}\Theta^*}\right)^{\frac{1}{2}} \tag{5.55}
\]

\[
R_{RCH2OH} = L_i k_3\Theta_{RCH2OH}\Theta^*\left(\frac{k_7\Theta_o + k_{11}\Theta_{ox}\Theta^*}{2k_3\Theta_{RCH2OH}\Theta^*}\right)^{\frac{1}{2}} \tag{5.56}
\]

It turns out that these simplified model equations resemble the kinetic model equations of Markusse et al. [31]. In previous work, it was found that some of the kinetic parameters, especially \(k_3\) and \(k_7\), of this model are highly correlated (approximate correlation \(> 0.9\)) [48]. For the reliable estimation of these parameters, the lumped parameters \((k_3 k_7)^{\frac{1}{2}}\) and \((k_3 k_{11})^{\frac{1}{2}}\) are identified, which can be recognised in the Equations 5.54, 5.55, and 5.56. In addition to that, to include the measured reaction rate data at 10 kPa oxygen partial pressure and initial reaction conditions, the influence of gas-to-liquid mass transport limitation has to be accounted for in the model for accurate parameter estimation [48]. The mass transport equations that need to be considered are as follows:

**Gas phase (G) mass balance.**

Oxygen mass transport from the gas phase to the liquid phase:

\[
\frac{V_G}{RT} \frac{dP_{o2}}{dt} = \frac{F_G(P_{o2}^{in} - P_{o2})}{RT} - k_{GL}a_{GL}V_L(HP_{o2} - C_{o2,L}) \tag{5.57}
\]

where \(V_G [m^3]\) is the volume of gas in the reactor, \(P_{o2} [kPa]\) is the oxygen partial pressure in the reactor, \(F_G [m^3 s^{-1}]\) is the total volumetric gas flow rate, \(k_{GL}a_{GL} [s^{-1}]\) is the volumetric gas-to-liquid mass transport coefficient, \(H [mol m^{-3} Pa^{-1}]\) is the Henry coefficient, and \(C_{o2,L} [mol m^{-3}]\) is the oxygen concentration in the liquid phase.

**Liquid phase (L) mass balance.**

Oxygen mass transport from the liquid phase to the solid phase:

\[
V_L \frac{dC_{o2,L}}{dt} = k_{GL}a_{GL}V_L(HP_{o2} - C_{o2,L}) - V_LR_{v,o2} \tag{5.58}
\]

where \(V_L [m^3]\) is the total liquid volume, and \(R_{v,o2}\) is the overall volumetric oxygen consumption rate, determined by Equation 5.48.

A generalised non-linear least square routine of MATLAB, which uses the Levenberg-Marquardt algorithm [49] is used for the optimization. The residual sum of squares that is minimised is:

\[
resid_{CSTR} = \Sigma(R_{RCH2OH,t(model)} - R_{RCH2OH,t(exp)})^2 \tag{5.59}
\]

The regression analysis is performed in two parts. First, the initial oxidation rate data (after 50 s) are used to obtain estimates for the parameters of the initial rate model. Next, the regression analysis is extended to the entire oxidation rate data in the time interval between 50 and 10000 s, estimating all parameters simultaneously.
Initial oxidation rate data

For the regression analysis, it is assumed that the catalyst deactivation due to over-oxidation is absent, i.e. $\Theta_{ox} = 0$. Hence, the oxide formation, step VIII, and oxide reduction, step XI, can be eliminated from the model. The reversible steps II and X are considered to be in quasi-equilibrium. Equation 5.51 then simplifies to:

$$E = \frac{RT}{2F} \ln\left(\frac{R_{oxid}}{2R_{red}}\right)$$

which leads to:

$$\exp\left(\frac{EF}{RT}\right) = \left(\frac{k_7\Theta_o}{2k_3\Theta_{RCH2OH}\Theta^*}\right)^{\frac{1}{2}}$$

By substituting the above equation in Equations 5.37 and 5.49 results in:

$$\frac{d\Theta_o}{dt} = 2k_1C_{O_2}\Theta^2 - (k_3k_7)^{\frac{1}{2}}(2\Theta_{RCH2OH}\Theta^*\Theta_o)^{\frac{1}{2}}$$

$$R_{RCH2OH} = L_1(k_3k_7)^{\frac{1}{2}}(0.5\Theta_{RCH2OH}\Theta^*\Theta_o)^{\frac{1}{2}}$$

Table 5.4: Kinetic parameters with their individual 95 % confidence intervals and correlation matrix, obtained with initial rate (after 50 s) data of MGP oxidation in CSTR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction step</th>
<th>Pt/Gr (dispersion 43 %)</th>
<th>Correlation matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ [$m^3mol^{-1}s^{-1}$]</td>
<td>oxygen adsorption</td>
<td>(1.76 ± 4.30)</td>
<td>1 0.16 0.06 -0.11</td>
</tr>
<tr>
<td>$K_2$ [$m^3mol^{-1}$]</td>
<td>alcohol adsorption</td>
<td>(6.51 ± 8.60) × $10^{-3}$</td>
<td>0.16 1 0.43 -0.83</td>
</tr>
<tr>
<td>$K_{10}$ [$m^3mol^{-1}$]</td>
<td>acid adsorption</td>
<td>(9.75 ± 13.67) × $10^{-2}$</td>
<td>0.06 0.43 1 0.10</td>
</tr>
<tr>
<td>$(k_3k_7)^{\frac{1}{2}}$ [s$^{-1}$]</td>
<td>alcohol oxidation</td>
<td>(1.58 ± 0.66) × $10^{-1}$</td>
<td>-0.11 -0.83 0.10 1</td>
</tr>
</tbody>
</table>

For the parameter estimation, the kinetic model Equations 5.62 and 5.63 are solved in combination with the gas-to-liquid mass transport Equations 5.57 and 5.58. The regression analysis is performed with experimental data obtained after 50 s. The estimated kinetic parameters along with their confidence intervals are presented in Table 5.4. The confidence intervals for the first three parameters ($k_1$, $K_2$, and $K_{10}$) are quite wide, which suggests that the measured data available for the regression analysis are not sufficient and the parameter estimates are preliminary. The fitting of the model is illustrated in Figures 5.1a and 5.1b, which shows the effect of MGP concentration and oxygen partial pressure on the initial oxidation rate, respectively. It is found that the kinetic parameters obtained in previous work [48] are present within the confidence interval of newly estimated parameters. The correlation matrix, which gives indication of the degree of interdependence between the estimated parameters, is also presented in Table 5.4. The mutual correlation between the parameters is low except between parameters $(k_3k_7)^{\frac{1}{2}}$ and $K_2$, $K_{10}$.
which corresponds to 0.83. This can be explained by the structure of the model, since substituting Equation 5.34 in Equation 5.56 shows that the rate is mainly determined by the product of $(k_3 k_7)^{1/2}$ and $K_2^{1/2}$.

![Graph showing MGP oxidation rate vs. MGP concentration and oxygen partial pressure.](image)

**Figure 5.1:** Effect of (a) MGP concentration and (b) oxygen partial pressure, on experimental (symbols) and model predicted (solid lines), MGP oxidation rates obtained after 50 s. Data used: (a) $P_o = 40$ kPa, $L_t = 0.073$ mol/kg_{cat} and (b) $C_{MGP} = 90$ mol/m$^3$, $C_{MG} = 10$ mol/m$^3$, $L_t = 0.073$ mol/kg_{cat}.

### Oxidation rate data including deactivation

The initial kinetic parameters, presented in Table 5.4, are used as starting values for the parameter estimation with entire oxidation data, $t > 50$ s.

**Table 5.5:** Kinetic parameters with their individual 95% confidence intervals and correlation matrix, obtained with the rate data, in the interval of 50 - 10000 s, of MGP oxidation in CSTR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction step</th>
<th>Pt/Gr (disp. 43 %)</th>
<th>Correlation matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ [m$^3$ mol$^{-1}$s$^{-1}$]</td>
<td>oxygen adsorption</td>
<td>$9.11 \pm 0.94 \times 10^{-1}$</td>
<td>1 0.1 0.1 0.2 -0.4 -0.1</td>
</tr>
<tr>
<td>$K_2$ [m$^3$ mol$^{-1}$]</td>
<td>alcohol adsorption</td>
<td>$8.50 \pm 1.00 \times 10^{-3}$</td>
<td>0.1 1 0.5 -0.7 -0.01 0.1</td>
</tr>
<tr>
<td>$K_{10}$ [m$^3$ mol$^{-1}$]</td>
<td>acid adsorption</td>
<td>$1.29 \pm 0.16 \times 10^{-1}$</td>
<td>0.1 0.5 1 0.03 -0.1 0.03</td>
</tr>
<tr>
<td>$(k_3 k_7)^{1/2}$ [s$^{-1}$]</td>
<td>alcohol oxidation</td>
<td>$1.64 \pm 0.06 \times 10^{-1}$</td>
<td>0.2 -0.7 0.03 1 0.2 0.01</td>
</tr>
<tr>
<td>$(k_8)$ [s$^{-1}$]</td>
<td>oxide formation</td>
<td>$1.15 \pm 0.08 \times 10^{-3}$</td>
<td>-0.4 -0.01 -0.1 0.2 1 0.7</td>
</tr>
<tr>
<td>$(k_3 k_{11})^{1/2}$ [s$^{-1}$]</td>
<td>oxide reduction</td>
<td>$5.61 \pm 3.54 \times 10^{-5}$</td>
<td>-0.1 0.1 0.03 0.01 0.7 1</td>
</tr>
</tbody>
</table>

The model predictions are obtained using gas-to-liquid mass transport Equations 5.57 and 5.58 and kinetic Equations 5.54, 5.55, and 5.56. For the parameter estimation the kinetic equations are simplified.
It is assumed that during alcohol oxidative dehydrogenation in the presence of oxygen, the catalyst potential is mainly determined by the oxygen reduction ($R_{\text{oxid1}}$) and alcohol dehydrogenation ($R_{\text{red1}}$) reactions, i.e. in Equation 5.51, $R_{\text{oxid1}} \gg R_{\text{oxid2}}$. However, with respect to catalyst reactivation by oxide removal, the catalyst potential is determined by oxide reduction ($R_{\text{oxid2}}$) and alcohol dehydrogenation ($R_{\text{red1}}$), since oxygen is removed and $\Theta_o$ quickly becomes very low. This means in Equation 5.51, $R_{\text{oxid2}} \gg R_{\text{oxid1}}$. The estimated kinetic parameters along with their confidence intervals are presented in Table 5.5. The kinetic parameters are obtained within the confidence interval of the initial kinetic parameters of Table 5.4. The correlation matrix is also presented in Table 5.5. The mutual correlation between the same parameters as discussed in the previous section is low and maximum correlation amounts to only 0.73. Figures 5.2a and 5.2b show the effect of MGP concentration and oxygen partial pressure on the rate of oxidation and catalyst deactivation, respectively. It can be seen that the model with the estimated kinetic parameters well describes the observed experimental data.

**Modelling catalyst reactivation**

Vleeming et al. showed that the catalyst activity can be recovered by reducing the catalyst in-situ, through shutting off the oxygen supply, for about 1000 s [28]. However, due to insufficient information on experimentally observed reactivation times, an insignificant oxide reduction parameter ($k_3k_{11}$)$^{\frac{1}{2}}$ is obtained, as presented in Table 5.5. In order to model the experimentally observed catalyst reactivation times, the parameter estimation is repeated but this time the individual oxide reduction parameter, $k_{11}$, is used. The value of this parameter is selected from previous work [48] and kept fixed ($k_{11} = 1.50 \times 10^3 \text{ s}^{-1}$),
Table 5.6: Kinetic parameters with their individual 95% confidence intervals for the catalyst reactivation of MGP oxidation in CSTR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction step</th>
<th>Pt/Gr (dispersion 43%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_3$ [s$^{-1}$]</td>
<td>alcohol dehydrogenation</td>
<td>$(5.28 \pm 3.02) \times 10^{-9}$</td>
</tr>
<tr>
<td>$k_7$ [s$^{-1}$]</td>
<td>oxygen reduction</td>
<td>$(5.10 \pm 2.96) \times 10^6$</td>
</tr>
<tr>
<td>$k_8$ [s$^{-1}$]</td>
<td>oxide formation</td>
<td>$(1.13 \pm 0.08) \times 10^{-3}$</td>
</tr>
<tr>
<td>$k_{11}$ [s$^{-1}$]</td>
<td>oxide reduction</td>
<td>$1.5 \times 10^3$</td>
</tr>
</tbody>
</table>

while the rest of the parameters are re-estimated. It is found that the adsorption parameters, $k_1$, $K_2$, and $K_{10}$ remain unchanged. However, new estimates for $k_3$, $k_8$, and $k_7$ are obtained, as presented in Table 5.6. It is to be noted that during regression the lumped parameter $(k_3k_7)^{1/2}$ remains the same. The results of the model simulations for catalyst deactivation and subsequent reactivation, which is known as redox cycle, are shown in Figures 5.3a and 5.3b. The details of the model simulation procedure for the redox cycle can be found elsewhere [32]. The oxide reduction parameter ($k_{11}$) can be safely used within the range of $(1.5 - 2.2) \times 10^3$ s$^{-1}$ with corresponding reactivation times of 1349-1574 s, which is close to the experimentally observed reactivation time of 1000 s [28].

### 5.5.2 pH dependent kinetic parameters

For the estimation of the pH dependent parameters, a set of six experiments performed in a semi-batch reactor with two different catalysts, Pt on carbon (42% dispersion) and Pt on graphite (15% dispersion), are used. Each experiment contains 10 acid formation rate data obtained at

Figure 5.3: Simulated (a) specific rate of consumption of MGP and (b) oxide coverage, to illustrate catalyst deactivation and reactivation by removing oxygen, on MGP oxidation rates. Data used: $P_{O_2} = 40$ kPa, $L_t = 0.073$ mol/kg$_{cat}$, $C_{MGP} = 90$ mol/m$^3$, $C_{MG} = 10$ mol/m$^3$, and $P_{O_2} = 0$ after 7200 s.
different pH conditions. The catalyst properties and experimental conditions are presented in Tables 5.2 and 5.3, respectively. Furthermore the complete kinetic model presented in Table 5.1 is used. To avoid over-parameterisation, and depending on the type of catalyst used, the kinetic parameters, estimated and discussed in the previous section, are kept fixed or adjustable, as shown in Table 5.7. For example, in case of the carbon supported Pt catalyst, the adsorption parameters of the organic reactants ($K_2$ and $K_{2a}$) are kept adjustable, while the acid product adsorption parameter ($K_{10}$) is kept fixed. It is found that as a result of stronger adsorption for organic reactants, the carbon supported catalyst gives a higher initial rate of reaction as compared to the graphite supported catalyst [48]. In case of the graphite supported Pt catalyst, the adsorption parameters are kept fixed while the oxygen reduction parameter is kept adjustable due to the lower dispersion, i.e. larger Pt crystallites compared to the carbon supported Pt catalyst. Throughout, it is considered that the aldehyde adsorption parameter is of the same magnitude as the alcohol adsorption parameter. This is acceptable because aldehyde and alcohol have nearly equal molar mass and they are considered to be adsorbed in a similar manner.

The complete kinetic model combined with mass transport equations is implemented in a laboratory scale semi-batch reactor model for the estimation of the kinetic parameters. The residual sum of squares that is minimised using the Levenberg-Marquardt algorithm is:

$$resid_{semi\text{-}batch} = \Sigma (R_{RCOOH, t(model)} - R_{RCOOH, t(exp)})^2$$  \hspace{1cm} (5.64)

The estimates of the kinetic parameters along with their confidence intervals are presented in Table 5.7. The estimated mutual correlation between the parameters is found to be low and the maximum correlation obtained corresponds to only 0.74. Examples of fitting results of the complete model are discussed and compared with experimental data in sections 5.5.3 and 5.5.4. It can be seen from Table 5.7 that for the Pt on carbon catalyst, nearly five to seven times higher adsorption parameters ($K_2$ and $K_{2a}$) of the organic reactants are estimated compared to the graphite supported Pt catalyst. In addition to this, the overall ($k_5 + k_6 COH$) aldehyde disappearance rate parameter is estimated to be two orders of magnitude higher than the overall ($k_3 + k_4 COH$) alcohol dehydrogenation rate parameter, at pH $> 7$. This has been experimentally also shown by Schuurman et al. [8].

For the graphite supported Pt catalyst (15 % dispersion), which has a lower dispersion compared to the carbon supported Pt catalyst (42 % dispersion), a nearly ten times higher oxygen reduction parameter ($k_7$) is obtained. This can be a consequence of the decrease in the oxygen adsorption enthalpy [50], or the increase in the electrochemical reduction rate of oxygen at platinum electrodes [51, 52], due to larger metal crystallites.
5.5. Kinetic parameter estimation

Table 5.7: Kinetic parameter estimates with their individual 95 % confidence intervals by regression of experimental data obtained at pH = 6-10 and T = 323 K, for MGP oxidation in semi-batch reactor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction step</th>
<th>Pt/C (disp. 42 %)</th>
<th>Pt/Gr (disp. 15 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ [m$^3$ mol$^{-1}$s$^{-1}$]</td>
<td>oxygen adsorption</td>
<td>$9.10 \times 10^{-1}$ (fixed)</td>
<td>$9.10 \times 10^{-1}$ (fixed)</td>
</tr>
<tr>
<td>$K_2$ [m$^3$ mol$^{-1}$]</td>
<td>alcohol adsorption</td>
<td>$(5.8 \pm 2.3) \times 10^{-2}$ (fixed)</td>
<td>$8.50 \times 10^{-3}$ (fixed)</td>
</tr>
<tr>
<td>$K_{2a}$ [m$^3$ mol$^{-1}$]</td>
<td>aldehyde adsorption</td>
<td>$(5.8 \pm 2.3) \times 10^{-2}$ (fixed)</td>
<td>$8.50 \times 10^{-3}$ (fixed)</td>
</tr>
<tr>
<td>$K_{10}$ [m$^3$ mol$^{-1}$]</td>
<td>acid adsorption</td>
<td>$1.29 \times 10^{-1}$ (fixed)</td>
<td>$1.29 \times 10^{-1}$ (fixed)</td>
</tr>
<tr>
<td>$k_3$ [s$^{-1}$]</td>
<td>alcohol dehydrogenation</td>
<td>$5.28 \times 10^{-9}$ (fixed)</td>
<td>$5.28 \times 10^{-9}$ (fixed)</td>
</tr>
<tr>
<td>$k_4$ [m$^3$ mol$^{-1}$s$^{-1}$]</td>
<td>alcohol dehydro. (pH)</td>
<td>$(3.4 \pm 0.62) \times 10^{-4}$ (fixed)</td>
<td>$(5.8 \pm 4.7) \times 10^{-4}$ (fixed)</td>
</tr>
<tr>
<td>$k_5$ [s$^{-1}$]</td>
<td>aldehyde oxidation</td>
<td>$(4.9 \pm 1.72) \times 10^{-7}$ (fixed)</td>
<td>$(6.4 \pm 6.9) \times 10^{-8}$ (fixed)</td>
</tr>
<tr>
<td>$k_6$ [m$^3$ mol$^{-1}$s$^{-1}$]</td>
<td>aldehyde oxidation (pH)</td>
<td>$1.60 \pm 1.18$ (fixed)</td>
<td>$3.68 \pm 5.08$ (fixed)</td>
</tr>
<tr>
<td>$k_7$ [s$^{-1}$]</td>
<td>oxygen reduction</td>
<td>$5.10 \times 10^{6}$ (fixed)</td>
<td>$(4.57 \pm 1.28) \times 10^{7}$ (fixed)</td>
</tr>
<tr>
<td>$k_8$ [s$^{-1}$]</td>
<td>oxide formation</td>
<td>$1.13 \times 10^{-3}$ (fixed)</td>
<td>$1.13 \times 10^{-3}$ (fixed)</td>
</tr>
<tr>
<td>$k_9$ [m$^3$ mol$^{-1}$]</td>
<td>oxide formation (pH)</td>
<td>$(9.4 \pm 3.44) \times 10^{-7}$ (fixed)</td>
<td>$(6.0 \pm 6.06) \times 10^{-7}$ (fixed)</td>
</tr>
<tr>
<td>$k_1$ [s$^{-1}$]</td>
<td>oxide reduction</td>
<td>$1.50 \times 10^{3}$ (fixed)</td>
<td>$1.50 \times 10^{3}$ (fixed)</td>
</tr>
</tbody>
</table>

5.5.3 MGP oxidation with Pt on carbon catalyst

Figure 5.4a shows the acid formation rate as a function of time for the egg shell type of Pt on carbon catalyst at different pH conditions. The rate of acid formation increases with increase in pH. It can also be seen that with increase in pH the rate of catalyst deactivation increases. To understand the observed catalyst deactivation, the catalyst potential against time is presented in Figure 5.4b. The catalyst potential increases with increase in pH. It can be seen that starting from a reduced catalyst (0.1 V potential) surface, the catalyst potential instantly increases to 0.83 V for pH = 6, and 0.93 V for pH = 8 and 10, as soon as the oxygen reaches to the catalyst surface and stabilizes to higher level, around 0.87 V for pH = 6, 0.97 V for pH = 8, and 0.99 V for pH = 10. This indicates that the catalyst deactivates very fast, i.e. due to a high oxide coverage, with increase in pH. Figure 5.4a shows that the developed model, with the rate constants as given in Table 5.7, is well able to describe the observed reaction rates at different pH conditions.
The increase of the reaction rate with increase in pH, is followed by strong catalyst deactivation caused by over-oxidation. The deactivation due to over-oxidation can be seen also through the simulated oxide coverage against time, in Figure 5.4c. After 5000 s, at pH = 6, approximately 70 % (\(\Theta_{\text{ox}} = 0.7\)), whereas at pH = 10, approximately 80 % (\(\Theta_{\text{ox}} = 0.8\)) of the catalyst surface is covered with inactive platinum oxide. This means with increase in pH from 6 to 10, the rate of catalyst deactivation due to over-oxidation increases approximately by 10 %, as indicated by the oxide coverage.

Figure 5.4d shows the simulated intermediate aldehyde concentration against time. The aldehyde concentration decreases with increase in pH of the reaction medium. Under the present conditions the maximum aldehyde concentration obtained is around 1 \(\text{mol/m}^3\) at pH = 6, and it decreases to approximately 0.02 \(\text{mol/m}^3\) at pH = 10. Figure 5.4e shows the simulated oxygen coverage with time. It can be seen that the initial oxygen coverage decreases with increase in pH and a maximum coverage of around 0.6 is observed at pH = 6.

Figure 5.4f shows the simulated concentration of the reactant alcohol, MGP, as a function of time. It can be seen that at lower pH the calculated conversion, from MGP concentration data, is around 25 % over 5000 s period of the reaction. Within this conversion, it can be accepted that the MGP oxidation has close to 100 % selectivity, while at the higher pH = 10, the conversion is 40 %, at which the experimentally observed selectivity is close to 90%. It was verified that carbon balance does not deviate significantly from 100 % and the alkali consumption is completely accounted for by the total amount of carboxylic anions analysed [11]. Considering these facts and the model performance, it can be said that the developed model accurately describes the observed pH effect on MGP oxidation.

It is to be noted that Schuurman et al. also found that the rate of MGP oxidation increases linearly with increase in pH above 8.5, while at low pH, between pH 6 and 8, no difference in the oxidation rates was observed [8]. This latter observation is also verified through model simulation showing that at pH 6 and 8, there is no difference in the MGP oxidation rates, which can be seen from MGP conversion, Figure 5.4f. However, it is noted that the acid formation rate presented in Figure 5.4a is a measure of the aldehyde disappearance rate and hence shows slight differences in the initial rates at pH 6 and 8. This effect can also be seen from the change in the aldehyde concentrations, presented in Figure 5.4d. The rate of aldehyde disappearance increases with increase in pH. A similar observation has been shown in literature [11, 53]. The observed catalyst deactivation with increase in pH is a well known phenomenon in electrochemistry, referred to as corrosion [41, 44]. This suggests that the oxygen species responsible for the high oxide coverage at pH = 10, originate from hydroxyl species.
5.5. Kinetic parameter estimation

Figure 5.4: Effect of pH on: (a) the acid formation rate; (b) the electrochemical catalyst potential; (c) the platinum oxide coverage; (d) the aldehyde concentration; (e) the oxygen coverage; (f) the MGP concentration, during Pt/Carbon catalysed MGP oxidation. Symbols represent experimental data, i.e. circles pH = 6, triangles pH = 8, and squares pH = 10. Lines represent modelling results, i.e. dashed-dotted line pH = 6, continuous line pH = 8, and dashed line pH = 10. Data used: $P_{O_2} = 40\, kPa$, $L_t = 0.0385\, mol/kg_{cat}$, and $C_{MGP, ini} = 100\, mol/m^3$. 
5.5.4 MGP oxidation with Pt on graphite catalyst

Figure 5.5a shows the acid formation rate as a function of time for the egg shell type of Pt on graphite catalyst at different pH. It can be seen from the experimental results that the initial rate of reaction increases with increase in pH, similar to the carbon supported catalyst. However, the reaction rates are nearly two times lower compared to the carbon supported Pt catalyst. Figure 5.5b shows the measured catalyst potentials as a function of time. It can be seen that for the graphite supported catalyst, with increase in pH, the potential increases along with the increase in the reaction rate, but also the rate of catalyst deactivation due to over-oxidation increases.

It can be seen that starting from a reduced catalyst (0.1 V potential) surface, the catalyst potential instantly increases to 0.8 V for pH = 6, and 0.9 V for pH = 8 and 9, as soon as the oxygen reaches to the catalyst surface and stabilizes to a higher level, around 0.91 V for pH = 6, and around 0.94 V for pH = 8 and pH = 9. This increase in potential coincides with the catalyst deactivation due to over-oxidation. The lower initial catalyst potential compared to the carbon supported catalyst, indicates the lower initial acid formation rate. However, the magnitude of the measured potentials for the oxidised state appears to be lower, but in view of the limitation of the measurement technique, this is not considered as significant [54].

Figure 5.5a shows that the developed model, with the rate constants as given in Table 5.7, is well able to describe the observed reaction rates at different pH conditions. The increase of the reaction rate with increase in pH is followed by 80 % decrease for pH = 9, during a reaction period of 5000 s, due to strong catalyst deactivation caused by over-oxidation. The calculated potentials presented in Figure 5.5b, show the right magnitude for the increase of the reaction rate with increase in potential from the reduced state followed by catalyst deactivation with increase in pH corresponding to an oxidized potential level of approximately 1 V. The catalyst deactivation due to over-oxidation can be seen through the simulated oxide coverage against time in Figure 5.5c. After 5000 s, at pH = 6, approximately 60 % (Θ_{ox} = 0.62), whereas at pH = 9, approximately 80 % (Θ_{ox} = 0.72) of the catalyst surface is covered with inactive platinum oxide. This means with increase in pH from 6 to 9, the rate of deactivation due to over-oxidation increases by 20 %, higher than the carbon supported catalyst.
Figure 5.5: Effect of pH on: (a) the acid formation rate; (b) the intermediate aldehyde concentration; (c) the platinum oxide coverage; (d) the electrochemical catalyst potential; (e) the oxygen coverage; (f) the reactant MGP concentration, during Pt/Graphite catalysed MGP oxidation. Symbols represent experimental data, i.e. circles for pH = 6, triangles for pH = 8, and squares for pH = 9, whereas lines represent modelling results, i.e. dashed-dotted line for pH = 6, continuous line for pH = 8, and dashed line for pH = 9. Data used: $P_{o_2} = 40$ kPa, $L_t = 0.1077$ mol/kg$_{cat}$, and $C_{MGP, ini} = 100$ mol/m$^3$. 
Figure 5.5d shows the simulated concentration of the intermediate aldehyde, methyl α-D-aldehydoglucopyranoside, against time. It can be seen that the selectivity to the aldehyde decreases with increase in pH, as observed for the carbon supported catalyst. However, the maximum concentration of aldehyde (4.5 mol/m$^3$) is observed to be almost 4.5 times higher than for the carbon supported catalyst, at pH 6. This can be seen through the lower apparent aldehyde disappearance parameter ($k_5 + k_6C_{OH}$) for graphite supported catalyst compared to the carbon supported catalyst, at pH 6. The possible explanation for this can be, although intrinsic conditions are considered for organic compounds, that the rate of the intermediate aldehyde disappearance is relatively high and hence pore diffusion limitations might be present for the aldehyde transfer. Especially, in case of the carbon supported catalyst, which has higher active metal dispersion compared to the graphite supported catalyst.

Figure 5.5e shows the simulated oxygen coverage with time. It can be seen that the initial oxygen coverage decreases with increase in pH and a maximum coverage of around 0.4 is observed at pH = 6, compared to the coverage of 0.6 for the platinum on carbon catalyst. This is the result of a higher oxygen reduction rate for the graphite supported catalyst. Figure 5.5f shows the simulated concentration of the reactant alcohol, MGP, as a function of time. It can be seen that the calculated conversion, from MGP concentration data, is around 18-20 % over 5000 s of the reaction time. Within this conversion level, it can be accepted that the MGP oxidation has close to 100 % selectivity.

5.6 Conclusions

In the present work, a dynamic electrochemical kinetic model has been developed, which describes the observed pH effect and catalyst deactivation due to over-oxidation. The rate determining steps and the model parameters have been deduced from previous reaction rate measurements in a CSTR, with graphite supported Pt catalyst [28], and from stirred slurry semi-batch reaction rate data, with carbon and graphite supported Pt catalyst (this work). The effect of pH is incorporated by considering parallel reaction steps depending on the acidity or the alkalinity of the medium. Hydroxyl ions are mainly responsible for strong deactivation of the catalyst in alkaline medium, whereas in neutral or acidic medium the deactivation is due to strong adsorption of oxygen atoms only. In both cases, the formation of inactive platinum oxide is responsible for the catalyst deactivation. Both types of catalyst shows the same degree of vulnerability to deactivation due to over-oxidation. However, the carbon supported Pt catalyst gives higher initial reaction rates compared to the graphite supported catalyst. The modelling results confirm that the intermediate aldehyde is present at low pH and the selectivity towards the aldehyde decreases with increase in pH. The graphite supported Pt catalyst gives an almost four times higher intermediate aldehyde concentration compared to the carbon supported catalyst. How-
ever, pore diffusion limitation can result in too low estimates for the rate parameters of a highly reactive intermediate. The observed catalyst potential gives useful information on the oxidation state of the catalyst. The developed model can describe well the observed catalyst potential at different pH.
Bibliography


Chapter 6

Reaction start-up & catalyst deactivation and reactivation

This chapter is submitted for publication as:

Abstract

The influence of the reaction start-up procedure on the oxidation of a polyol, methyl α-D-glucopyranoside, is investigated. Results are obtained using semi-batch experiments in a stirred slurry reactor with a Pt on carbon catalyst and molecular oxygen as oxidant. Three types of reaction start-up procedures are applied with respect to the pretreatment of the catalyst slurry, viz. reduced, oxidised, and inert. The experimental results are described by a recently developed dynamic, pH dependent, electrochemical kinetic model.

The reduced start-up results in the highest initial catalyst activity, compared to the other start-up procedures. It is found that the catalyst needs pretreatment before starting the reaction, as the inert start-up results in no catalytic activity at all. Additionally, independent of the start-up procedure, under oxygen rich conditions, for a weak reducing compound, over-oxidation is found to be the main cause of catalyst deactivation. The rate of over-oxidation is lower in the absence of the dehydrogenation reaction, which is modelled by considering that over-oxidation (Pt corrosion) needs free sites in order to take place. The mechanism of catalyst deactivation is experimentally verified through intermediate catalyst reactivation. The model adequately describes this reactivation step.
6.1 Introduction

There is an increasing trend for heterogeneously catalysed liquid phase oxidations, towards replacement of stoichiometric quantities of inorganic oxidants [1]. The stoichiometric oxidation process suffers from a low atom efficiency and high toxic waste production [2]. Noble metal catalysed oxidations with molecular oxygen are an attractive alternative, as the oxidant is converted to water and the oxidations are in general more selective [3–5]. It is generally accepted that alcohol oxidation on noble metal catalysts takes place via a dehydrogenation mechanism followed by the oxidation of the adsorbed hydrogen atoms with dissociatively adsorbed oxygen [6–8].

Depending on the rate of transfer of molecular oxygen to the catalyst surface, two operating regimes can be distinguished: the so-called mass transport limited regime and the intrinsic kinetic regime. In the intrinsic kinetic regime, the reaction is independent of transport and diffusion limitations (gas-to-liquid transport, liquid-to-solid transport, and pore diffusion) and the reaction rate is only determined by chemical kinetics. In the oxygen mass transport limited regime, which takes place usually at low oxygen concentrations, diffusion and transport limitations play a role [9]. Both regimes have an influence on the catalyst behavior and especially on the catalyst deactivation, which is one of the major obstacles for large-scale operation of this process [10].

In the oxygen mass transport limited regime, the catalyst surface is reduced, i.e. shows a low electrochemical potential (0.2 - 0.7 V vs reversible hydrogen electrode (RHE)), and the catalyst may deactivate by adsorption of carbonaceous deposits and CO [11, 12]. This phenomenon is more pronounced when the catalyst is prereduced by the organic reactant [13, 14]. In the intrinsic kinetic regime, the catalyst surface is oxidised, i.e. high catalyst potential (∼ 1 V vs RHE), and the catalyst deactivates due to over-oxidation [15–17]. Depending on the type of reaction and conditions applied, other type of catalyst deactivation mechanisms may exist, such as aldol condensation (polymerisation or coking), crystalline growth (Ostwald ripening), and metal dissolution (leaching) [10, 18].

At an early stage, Dirkx et al. [19, 20] have clearly demonstrated the importance of the start-up procedure on the catalyst activity. It was found that for gluconic acid (weak reducing agent) oxidation on a Pt catalyst in a semi-batch reactor, starting with a reduced catalyst resulted in a 14 times higher activity than while starting with an oxidised catalyst. However, for glucose (strong reducing agent) oxidation on Pt catalyst, the catalyst activity difference between the two procedures amounted to a factor of 1.4 only. Furthermore, Dijkgraaf et al. [16, 21] presented an elementary model, for a catalyst deactivation and regeneration process, considering the Pt catalysed oxidation of sodium-D-gluconate (weak reducing agent).
It is clear that the reaction start-up procedure has a significant influence on the catalytic activity, especially for weakly reducing compounds. However, research so far lacks a detailed quantitative analysis. The goal of this study is to demonstrate with the help of experiments and a recently developed kinetic model, that over-oxidation is the main cause of catalyst deactivation, under oxygen rich conditions. Results are obtained in a three phase stirred slurry semi-batch reactor using Pt catalysed oxidation of methyl α-D-glucopyranoside, a weakly reducing compound, as a test reaction. Experiments are performed at a constant pH of 8 and a sufficiently high oxygen partial pressure of 40 kPa. A detailed semi-batch reactor model is used to describe and validate the observed catalytic reaction rates. Long term catalyst deactivation by coking, attrition, crystalline growth, or leaching is not subject of this study. These types of deactivations are negligible at the chosen experimental conditions.

6.2 Modelling

6.2.1 Kinetic model

In this chapter, our recently developed dynamic electrochemical kinetic model is used, which is applicable at different pH conditions. The reaction mechanism with the reaction rate equations are presented in Table 6.1 [22]. Based upon the non-steady state site balances and the rate equations given in Table 6.1, the rates of change of oxygen coverage and oxide coverage (measure of the catalyst deactivation due to overoxidation), are determined by the following differential equations:

\[
\frac{d\Theta_o}{dt} = 2k_1C_{o2}\Theta^2 - k_7\Theta_o\exp\left(-\frac{EF}{RT}\right) - k_8\Theta_o(1 - \Theta_{ox}) \quad (6.1)
\]

\[
\frac{d\Theta_{ox}}{dt} = k_8\Theta_o(1 - \Theta_{ox}) + k_9C_{OH}\Theta_\ast\exp\left(\frac{EF}{RT}\right) - k_{11}\Theta_{ox}\Theta_\ast\exp\left(-\frac{EF}{RT}\right) \quad (6.2)
\]

where \(\Theta_o\) is the oxygen surface coverage, \(\Theta_{ox}\) is the oxide surface coverage, \(\Theta_\ast\) is the free site surface coverage, \(k_i\) are the reaction rate parameters defined in Table 6.2, \(C_{o2}\) [\(mol\ m^{-3}\)] is the oxygen concentration at the catalyst surface, \(E\) [V] is the electrochemical catalyst potential, \(F\) [\(C\ mol^{-1}\)] is Faraday’s constant, \(R\) [\(J\ mol^{-1}\ K^{-1}\)] is the ideal gas constant, \(T\) [K] is the reaction temperature, and \(t\) [s] is time.

The catalyst potential is determined by balancing the rate of electrons produced (\(R_3 + R_4 + R_5 + R_6 + R_9\)) per volume of the catalyst and the rate of electrons consumed (\(R_7 + R_{11}\)) per volume of the catalyst as:

\[
E(t) = \frac{RT}{2F} \ln\left(\frac{R_{oxid1} + R_{oxid2}}{R_{red1} + R_{red2} + R_{red3} + R_{red4} + R_{red5}}\right) \quad (6.3)
\]
where,

\[
R_{\text{oxid}1} = k_7 L_t \rho_p \Theta_o 
\]

(6.4)

\[
R_{\text{oxid}2} = k_{11} L_t \rho_p \Theta_o \Theta^* 
\]

(6.5)

\[
R_{\text{red}1} = k_3 L_t \rho_p \Theta_{RCH_2OH} \Theta^* 
\]

(6.6)

\[
R_{\text{red}2} = k_4 L_t \rho_p C_{\text{OH}} \Theta_{RCH_2OH} \Theta^* 
\]

(6.7)

\[
R_{\text{red}3} = k_5 L_t \rho_p \Theta_{RCHO} \Theta^* 
\]

(6.8)

\[
R_{\text{red}4} = k_6 L_t \rho_p C_{\text{OH}} \Theta_{RCHO} \Theta^* 
\]

(6.9)

\[
R_{\text{red}5} = k_9 L_t \rho_p C_{\text{OH}} \Theta^* 
\]

(6.10)

\(k_i\) are the reaction rate parameters defined in Table 6.2, \(L_t\) is the specific number of platinum surface atoms, i.e. \(\text{mol Pt}_\text{s}/\text{kg catalyst}\), based on the assumption that one Pt surface atom equals one catalytic site, \(\rho_p\) [\(\text{kg/m}^3\)] is the catalyst particle density, \(\Theta_{RCH_2OH}\) [-] is the reactant alcohol surface coverage, \(\Theta_{RCHO}\) [-] is the intermediate aldehyde surface coverage, and \(C_{\text{OH}}\) [\(\text{mol/m}^3\)] is the hydroxyl concentration. It should be noted that two important phenomena limit the range of the catalyst potential. Firstly, below a potential of 0.4 V RHE, hydrogen gas evolves, due to water reduction, and CO formation is possible. Secondly, above a potential of 1.5 V RHE, oxygen gas evolves, due to water oxidation. Since these reactions are not taken into account in the kinetic model presented in Table 6.1, Equation 6.3 can only be applied, if:

\[
0.4\text{VRHE} < E < 1.5\text{VRHE} 
\]

(6.11)

### 6.2.2 Semi-batch reactor model

In practice, the oxidation reaction is generally carried out with the aqueous alcohol reactant in a batch mode and the gaseous oxidant, molecular oxygen, in a continuous mode. For the reaction to take place, oxygen has to be transferred from the gas phase to the liquid phase, through the liquid to the catalyst particle, and finally has to diffuse through the pores to the catalytic site inside the particle. For this work, it was verified that liquid-to-solid mass transport limitation and intra-particle diffusion limitation are not present and hence were not taken into account [23]. The transient material balance equations for oxygen in the gas phase and in the liquid phase are as follows:

\[
\frac{V_G}{RT} \frac{dP}{dt} = F_{V,G} \frac{P^\text{in}}{RT} - k_{GL} a_{GL} V_L (HP - C_L) \quad \text{Gas phase (G)} 
\]

(6.12)

\[
\frac{V_L}{dt} = k_{GL} a_{GL} V_L (HP - C_L) - V_L R_{V,o2} \quad \text{Liquid phase (L)} 
\]

(6.13)
Table 6.1: Reaction steps and rate equations for the alcohol oxidation mechanism (Gangwal et al. [22]).

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Rate equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2 + 2* \rightarrow 2O*$</td>
<td>$R_1 = k_1 C_{o2} \Theta_s^2$ (I)</td>
</tr>
<tr>
<td>$RCH_2OH + <em>_p \rightleftharpoons RCH_2OH</em>_{p}$</td>
<td>$\Theta_{RCH_2OH} = K_2 C_{RCH_2OH} \Theta_s$</td>
</tr>
<tr>
<td>$RCH_2OH<em>_{p} \rightleftharpoons RCHO</em>_{p}$</td>
<td>$\Theta_{RCHO} = K_2 C_{RCHO} \Theta_s$</td>
</tr>
<tr>
<td>$RCH_2OH<em>_{p} + * + RCHO</em>_{p} + 2H^+ + 2e^- + *$</td>
<td>$R_3 = k_3 \Theta_{RCH_2OH} \Theta_s \exp \left( \frac{EF}{RT} \right)$</td>
</tr>
<tr>
<td>$RCH_2OH<em>_{p} + * + OH^- \rightarrow RCHO</em>_{p} + H_2O + H^+ + 2e^- + *$</td>
<td>$R_4 = k_4 \Theta_{RCH_2OH} \Theta_s C_{OH} \exp \left( \frac{EF}{RT} \right)$</td>
</tr>
<tr>
<td>$RCHO<em>_{p} + * + H_2O \rightarrow RCOOH</em>_{p} + 2H^+ + 2e^- + *$</td>
<td>$R_5 = k_5 \Theta_{RCHO} \Theta_s \exp \left( \frac{EF}{RT} \right)$ (V)</td>
</tr>
<tr>
<td>$O* + H_2O + 2e^- \rightarrow 2OH^- + *$</td>
<td>$R_7 = k_7 \Theta_o \exp \left( -\frac{EF}{RT} \right)$ (VII)</td>
</tr>
<tr>
<td>$O* + <em>_s \rightarrow O</em>_{s} + *$</td>
<td>$R_8 = k_8 \Theta_o (1 - \Theta_{ox})$ (VIII)</td>
</tr>
<tr>
<td>$O* + * + O*_{s} + *$</td>
<td>$R_{8a} = k_{8a} \Theta_o \Theta_s$ (VIIIa)</td>
</tr>
<tr>
<td>$OH^- + * + O*_{s} + H^+ + 2e^-$</td>
<td>$R_9 = k_9 C_{OH} \Theta_s \exp \left( \frac{EF}{RT} \right)$ (IX)</td>
</tr>
<tr>
<td>$RCOOH + <em>_{p} \rightleftharpoons RCOOH</em>_{p}$</td>
<td>$\Theta_{RCOOH} = K_{10} C_{RCOOH} \Theta_s^*$</td>
</tr>
<tr>
<td>$O*<em>{s} + H_2O + 2e^- + * \rightarrow 2OH^- + * + *</em>{s}$</td>
<td>$R_{11} = k_{11} \Theta_{ox} \Theta_s \exp \left( -\frac{EF}{RT} \right)$ (XI)</td>
</tr>
<tr>
<td>$O*<em>{s} + H_2O + 2e^- + * \rightarrow 2OH^- + * + *</em>{s}$</td>
<td>$R_{11} = k_{11} \Theta_{ox} \Theta_s \exp \left( -\frac{EF}{RT} \right)$ (XI)</td>
</tr>
</tbody>
</table>
Table 6.2: Kinetic parameters for the reaction steps defined in Table 6.1 (Gangwal et al. [22]).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction step</th>
<th>Pt/C (dispersion 42%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1 ,[,m^3,mol^{-1} ,s^{-1}]$</td>
<td>oxygen adsorption</td>
<td>9.10 $\times$ 10$^{-1}$</td>
</tr>
<tr>
<td>$K_2 ,[,m^3,mol^{-1}]$</td>
<td>alcohol adsorption</td>
<td>5.78 $\times$ 10$^{-2}$</td>
</tr>
<tr>
<td>$K_{2a} ,[,m^3,mol^{-1}]$</td>
<td>aldehyde adsorption</td>
<td>5.78 $\times$ 10$^{-2}$</td>
</tr>
<tr>
<td>$K_{10} ,[,m^3,mol^{-1}]$</td>
<td>acid adsorption</td>
<td>1.29 $\times$ 10$^{-1}$</td>
</tr>
<tr>
<td>$k_3 ,[,s^{-1}]$</td>
<td>alcohol dehydrogenation</td>
<td>5.28 $\times$ 10$^{-9}$</td>
</tr>
<tr>
<td>$k_4 ,[,m^3,mol^{-1} ,s^{-1}]$</td>
<td>alcohol dehydrogenation (pH)</td>
<td>3.40 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>$k_5 ,[,s^{-1}]$</td>
<td>aldehyde dehydrogenation</td>
<td>4.88 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>$k_6 ,[,m^3,mol^{-1} ,s^{-1}]$</td>
<td>aldehyde dehydrogenation (pH)</td>
<td>1.60</td>
</tr>
<tr>
<td>$k_7 ,[,s^{-1}]$</td>
<td>oxygen reduction</td>
<td>5.10 $\times$ 10$^{6}$</td>
</tr>
<tr>
<td>$k_8 ,[,s^{-1}]$</td>
<td>oxide formation</td>
<td>1.13 $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>$k_{8a} ,[,s^{-1}]$</td>
<td>modified oxide formation</td>
<td>(2.63 $\pm$ 0.09) $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>$k_9 ,[,m^3,mols^{-1}]$</td>
<td>oxide formation (pH)</td>
<td>9.39 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>$k_{11} ,[,s^{-1}]$</td>
<td>oxide reduction</td>
<td>(1.50 $-$ 2.00) $\times$ 10$^{3}$</td>
</tr>
</tbody>
</table>

where $V_G \,[\,m^3]\,$ is the volume of gas in the reactor, $P \,[\,Pa]\,$ is the oxygen partial pressure in the reactor, $F_{V,G} \,[\,m^3 \,s^{-1}]\,$ is the total volumetric gas flow rate, $k_{GLaGL} \,[\,s^{-1}]\,$ is the volumetric gas-to-liquid mass transport coefficient, $H \,[\,mol \,m^{-3} \,Pa^{-1}]\,$ is the Henry coefficient, $C_L \,[\,mol \,m^{-3}]\,$ is the oxygen concentration in the liquid phase, $V_L \,[\,m^3]\,$ is the total liquid volume. $R_{V,o2} \,[\,mol \,m^{-3} \,s^{-1}]\,$ is the overall volumetric oxygen consumption rate:

$$R_{V,o2} = C_{cat}L_{t}k_1\Theta^2C_L$$  \hspace{1cm} (6.14)

where $C_{cat} \,[\,kg \,m^{-3}]\,$ is the catalyst concentration. The weight specific dehydrogenation rate of the reactant alcohol, $R_{RCH_2OH} \,[\,mol \,kg^{-1} \,s^{-1}]\,$ from Equations (III) and (IV) of Table 6.1, can be determined as:

$$R_{RCH_2OH} = L_{t}(k_3 + k_4COH)\Theta_{RCH_2OH}\Theta^*\exp\left(\frac{EF}{RT}\right)$$  \hspace{1cm} (6.15)

The liquid reactant alcohol is in a batch mode and continuously converting to the product as the reaction progresses, e.g., methyl glucoside (MGP) gives methyl glucuronic acid (MG) with methyl aldehydo-glucoside (MAGP) as an intermediate. The material balances for the liquid reactant and the products are described as follows. The rate of disappearance of the alcohol to the aldehyde is:

$$\frac{dC_{RCH_2OH}}{dt} = -C_{cat}R_{RCH_2OH}$$  \hspace{1cm} (6.16)

$$\frac{dC_{RCHO}}{dt} = C_{cat}(R_{RCH_2OH} - R_{RCHO})$$  \hspace{1cm} (6.17)
$R_{RCHO}$ is the weight specific aldehyde disappearance rate, which is determined from Equations (V) and (VI) of Table 6.1, as:

$$R_{RCHO} = L_t (k_5 + k_6 C_{OH}) \Theta_{RCHO} \Theta^* \exp \left( \frac{E_F}{RT} \right) \quad (6.18)$$

The rate of acid formation, which is experimentally measured through the rate of alkali (NaOH) addition, is calculated from the rate of disappearance of the aldehyde as:

$$\frac{dC_{RCOOH}}{dt} = C_{cat} R_{RCHO} \quad (6.19)$$

The reactor model equations are solved with Matlab software, using the catalyst properties and the experimental conditions as given in Tables 6.3 and 6.4. The differential equations, Equations 6.12, 6.13, 6.16, 6.17, and 6.19 are solved using the stiff ordinary differential equations solver routine (ode23s).

### 6.3 Experimental

#### 6.3.1 Conditions

In this chapter, experiments are performed in a stirred three-phase semi-batch reactor. The aqueous alcohol reactant is added in a batch mode. The gaseous oxidant (molecular oxygen) is supplied continuously by a mass flow controller. The oxygen partial pressure is set by the nitrogen flow, also supplied by a mass flow controller. The pH of the reaction medium is kept at a constant level (pH=8), by controlled addition of a known concentration of an alkali (NaOH). During the reaction, the alcohol reactant is converted to the acid product with time. The acid formation rate is measured through the rate of addition of the alkali. The oxygen concentration in the liquid phase is measured using an oxygen electrode. The open circuit electrochemical catalyst potential is measured with a smooth Pt wire as working electrode and Ag/AgCl, saturated KCl as a reference electrode. Experiments were performed at the set of reaction conditions as presented in Table 6.4, and further details of the experimental procedure are described in Chapter 3 (section 3.4.2). A commercial non-uniform (egg shell), 5 wt % Pt on carbon (Engelhard, code-43545) catalyst is used. The properties of the catalyst are presented in Table 6.4.

#### 6.3.2 Reaction start-up procedure

Three different reaction starting procedures are investigated, depending on the pretreatment of the catalyst:

1. **Reduced start-up**
   
   For the reduced start-up procedure, the catalyst slurry is pre-reduced in a hydrogen atmosphere for about 1800 s at 323 K. After flushing with nitrogen, the liquid reactant,
aqueous alcohol, is added to the slurry and the experiment is started by setting a specific partial pressure of oxygen in the gas inlet to the reactor.

2. Oxidised start-up
For the oxidised start-up procedure, the catalyst pretreatment is similar to the reduced start-up. However, before starting the reaction, the catalyst slurry is oxidised by exposing it to a 40 kPa partial pressure of gaseous oxygen, for a specific time of 1800 s. The reaction is then started in the oxidising medium, by adding a solution with a known concentration of the aqueous alcohol to the reactor.
3. Inert start-up

The term 'inert' means starting the reaction without any pretreatment of the catalyst. The catalyst slurry is brought to the reaction temperature in a nitrogen atmosphere. The liquid reactant, aqueous alcohol, is added to the aqueous catalyst slurry, at the reaction temperature, and the experiment is started by simultaneous addition of oxygen to the reactor.

6.4 Results and discussion

6.4.1 Reduced start-up

Figure 6.1a shows the experimentally observed acid formation rate as a function of time for the reduced start-up procedure. The initial acid formation rate obtained is 5.6 mmol/kgs. As the reaction progresses the reaction rate clearly drops. This drop is not only because of conversion of the liquid reactant but also because of strong catalyst deactivation. To visualise this catalyst deactivation phenomenon, the observed catalyst potential against time is presented in Figure 6.1c. Starting from a reduced catalyst (0.1 V potential) surface, the catalyst potential instantly increases to 0.9 V as soon as the oxygen reaches the catalyst surface, thereafter it slowly increases further and stabilises around 0.97 V. This further increase in the catalyst potential indicates that the catalyst deactivates due to over-oxidation [24, 25].

In literature, it has been argued that over-oxidation is the result of catalyst deactivation due to carbonaceous deposition and that over-oxidation is not the direct cause of catalyst deactivation [4]. The simplest way to verify the main cause of the deactivation is to restore the initial rate of reaction by interruption of the oxygen supply to the reactor or by stopping the gas-inducing stirrer for a few minutes [16], which facilitates the reduction of the catalyst by the alcohol reactant. Figure 6.1a shows that after 2500 s of reaction time, the oxygen supply to the reactor was stopped for about 1100 s, and then was started again. There is a temporary sharp increase in the reaction rate, from 1.75 mmol/kgs to 2.23 mmol/kgs, at the initial stage of the regeneration and then the reaction rate immediately drops. After resuming the oxygen supply, the rate of reaction restores to the level of the fresh active catalyst. The catalyst is regenerated by a simple in-situ reduction process, which shows that over-oxidation is the main cause of deactivation and not the deposition of carbonaceous compounds. However, the magnitude of the recovered reaction rate is not the same as at the beginning of the reaction, which is because of the drop in the reactant concentration (conversion 17 %). The temporary increase in the reaction rate, shortly after stopping the oxygen supply, may be an indication of consumption of the inactive oxide together with the negative order dependency on the oxygen concentration, which has been demonstrated in our previous modelling work [9]. The reduction of the catalyst can also be seen through the
drop in the measured electrochemical catalyst potential (Figure 6.1c), which reaches to 0.4 V. As soon as the oxygen flow is resumed, the catalyst potential follows its previous track, however it reaches to a higher level of 0.97 V, more quickly.

Figure 6.1a shows that the dynamic semi-batch reactor model, which considers over-oxidation as the main cause for catalyst deactivation, is well able to describe the observed reaction rates. The high initial catalytic activity followed by the strong catalyst deactivation accompanied with reactant conversion is accurately described by the model. In order to mimic the experimental data, after a simulation time of 2500 s, the gas phase oxygen partial pressure in the model was forced to zero for 1100 s and then switched back to its original value. The reactor model with the electrochemical kinetics clearly demonstrates that the catalyst activity is fully regenerated and over-oxidation is the main cause of the deactivation. In order to describe the temporary increase in the acid formation rate as observed in the experiment at the beginning of the re-activation period, diffusion limitation inside the catalyst particle has to be considered in the model [9]. Immediately, after setting the oxygen partial pressure to zero, the model shows a temporary increase in the reaction rate (Figure 6.1b). However, the magnitude of this increased rate is lower than observed in the experiment. This may be due to the fact that the model insuffi- ciently accounts for the oxygen storage capacity of the catalyst support and the platinum oxide.

The calculated potentials presented in Figure 6.1c, show the right magnitude for the increase of the reaction rate with increase in potential from the reduced state followed by catalyst deacti-vation with time, corresponding to an oxidised potential level of approximately 1 V. During the reduction period, the drop in the model predicted potential is slower, compared to the measured catalyst potential. However, after some time, the model shows a rapid drop in the potential to the level of 0.4 V. The discrepancy between the model and the experiments is because the mea-sured electrochemical catalyst potential is quite dynamic, as it is a mixed potential of colliding catalyst particles, the reaction mixture, and the smooth Pt wire, whereas in the model removal of oxide is a comparatively slow process. As soon as the oxygen pressure is switched back to its original value, the potential increases faster and stabilizes to a slightly higher level (1 V) than the original level (0.99 V), similar to the experimentally measured catalyst potential.
Figure 6.1: Effect of the reduced startup procedure: (a) acid formation rate; (b) enlarged view of the acid formation rate, at the beginning of the reactivation period; (c) electrochemical catalyst potential; (d) oxide coverage; (e) oxygen coverage; (f) MGP concentration. The oxygen supply stopped from 2500 s to 3600 s. Symbols represent experimental data and lines represent model results.
The degree of catalyst deactivation due to over-oxidation is presented as the simulated oxide coverage against time in Figure 6.1d. After 2500 s, approximately 60 % (Θ_{ox} = 0.58) of the catalyst surface is covered with inactive platinum oxide. During the reduction time, the drop in oxide coverage coincides with the catalyst potential. It can be seen from the figure that at 3200 s the oxide coverage reduces to zero, which means 700 s of reduction time is sufficient for regenerating the catalyst. That means using this model the reduction period can be optimised, which is essential in order to avoid carbonaceous deposits due to prolonged exposure of the reduced catalyst to the organic compounds [13, 14].

Figure 6.1e shows the simulated oxygen coverage with time. The initial oxygen coverage (approx. 0.5) decreases with time due to increase in oxide formation. During the reduction period the coverage drops fast to zero. As soon as the oxygen pressure is switched to its original value, the oxygen coverage at the catalyst surface increases and goes to a higher level due to lower alcohol coverage (conversion), and drops again due to over-oxidation. Figure 6.1f shows the simulated concentration of the reactant alcohol, MGP, as a function of time. It can be seen that the calculated conversion, from MGP concentration data, is around 26 % over 5000 s of the simulation time. Within this conversion level, it can be accepted that the MGP oxidation has close to 100 % selectivity [24].

6.4.2 Oxidised start-up

Figure 6.2a shows the experimentally observed acid formation rate as a function of time for the oxidised start-up procedure. The catalyst slurry, after reduction with hydrogen, is oxidised with a 40 kPa partial pressure of oxygen, for about 1800 s, in the absence of the alcohol reactant. The reaction is started by adding a known amount of alcohol reactant to the catalyst slurry, in the presence of oxygen. The initial acid formation rate obtained is 4.21 mmol/kgs, which is 1.3 times lower than the initial rate for the reduced start-up. As the reaction progresses the drop in the reaction rate can be clearly seen. This drop is not only because of conversion of the reactant but also because of strong catalyst deactivation. Again to visualise the catalyst deactivation, the observed catalyst potential against time is presented in Figure 6.2b. In the oxidising medium the catalyst has a potential of about 1.1 V, and as soon as the alcohol reactant is added to the catalyst slurry the potential drops to 0.9 V, while thereafter it slowly increases to 0.97 V and stabilises. This increase in the catalyst potential indicates that the catalyst has deactivated.

To verify the mechanism of deactivation, the regeneration procedure as described in the previous section is followed. Figure 6.2a shows that after 4000 s of run time, the oxygen supply to the reactor was stopped for about 800 s and started again. There is a temporary increase in the reaction rate, from 1.95 mmol/kgs to 3.45 mmol/kgs, at the initial stage of the regeneration and then the reaction rate immediately drops. This temporary increase in the reaction rate is almost 3 times higher than for the reduced start-up. After resuming the oxygen supply, the rate of reaction has restored to the level of the fresh active catalyst. The catalyst is regenerated by the
simple in-situ reduction process, which confirms that over-oxidation is the main cause of deactivation. The reduction of the catalyst can also be seen through the drop in the measured catalyst potential (Figure 6.2b), which reaches to 0.4 V. As soon as the oxygen flow is resumed, the catalyst potential follows its previous track, however it reaches rather quickly to a higher level of 0.97 V. For modelling the oxidised start-up, the semi-batch reactor model has been modified, containing two parts. First, the preoxidising period (no reaction), where the reactant alcohol is not present, Equations 6.1, 6.2, 6.12, and 6.13 are used. The catalyst potential Equation 6.3 is also modified, due to the absence of the alcohol reactant and the reaction products, as follows:

$$E = \frac{RT}{2F} \ln\left(\frac{R_{\text{oxid}1} + R_{\text{oxid}2}}{R_{\text{red}5}}\right)$$

(6.20)

For the second part, where reaction is involved, the standard set of equations are used. It is found that during the preoxidising period, in the absence of the alcohol reactant, the model predicts a high degree of catalyst deactivation ($\Theta_{\text{ox}} = 0.8$), which resulted in a much lower reaction rate compared to the observed reaction rate. However, after the reduction period, the model showed complete regeneration of the catalytic activity and gave an accurate description of the reaction rates thereafter, which duplicates the reduced start-up. In order to describe the initial observed reaction rates, for the oxidised start-up, it is considered that over-oxidation described by step VIII in Table 6.1, needs free sites for transformation of chemisorbed oxygen into the inactive platinum oxide. It can be envisaged that chemisorbed oxygen, in the absence of co-reactants, forms a regular layer on the platinum surface, which only decomposes into inactive oxide depending on the degree of layer disruption (creation of free sites). This is similar to the 'oxygen passivation' phenomena in corrosion, or place exchange mechanisms observed in electrochemistry [26]. This is also in agreement with Dirkx et al. [19], who have found that catalyst deactivation due to over-oxidation is higher in the presence of the reactant alcohol (during reaction). The kinetic parameter, $k_{8a}$, of the modified step, VIIIa in Table 6.1, is estimated using former experimental data, obtained at different pH conditions [22] and keeping the other parameters fixed. It is verified that the results presented for the reduced start-up are not altered due to modification in this step. It can be considered that $k_{8a}$ is exchanged for $k_{8a} \times \overline{\Theta^*}$ in the model, and the average free site coverage, $\overline{\Theta^*}$, during the reaction is approximately 0.43, which results in $k_{8a} \sim 2.35 \times k_8$. 
Figure 6.2: Effect of the oxidised startup procedure: (a) acid formation rate; (b) electrochemical catalyst potential; (c) oxide coverage; (d) oxygen (continuous line) and free site coverage (dashed line); (e) MGP concentration. The reactant alcohol, MGP, is added after 1800 s and the oxygen supply stopped from 4000 s to 4800 s. Symbols represent experimental data and lines represent model results.
Figure 6.2a shows that the reactor model is well able to describe the observed reaction rates. Especially, the acid formation rate after the pre-oxidation period (no reaction), is now properly simulated. In order to mimic the experimental data, after a simulation time of 4000 s, the gas phase oxygen partial pressure in the model was forced to zero for 800 s and then switched back to its original value. The model clearly demonstrates that the catalyst activity is fully regenerated and over-oxidation is the main cause of catalyst deactivation. Immediately, after setting the oxygen partial pressure to zero, the model shows a temporary increase in the reaction rate. However, the magnitude of the increased rate is lower than observed in the experiment, similar to the reduced start-up simulations.

Figure 6.2b shows that the model adequately describes the measured electrochemical catalyst potentials. In the oxidised period the electrochemical catalyst potential reaches to a high value, around 1.2 V, compared to the reaction period. The potential decreases to a lower value of 0.99 V with the addition of the alcohol reactant. However, during the reduction period, the model predicts a slower drop in the catalyst potential compared to the measured potential, similar as for the reduced start-up.

The degree of catalyst deactivation due to over-oxidation is presented as the simulated oxide coverage against time in Figure 6.2c. During the pre-oxidation period of 1800 s, approximately 22 % (Θ_{ox} = 0.22) of the catalyst surface is covered with inactive platinum oxide. It can be determined that approximately after 33 hrs of continuous exposure of the catalyst to the oxygen supply, full coverage with inactive platinum oxide (Θ_{ox} = 1) is obtained. After the addition of the reactant alcohol, the reaction starts but the level of the oxide coverage remains the same. This shows that the reactant alcohol is unable to reduce the oxide in the presence of oxygen, which confirms that the reactant MGP is a weak reducing compound. However, the oxygen coverage presented in Figure 6.2d drops from 0.8 to below 0.4, which has a slight effect on the catalyst potential lowering its value from 1.2 V to 1 V (Figure 6.2b).

After 4000 s of simulation time the model shows 60 % of catalyst deactivation, whereas the same degree of catalyst deactivation (60 %) was obtained after 2500 s, for the reduced start-up. This means that a higher catalyst deactivation rate is observed with reaction than without reaction. In practice, catalyst deactivation seems to be proportional to the turnover number [19]. This can be understood by considering that the dehydrogenation rate, step III in Table 6.1, and the over-oxidation rate, steps VIIIa and IX, all are proportional to the number of available free sites. During the reduction time, the drop in oxide coverage coincides with the catalyst potential. The oxide is completely removed after 800 s of catalyst reduction, which indicates complete regeneration of the catalyst.
Figure 6.2d shows the simulated oxygen coverage and free site coverage with time. The oxidised start-up leads to a higher initial oxygen coverage (approx. 0.9) than the reduced start-up (approx. 0.5). As soon as the reactant alcohol is added to the slurry, the oxygen coverage drops from a level of 0.8 to below 0.4, whereas the free site coverage increases to 0.38. The oxygen coverage further decreases with time due to an increase in oxide formation. The increased number of available free sites contributes to over-oxidation during the reaction, through kinetic steps VIIIa and IX in Table 6.1. During the reduction period the oxygen coverage drops fast to zero and the free site coverage reaches to 1. When the oxygen pressure is switched to its original value, the oxygen coverage at the catalyst surface increases and goes to a higher level (approx. 0.6), due to a lower alcohol coverage (conversion), and drops again due to over-oxidation. Figure 6.2e shows the simulated concentration of the reactant alcohol, MGP, as a function of time. It can be seen that the calculated conversion, from MGP concentration data, is around 22% over 6000 s of the simulation time.

### 6.4.3 Inert start-up

Figure 6.3a shows the experimentally observed acid formation rate as a function of time for the inert start-up procedure, i.e. using the catalyst from the shelf. It can be seen that the catalyst shows hardly any activity. The inert start-up represents an extreme case of the oxidised start-up. The initial rate obtained is only 0.3 mmol/kgs, which is nearly 19 times lower than the reduced start-up and 14 times lower than the oxidised start-up. Also here, to understand the cause of such a low activity, the oxygen flow was stopped after 3500 s for about 1000 s and started again. It can be seen from the figure that the catalyst has been fully regenerated and an acid formation rate of 5.8 mmol/kgs was obtained, which is of the same magnitude as for the reduced start-up. This shows that with the inert start-up procedure, before starting the reaction, the catalyst was fully over-oxidised. The initial reaction rate is close to the reaction rate obtained by Dirkx et al. [20] for an over-oxidised catalyst. The complete reactivation of the catalyst confirms that over-oxidation is the main cause of the catalyst deactivation. The temporary increase in the reaction rate, from 0.5 mmol/kgs to 1.1 mmol/kgs, at the initial stage of the regeneration, matches with the other start-up procedures.

To understand the catalyst deactivation, the observed electrochemical catalyst potential against time is presented in Figure 6.3b. Starting from an oxidised surface with potential around 1 V, after addition of the reactant, the potential drops to a lower value of 0.9 V. The catalyst potential stays at the same level over the reaction time.
Figure 6.3: Effect of the inert startup procedure: (a) acid formation rate; (b) electrochemical catalyst potential; (c) oxide coverage; (d) oxygen coverage; (e) MGP concentration. The oxygen supply stopped from 3500 s to 4600 s. Symbols represent experimental data and lines represent model results.
This inertness of the catalyst potential corresponds to the unaltered concentration (no conversion) of the reactant alcohol. During the reduction period, the catalyst potential drops to 0.4 V. As soon as the oxygen flow is resumed, the catalyst potential instantaneously increases to 0.9 V and quickly reaches to the level of 0.97 V during the reaction, where it stabilises, confirming the over-oxidation. For modelling the inert start-up, it is considered that the catalyst is fully oxidised, i.e. high coverage of oxide (approximately, $\Theta_{ox}=0.9$). Figure 6.3a shows that the reactor model is well able to describe the observed low reaction rates.

In order to mimic the experimental data, after a simulation time of 3500 s, the gas phase oxygen partial pressure in the model was forced to zero for 1000 s and then switched back to its original value. The model clearly demonstrates that the catalyst activity is fully regenerated and over-oxidation is the main cause of the deactivation. Immediately, after setting the oxygen partial pressure to zero, the model shows a temporary increase in the reaction rate. However, the magnitude of the increased rate is lower than observed in the experiment, similar as for the reduced start-up. The calculated potentials presented in Figure 6.3b, properly describe the observed electrochemical catalyst potential. During the reduction period the drop in the model predicted potential is slower compared to the measured catalyst potential, as observed for the other start-ups. The potential then drops to the level of 0.4 V and as soon as the oxygen pressure is switched back to its original values, the potential increases faster and stabilizes to a higher level (1 V) than the original level (0.95 V), similar to the experimentally measured catalyst potential.

Figure 6.3c shows the simulated oxide coverage against time. The oxide coverage remains at a high level, for a long period, as assumed at the beginning of the reaction ($\Theta_{ox}=0.9$). During the reduction period, the oxide coverage drops and reduces to zero after 1000 s. The model clearly demonstrates that the catalyst activity is fully regenerated. Figure 6.3d shows the simulated oxygen coverage with time. It can be seen that the oxygen has insignificant coverage on the catalyst surface, which is due to a high oxide coverage. This also indicates a low activity of the catalyst. During the reduction period, the coverage becomes zero. As soon as the oxygen pressure is switched to its original value, the oxygen coverage at the catalyst surface increases and goes to a higher level of 0.5, similar as for the reduced start-up. It can also be seen that the oxygen coverage further decreases due to over-oxidation. Figure 6.3e shows the simulated concentration of the reactant alcohol, MGP, as a function of time. It can be seen that the calculated conversion, from MGP concentration data, is around 15% over 6000 s of the simulation time.
6.5 Conclusions

In this chapter the effect of the reaction start-up procedure on the oxidation of methyl α-D-glucopyranoside has been investigated. Results have been obtained by performing experiments in a stirred slurry semi-batch reactor with Pt on carbon catalyst and molecular oxygen as oxidant. The reduced start-up case gives a nearly 1.3 times higher initial reaction rate than the oxidised start-up case and a nearly 19 times higher initial rate than the inert start-up case. It has been demonstrated, with the help of experiments and the recently developed electrochemical reaction model, that independent of the start-up procedure, over-oxidation is the main cause of catalyst deactivation. These results can be generalised for the oxidation of weakly reducing compounds, under oxygen rich conditions in a weakly alkaline medium. As the reaction progresses, the conversion of the reactant alcohol increases, the rate of oxygen supply becomes higher than the rate of reaction, and the catalyst deactivates due to over-oxidation. The results obtained in experiments are validated with the electrochemical model. The experimental regeneration period can be optimised with the model, in order to avoid carbonaceous deposits on the reduced catalyst. The observed catalyst potential gives useful information on the oxidation state of the catalyst. The model can describe well the observed catalyst potential at different start-up conditions. A modified kinetic step, which considers that free sites are needed for transformation of chemisorbed oxygen into inactive oxide, gave a good description of the oxidised start-up. Investigation on the effect of varying oxygen partial pressure, length of the pre-oxidising period, pH, and metal crystallite size, on the initial reaction rate, would give useful additional data to verify or adjust the kinetic equations, that describe over-oxidation.
Bibliography


Chapter 7

Process improvement by periodic operation and product removal

Abstract

A periodically operated process for the platinum catalysed selective oxidation of methyl α-D-glucopyranoside (MGP) to 1-O-methyl α-D-glucuronate (MG) has been presented. The benefits of periodic operation are demonstrated through lab scale experiments in a three phase stirred semi-batch reactor. Experiments are performed at a constant pH of 8 and a sufficiently high oxygen partial pressure of 20 kPa. A recently developed dynamic electrochemical kinetic model, implemented in a reactor model, is used to describe and validate the observed catalytic reaction rates. In addition, a model based process design is presented for MGP oxidation on an industrial scale in a continuous stirred tank reactor.

7.1 Introduction

Noble metal catalyzed selective alcohol oxidation is an attractive process because besides the use of clean oxidants, such as molecular oxygen or air, high selectivities can be obtained [1–3]. The reaction is carried out typically at temperatures below 90°C and at atmospheric pressure, in neutral or slightly alkaline media. Traditionally, due to fast production demands and one pot operation, synthesis routes of fine chemical and pharmaceutical compounds have been based on alcohol oxidation with stochiometric quantities of inorganic oxidants. This oxidation process suffers from low atom efficiency and high toxic waste production [4]. Alcohol oxidation by enzymes is practiced as an environmentally friendlier alternative, however product separation and waste production remain a problem. Homogeneous catalysis is an efficient alternative, however catalyst recovery, reactant recycling, and reactor corrosion limit its industrial scale utilization [5].
Noble metal catalysed alcohol oxidation provides useful carbonyl compounds and carboxylic acids for various applications in fine chemistry. The platinum catalysed oxidation of methyl α-D-glucopyranoside (MGP), a polyol, which is subject of the present study, opens a route to D-glucuronic acid, which has pharmaceutical applications and is a component of energy drinks. However, it is not performed on an industrial scale for several reasons, e.g., the selectivity for the main reaction product is only 70% at 100% conversion [1, 6], and catalyst deactivation results in a low catalyst activity [6, 7]. The selectivity problem can be overcome by keeping high alcohol levels and low carboxylic acid concentrations, with which the secondary oxidation steps are suppressed [8]. Kunz and Recker [8] demonstrated a selectivity of $> 99\%$ in a continuous oxidation process of methyl α-D-glucopyranoside, based on a fixed bed reactor. Schuurman et al. [6] and Vleeming et al. [7] have reported that at low conversion level, about 10%, a selectivity level of more than 95% can be obtained. A process, operated at low conversion level necessitates selective removal of the oxidation product from the liquid stream and recycling of the alcohol reactant, methyl α-D-glucopyranoside. This can for example be accomplished by ion exchange over a strong alkaline ion exchanger [9] or by electrodialysis [8, 10]. Electrodialysis with bipolar membranes has been found to be a more suitable separation technique [8, 11, 12], due to cost effectiveness and reproducibility.

Catalyst deactivation is often a major bottleneck for commercialization. It represents a technical as well as an economic factor in the process. The nature of the deactivation, whether it can be reversed under the normal operation or a separate regeneration treatment is required, as well as the time-scale of the deactivation determine the type of feasible technology and process options like reactor type and process configuration [13]. In liquid phase alcohol oxidation, catalysts can lose their activity for a variety of reasons [14]. Most common reasons are over-oxidation (corrosion), decarbonylation (CO formation) or carbonaceous deposition, aldol condensation (polymerisation or coking), crystalline growth (Ostwald ripening), and metal dissolution (leaching) [15].

Recently, it has been verified through experiments and modelling that for the oxidation of a weakly reducing compound like methyl α-D-glucopyranoside, under oxygen rich conditions, over-oxidation is the main cause of catalyst deactivation [16]. This type of deactivation is reversible and can be easily overcome through reduction of the catalyst, which can often be applied in-situ at mild conditions [6, 7, 17]. Markusse et al. [18] have demonstrated that by proper selection of the oxidation period and the catalyst reduction period, and by performing periodic process (redox-cycle) operation, the catalyst activity and the process productivity can be increased substantially. Periodic operation of chemical reactors is hardly new. Any heterogeneous catalytic reactor in which the catalyst is regenerated in-situ, operates periodically [19]. It
is a contacting technique for control of conversion or selectivity, which forces a reaction system to proceed under transient conditions [20]. The process production becomes a time-average quantity under this type of operation.

In addition to periodic operation, in the literature, several possible solutions have been presented to overcome or prevent catalyst deactivation by over-oxidation [5]. In general, over-oxidation can be prevented by control of the oxygen supply [21, 22], application of diffusion stabilized or core catalysts [23, 24], or addition of promoter metals to the catalyst [25, 26]. However, in the former two situations, when the rate of reaction is controlled by oxygen transport, the active platinum surface area is more likely to suffer from deposition of carbonaceous species [27–29]. This phenomenon is more pronounced when the catalyst is prereduced by the organic reactant [28]. In the case promoter metals are used, deactivation may occur due to leaching of promoter metal, which may take place at considerable levels as was observed by Bronnimann et al. [29] for bismuth and lead promoted catalysts.

It is clear from the above discussion that through periodic operation high catalytic activity can be maintained, whereas by removing the primary reaction product or by keeping low conversion levels, selectivity can be improved. However, research so far lacks detailed quantitative analysis. The purpose of this work is to present a detailed quantitative account of process performance, subject to periodic operation with product removal. The benefits of periodic operation are demonstrated through lab scale experiments in a three phase stirred semi-batch reactor. The Pt catalysed oxidation of methyl α-D-glucopyranoside (MGP), is used as a test reaction. Experiments are performed at a constant pH of 8 and a sufficiently high oxygen partial pressure of 20 kPa. A recently developed dynamic electrochemical kinetic model, implemented in a reactor model, is used to describe and validate the observed catalytic reaction rates. In addition, a model based process design is presented for the MGP oxidation on an industrial scale.

### 7.2 Lab scale process operation

#### 7.2.1 Modelling

**Kinetic model**

In this work, a recently developed dynamic electrochemical kinetic model is used. The reaction mechanism with the reaction rate equations are presented in Table 7.1. The details of the mechanism and the model are described elsewhere [30]. Based upon the non-steady state site balances and the rate equations given in Table 7.1, the rates of change of the oxygen coverage and the oxide coverage (measure of the catalyst deactivation due to overoxidation), are determined by
the following differential equations:

\[
\frac{d\Theta_o}{dt} = 2k_1C_o \Theta_o^2 - k_7\Theta_o\exp\left(-\frac{EF}{RT}\right) - k_8\Theta_o\Theta^* \\
\frac{d\Theta_{ox}}{dt} = k_8\Theta_o\Theta^* + k_9C_{OH}\Theta^*\exp\left(\frac{EF}{RT}\right) - k_{11}\Theta_{ox}\Theta^*\exp\left(-\frac{EF}{RT}\right)
\] (7.1) (7.2)

where \(\Theta_o\) is the oxygen surface coverage, \(\Theta_{ox}\) is the oxide surface coverage, \(\Theta^*\) is the free site surface coverage, \(k_i\) are the reaction rate parameters defined in Table 7.1, \(C_o\) [mol m\(^{-3}\)] is the oxygen concentration at the catalyst surface, \(E\) [V] is the electrochemical catalyst potential, \(F\) [C mol\(^{-1}\)] is the Faraday’s constant, \(R\) [J mol\(^{-1}\) K\(^{-1}\)] is the ideal gas constant, and \(T\) [K] is the reaction temperature. The catalyst potential is determined by balancing the rate of electrons produced \((R_3 + R_4 + R_5 + R_6 + R_9)\) per volume of the catalyst and the rate of electrons consumed \((R_7 + R_{11})\) per volume of the catalyst as:

\[
E(t) = \frac{RT}{2F} \ln\left(\frac{R_{oxid1} + R_{oxid2}}{R_{red1} + R_{red2} + R_{red3} + R_{red4} + R_{red5}}\right)
\] (7.3)

where,

\[
R_{oxid1} = k_7L_t\rho_p\Theta_o \\
R_{oxid2} = k_{11}L_t\rho_p\Theta_{ox}\Theta^* \\
R_{red1} = k_3L_t\rho_p\Theta_{RCH_2OH}\Theta^* \\
R_{red2} = k_4L_t\rho_pCOH\Theta_{RCH_2OH}\Theta^* \\
R_{red3} = k_5L_t\rho_p\Theta_{RCHO}\Theta^* \\
R_{red4} = k_6L_t\rho_pCOH\Theta_{RCHO}\Theta^* \\
R_{red5} = k_9L_t\rho_pCOH\Theta^* 
\] (7.4) (7.5) (7.6) (7.7) (7.8) (7.9) (7.10)

where \(L_t\) is the specific number of platinum surface atoms, i.e. mol Pt s/kg catalyst, based on the assumption that one Pt surface atom equals one catalytic site, and \(\rho_p\) mol/m\(^3\) is the catalyst particle density. It should be noted that two important phenomena limit the range of the catalyst potential. First, below a potential of 0.4 V RHE, hydrogen gas evolves, due to water reduction. Second, above a potential of 1.5 V RHE, oxygen gas evolves, due to water oxidation. Since these reactions are not taken into account in the kinetic model presented in Table 7.1, Equation 7.3 can only be applied, if:

\[0.4VRHE < E < 1.5VRHE\] (7.11)

**Semi-batch reactor model**

In practice, the oxidation reaction is generally carried out with the aqueous alcohol reactant in a batch mode and the gaseous oxidant, molecular oxygen, in a continuous mode. For the reaction to take place, oxygen has to be transferred from the gas phase to the liquid phase, through the
### Table 7.1: Reaction steps and rate equations for the alcohol oxidation mechanism (Gangwal et al. [16, 30]).

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Rate equation</th>
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<tbody>
<tr>
<td>(O_2 + 2* \rightarrow 2O*)</td>
<td>(R_1 = k_1 C_{O_2} \Theta^2)</td>
</tr>
<tr>
<td>(RCH_2OH + <em>_p \rightleftharpoons RCH_2OH</em>_p)</td>
<td>(\Theta_{RCH_2OH} = K_2 C_{RCH_2OH} \Theta*_p)</td>
</tr>
<tr>
<td>(RCHO + <em>_p \rightleftharpoons RCHO</em>_p)</td>
<td>(\Theta_{RCHO} = K_2a C_{RCHO} \Theta*_p)</td>
</tr>
<tr>
<td>(RCH_2OH<em>_p + * \rightarrow RCHO</em>_p + 2H^+ + 2e^- + *)</td>
<td>(R_3 = k_3 \Theta_{RCH_2OH} \Theta_* \exp\left(\frac{EF}{RT}\right))</td>
</tr>
<tr>
<td>(RCH_2OH<em>_p + * + OH^- \rightarrow RCHO</em>_p + H_2O + H^+ + 2e^- + *)</td>
<td>(R_4 = k_4 \Theta_{RCH_2OH} \Theta_* \exp\left(\frac{EF}{RT}\right))</td>
</tr>
<tr>
<td>(RCHO<em>_p + * + H_2O \rightarrow RCOOH</em>_p + 2H^+ + 2e^- + *)</td>
<td>(R_5 = k_5 \Theta_{RCHO} \Theta_* \exp\left(\frac{EF}{RT}\right))</td>
</tr>
<tr>
<td>(RCHO<em>_p + * + OH^- \rightarrow RCOOH</em>_p + H^+ + 2e^- + *)</td>
<td>(R_6 = k_6 \Theta_{RCHO} \Theta_* \exp\left(\frac{EF}{RT}\right))</td>
</tr>
<tr>
<td>(O^* + H_2O + 2e^- \rightarrow 2OH^- + *)</td>
<td>(R_7 = k_7 \Theta_o \exp\left(-\frac{EF}{RT}\right))</td>
</tr>
<tr>
<td>(O^* + * \rightarrow O^* + *)</td>
<td>(R_8 = k_8 \Theta_o \Theta^*)</td>
</tr>
<tr>
<td>(OH^- + * \rightarrow O^*_s + H^+ + 2e^-)</td>
<td>(R_9 = k_9 C_{OH} \Theta_* \exp\left(\frac{EF}{RT}\right))</td>
</tr>
<tr>
<td>(RCOOH + <em>_p \rightleftharpoons RCOOH</em>_p)</td>
<td>(\Theta_{RCOOH} = K_{10} C_{RCOOH} \Theta_*)</td>
</tr>
<tr>
<td>(O^*_s + H_2O + 2e^- + * \rightarrow 2OH^- + * + *_s)</td>
<td>(R_{11} = k_{11} \Theta_o \Theta_* \exp\left(-\frac{EF}{RT}\right))</td>
</tr>
</tbody>
</table>
Table 7.2: Kinetic parameters for the reaction steps defined in Table 7.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction step</th>
<th>Pt on carbon (Pt/C) (dispersion 42%)</th>
<th>Pt on graphite (Pt/Gr) (dispersion 15%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1 \ [m^3 mol^{-1} s^{-1}]$</td>
<td>oxygen adsorption</td>
<td>$9.10 \times 10^{-1}$</td>
<td>$9.10 \times 10^{-1}$</td>
</tr>
<tr>
<td>$K_2 \ [m^3 mol^{-1}]$</td>
<td>alcohol adsorption</td>
<td>$5.8 \times 10^{-2}$</td>
<td>$8.50 \times 10^{-3}$</td>
</tr>
<tr>
<td>$K_{2a} \ [m^3 mol^{-1}]$</td>
<td>aldehyde adsorption</td>
<td>$5.8 \times 10^{-2}$</td>
<td>$8.50 \times 10^{-3}$</td>
</tr>
<tr>
<td>$K_{10} \ [m^3 mol^{-1}]$</td>
<td>acid adsorption</td>
<td>$1.29 \times 10^{-1}$</td>
<td>$1.29 \times 10^{-1}$</td>
</tr>
<tr>
<td>$k_3 \ [s^{-1}]$</td>
<td>alcohol dehydrogenation</td>
<td>$5.28 \times 10^{-9}$</td>
<td>$5.28 \times 10^{-9}$</td>
</tr>
<tr>
<td>$k_4 \ [m^3 mol^{-1} s^{-1}]$</td>
<td>alcohol dehydro. (pH)</td>
<td>$3.4 \times 10^{-4}$</td>
<td>$5.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_5 \ [s^{-1}]$</td>
<td>aldehyde oxidation</td>
<td>$4.9 \times 10^{-7}$</td>
<td>$6.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>$k_6 \ [m^3 mol^{-1} s^{-1}]$</td>
<td>aldehyde oxidation (pH)</td>
<td>$1.60$</td>
<td>$3.68$</td>
</tr>
<tr>
<td>$k_7 \ [s^{-1}]$</td>
<td>oxygen reduction</td>
<td>$5.10 \times 10^{6}$</td>
<td>$4.57 \times 10^{7}$</td>
</tr>
<tr>
<td>$k_8 \ [s^{-1}]$</td>
<td>oxide formation</td>
<td>$1.13 \times 10^{-3}$</td>
<td>$1.13 \times 10^{-3}$</td>
</tr>
<tr>
<td>$k_9 \ [m^3 mol s^{-1}]$</td>
<td>oxide formation (pH)</td>
<td>$9.4 \times 10^{-7}$</td>
<td>$6.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>$k_1 \ [s^{-1}]$</td>
<td>oxide reduction</td>
<td>$1.50 \times 10^{3}$</td>
<td>$1.50 \times 10^{3}$</td>
</tr>
</tbody>
</table>

Liquid to the catalyst particle, and finally has to diffuse through the pores to the catalytic site inside the particle. For this work, it was verified that liquid-to-solid mass transport limitation and intra-particle diffusion limitation are not present and hence were not taken into account [31]. The transient material balance equations for oxygen in the gas phase and in the liquid phase are as follows:

\[ \frac{V_G}{RT} \frac{dP}{dt} = F_{V,G} \frac{P^{in} - P}{RT} - k_{GL}a_{GL}V_L(HP - C_L) \quad \text{Gas phase (G)} \tag{7.12} \]
\[ \frac{V_L}{dt} = k_{GL}a_{GL}V_L(HP - C_L) - V_L R_{V,o2} \quad \text{Liquid phase (L)} \tag{7.13} \]

where $V_G \ [m^3]$ is the volume of gas in the reactor, $P \ [Pa]$ is the oxygen partial pressure in the reactor, $F_{V,G} \ [m^3 s^{-1}]$ is the total volumetric gas flow rate, $k_{GL}a_{GL} \ [s^{-1}]$ is the volumetric gas-to-liquid mass transport coefficient, $H \ [mol m^{-3} Pa^{-1}]$ is the Henry coefficient, $C_L \ [mol m^{-3}]$ is the oxygen concentration in the liquid phase, and $V_L \ [m^3]$ is the total liquid volume. $R_{V,o2} \ [mol m^{-3} s^{-1}]$ is the overall volumetric oxygen consumption rate:

\[ R_{V,o2} = C_{cat}L_t k_1 \Theta^2 C_L \tag{7.14} \]

where $C_{cat} \ [kg m^{-3}]$ is the catalyst concentration. The weight specific dehydrogenation rate of the reactant alcohol, $R_{RCH_2OH} \ [mol kg^{-1} s^{-1}]$, from Equations (III) and (IV) of Table 7.1, can be determined as:

\[ R_{RCH_2OH} = L_t (k_3 + k_4 C_{OH}) \Theta_{RCH_2OH} \Theta^* \exp \left( \frac{EF}{RT} \right) \tag{7.15} \]
The liquid reactant alcohol is in a batch mode and continuously converting to the product as the reaction progresses, e.g., methyl glucoside (MGP) gives methyl glucuronic acid (MG) with methyl aldehydo-glucoside (MAGP) as an intermediate. The material balances for the liquid reactant and the products are described as follows. The rate of disappearance of the alcohol to the aldehyde is:

\[
\frac{dC_{RCH_2OH}}{dt} = -C_{cat}R_{RCH_2OH} \tag{7.16}
\]

\[
\frac{dC_{RCHO}}{dt} = C_{cat}(R_{RCH_2OH} - R_{RCHO}) \tag{7.17}
\]

\(R_{RCHO}\) is the weight specific aldehyde disappearance rate, which is determined from Equations (V) and (VI) of Table 7.1, as:

\[
R_{RCHO} = L_t(k_5 + k_6C_{OH})\Theta_{RCHO}\Theta^*\exp\left(\frac{EF}{RT}\right) \tag{7.18}
\]

The rate of acid formation, which is experimentally measured through the rate of alkali (NaOH) addition, is calculated from the rate of disappearance of the aldehyde as:

\[
\frac{dC_{RCOOH}}{dt} = C_{cat}R_{RCHO} \tag{7.19}
\]

The reactor model equations are solved with Matlab software, using the catalyst properties and the experimental conditions as given in Tables 7.3 and 7.4. The differential equations, Equations 7.12, 7.13, 7.16, 7.17, and 7.19 are solved using the stiff ordinary differential equations solver routine (ode23s).

### 7.2.2 Experimental

Experiments are performed in a stirred three-phase semi-batch reactor. The aqueous alcohol is added in a batch mode. The gaseous oxidant (molecular oxygen) is supplied continuously by a mass flow controller. The oxygen partial pressure is set by the nitrogen flow, also supplied by a mass flow controller. The pH of the reaction medium is kept at a constant level, by controlled addition of a known concentration of an alkali (NaOH). During the reaction, the alcohol reactant is converted to the product acid with time. The acid formation rate is measured through the rate of addition of alkali. The oxygen concentration in the liquid phase is measured using an oxygen electrode. The open circuit electrochemical catalyst potential is measured with a smooth Pt wire as working electrode and Ag/AgCl, saturated KCl as a reference electrode. Experiments were performed at the set of reaction conditions as presented in Table 7.4, and further details of the procedure are described in Chapter 3 (section 3.4.2). A commercial non-uniform (egg shell), 5 wt % Pt on Graphite (Johnson Mathhey - JM238) catalyst is used. The properties of the catalyst are presented in Table 7.3.
<table>
<thead>
<tr>
<th>Catalyst property</th>
<th>Pt/C (Engelhard, 43545)</th>
<th>Pt/Gr (Johnson Matthey: JM238)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dispersion [%]</td>
<td>42</td>
<td>15</td>
</tr>
<tr>
<td>B.E.T. area [m²/gm]</td>
<td>900</td>
<td>15</td>
</tr>
<tr>
<td>Pt content [weight %]</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>particle size [μm]</td>
<td>35-40</td>
<td>15</td>
</tr>
<tr>
<td>moisture content [%]</td>
<td>46.88</td>
<td>dry</td>
</tr>
<tr>
<td>porosity [%]</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>density [kg/m³]</td>
<td>1050</td>
<td>1350</td>
</tr>
</tbody>
</table>

Table 7.4: Experimental operating conditions.

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Semi-batch reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH [-]</td>
<td>8</td>
</tr>
<tr>
<td>degree of conversion [%]</td>
<td>5 - 30</td>
</tr>
<tr>
<td>temperature, T [K]</td>
<td>323</td>
</tr>
<tr>
<td>catalyst concentration, C_cat [kg m⁻³]</td>
<td>2</td>
</tr>
<tr>
<td>stirring speed [r.p.m]</td>
<td>1000</td>
</tr>
<tr>
<td>oxygen partial pressure, P^{in} [kPa]</td>
<td>40</td>
</tr>
<tr>
<td>initial MGP concentration, C_{MGP} [mol m⁻³]</td>
<td>100</td>
</tr>
<tr>
<td>initial MG concentration, C_{MG} [mol m⁻³]</td>
<td>0</td>
</tr>
<tr>
<td>liquid volume, V_L [m³]</td>
<td>0.5 × 10⁻³</td>
</tr>
<tr>
<td>gas volume, V_G [m³]</td>
<td>0.35 × 10⁻³</td>
</tr>
<tr>
<td>volumetric gas flow, F_{V,G} [m³ s⁻¹]</td>
<td>14 × 10⁻⁶</td>
</tr>
<tr>
<td>k_{GLaGL} [s⁻¹]</td>
<td>0.4</td>
</tr>
</tbody>
</table>
7.2.3 Process improvement

Figure 7.1a shows the experimentally observed acid formation rate as a function of time, for the normal and periodic feed oxygen operation. For periodic operation, the oxygen partial pressure is alternatively changed from 0 to 20 kPa. After each oxidation period of 500 s, the oxygen partial pressure is set to 0 for 300 s, i.e. only nitrogen is present in the gas feed. This period, in which the gas feed does not contain oxygen, will be referred to as the reduction period. It can be clearly seen that with periodic operation, a high acid formation rate can be maintained, compared to normal operation. For normal operation, the acid formation rate decreases by 67 %, after 2000 s, compared to 43 %, after 6000 s, in periodic operation.

Figure 7.1: Results for normal and periodic feed oxygen operation: (a) acid formation rate; (b) acid product (NaMG) concentration; (c) oxide coverage; (d) oxygen coverage as a function of time. Symbols represent the experimental results (■: normal operation; ▲: periodic operation) and lines represent the model results (dashed-dot line: normal operation; solid line: periodic operation; dotted line: periodic operation with product removal)
Figure 7.1b shows the acid product (NaMG) concentration as a function of time. The periodic operation (conversion = 22\%) gives approximately 6 \% higher conversion compared to the normal operation (conversion = 16\%), at the corresponding oxidation period of 2500 s. Figures 7.1a and 7.1b show that the developed electrochemical kinetic accurately describes the experimentally observed acid formation rates, for both types of operation. Figure 7.1c shows the calculated oxide coverage against time. The normal operation results in almost two times higher degree of catalyst deactivation due to over-oxidation. After 7000 s the oxide coverage is $\Theta_{\text{ox}} = 0.6$, compared to $\Theta_{\text{ox}} = 0.3$ for periodic operation. During the reduction period the model shows a drop in oxide coverage, however, the surface oxide is not removed completely. The model simulations suggest that the experimental reduction time, as it was found in previous work [16], is somewhat too short. In addition due to the consumption of the reactant alcohol, with time the alcohol surface coverage decreases and the surface oxide formation increases, which means the reduction period has to be increased. Figure 7.1d shows the oxygen coverage on the catalyst surface as a function of time. The periodic operation helps to maintain a constant level of oxygen coverage, whereas in the normal operation the coverage continuously decreases with time, which results in lower activity. Having gained confidence that the model can adequately describe periodic operation (Figure 7.1a), simulations have been performed with the model, incorporating product removal. It is considered that the product is removed as soon as it is formed, i.e. the acid concentration is considered to be zero ($C_{\text{RCOOH}} = 0$). In practice this can be achieved by applying a continuous mode of operation, which is discussed in the next section.

From Figure 7.1a, dashed line showing the simulated acid formation rate against time for the semi-batch reactor, it can be clearly seen that for the case of periodic operation, continuous product removal is beneficial. For normal operation also increase in the reaction rates is obtained with product removal (not shown in the figure), however these rates are lower than for the case of periodic operation only. Especially, for periodic operation, 35 \% increase in the reaction rate can be seen against 15 \% for the normal operation, after 7000 s of reaction time, using product removal. Figure 7.2c shows that for periodic operation with product removal the degree of catalyst deactivation is negligible compared to any other type of operation. This is demonstrated by a higher and constant oxygen coverage over the simulation time, as shown in Figure 7.2d.

### 7.3 Industrial scale process operation

It is clear from laboratory scale operation and simulations that periodic operation together with product removal considerably improves process productivity. Several possible industrial scale process options have been investigated, for the production of 1-O-methyl $\alpha$-D-glucuronate. Schuurman [9] designed a continuous three phase stirred tank reactor with an ion exchange
separation technique. Kunz and Recker [8] described a continuous oxidation process of methyl α-D-glucopyranoside based on a fixed bed reactor with an electrodialysis separation technique. Vleeming [10] and Markusse [32] extended the design of Schuurman with an adopted kinetic model, which includes catalyst deactivation and reactivation, and electrodialysis as a separation technique. Recently, Kluytmans et al. [33] presented a design based on the airlift loop redox cycle reactor.

In this work, the process for the production of 1-O-methyl α-D-glucuronate is designed on similar principles as used by Vleeming [10] and Markusse [32], using the improved kinetic model, as presented in Table 7.1.

### 7.3.1 Process description

Figure 7.2 shows the simplified process flow sheet for the oxidation of methyl α-D-glucopyranoside to 1-O-methyl α-D-glucuronate. The central part of the process consists of a continuous three-phase slurry reactor equipped with a microporous filter to retain the catalyst. The product concentration in the reactor is kept low, in order to perform the reaction with high selectivity. As discussed in the previous section, 1-O-methyl α-D-glucuronate is selectively removed from the liquid stream via electrodialysis with bipolar membrane (EDBM), through which only ions will move. In order to increase the concentration of the ionic species, conventional electrodialysis (EDC) is further used prior to EDBM. In this manner, the economic profitability of the EDBM step can be improved and the product can be removed selectively. To some extent, EDC can also simultaneously increase the purity of the target acid salt, since unreacted alcohol can be removed and recycled. The details of the EDC and EDBM techniques can be found elsewhere [11, 34]. A complete removal of sodium 1-O-methyl α-D-glucuronate is assumed. Also, removal of the product in the acid form, i.e. 1-O-methyl α-D-glucuronic acid, can be considered, because the use of electrodialysis with bipolar membranes allows this possibility, and then sodium hydroxide can be recycled for pH control [12]. The intermediate product, methyl α-D-6-aldehydoglucopyranoside, is not taken into account and is considered as a reactive intermediate. The reactor is operated at a constant pH through the addition of sodium hydroxide via a pH control loop. During reaction the catalyst is deactivating by over-oxidation. In order to overcome this deactivation, the reactor is operated periodically by reduction of the catalyst by a mild reductive treatment. This is done by feeding air and nitrogen periodically.

**Continuous tank reactor design equations**

The reactor equations are derived based on the following assumptions:

- The system is isothermal.
Figure 7.2: Simplified process layout. (1) Reactor, (2) Conventional Electrodialysis (EDC), and (3) Electrodialysis with bipolar membrane (EDBPM).

- The gas and aqueous phases are ideally mixed.
- The ideal gas law can be applied.
- The liquid feed flow contains no oxygen.
- Air contains 20% oxygen and 80% nitrogen.
- Catalyst particles are spherical with constant shape and porosity.
- For the egg shell catalyst the given amount of active metal is distributed in the outer 20 percent of the volume of the support particle.
- The partition coefficient, for which the oxygen concentration just within the surface of the solid may be higher than the oxygen concentration in the liquid just adjacent to the solid, is assumed to be equal to 1.
- Reactor is operated with constant volume.
- The solutes are not volatile.

The reaction rate equations required for estimating the catalyst surface coverages are presented in Table 7.1. For the reaction to take place, oxygen has to be transferred from the gas phase to the liquid phase, through the liquid to the catalyst particle, and finally has to diffuse through the pores to the catalytic site inside the particle.

The mass balance equation for oxygen in the gas phase is given by Equation 7.12, whereas for the liquid phase it is given as:

\[ V_L \frac{dC_L}{dt} = k_{GL}a_{GL}V_L(C_{\text{sat}} - C_L) - k_{LS}a_{LS}V_L(C_L - C_S) \] (7.20)
where \( k_{GLaGL} \) is the volumetric gas-to-liquid mass transport coefficient, \( C^{\text{Sat}} \) is the saturation oxygen concentration, \( C_L \) is the oxygen concentration in the liquid phase, \( k_{LSaLS} \) is the volumetric liquid-to-solid mass transport coefficient, \( C_S \) is the oxygen concentration at the solid particle.

The gas-to-liquid mass transport coefficient is estimated using the correlation developed by Yagi and Yoshida [35]:

\[
\frac{k_{GLaGL} d_I^2}{D_{O_2}} = 0.06 \left\{ \frac{d_I^2 N_I \rho_L}{\mu_L} \right\}^{1.5} \left\{ \frac{d_L^2 N_I^2}{g} \right\}^{0.19} \left\{ \frac{\mu_L}{\rho_L D_{O_2}} \right\}^{0.5} \left\{ \frac{\mu_L u_g}{\sigma_L} \right\}^{0.6} \left\{ \frac{d_I N_I}{u_g} \right\}^{0.32} \tag{7.21}
\]

The oxygen equilibrium concentration, \( C^{\text{Sat}} \), in the liquid phase is calculated by a semi-empirical correlation given by Battino [36]:

\[
C^{\text{Sat}} = 0.5483 \exp(-179.3439 + 8747.547/T + 24.45264 \ln(T)) P_{O_2} \tag{7.22}
\]

The liquid to solid mass transfer coefficient, \( k_{LS} \), is calculated according to the correlation given by Sano et al. [37]:

\[
Sh = \phi_c (2 + 0.4 \Re^{0.25} \Sc^{0.33}) = \frac{k_{LSd_p}}{D_{O_2}} \tag{7.23}
\]

where \( \phi_c \) is the Carman correction factor for the particle geometry, for spherical particles: \( \phi_c = 1 \). \( \Re \) is the dimensionless Reynolds number, which is given as:

\[
\Re = \frac{N_p d_I^5 N_I^3 d_p^4 \rho_L^3}{V_L \mu_L^3} \tag{7.24}
\]

and \( \Sc = \mu_L \rho_L^{-1} D_{O_2}^{-1} \) is the dimensionless Schmidt number. The volumetric liquid-solid interface surface area, \( a_{LS} \), is calculated as:

\[
a_{LS} = \frac{6 \text{Cat}}{d_p \rho_p} \tag{7.25}
\]

It is assumed that the catalytically active sites are located inside the pores of the catalyst particle. This is necessary to be able to differentiate between catalysts of different intra-particle activity distributions. For a uniformly activated spherical catalyst particle and constant oxygen diffusivity, the oxygen balance under isothermal conditions leads to:

\[
\frac{\partial C_{O_2}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_e r^2 \frac{\partial C_{O_2}}{\partial r} \right) - R_{V,O_2} \tag{7.26}
\]

with the following initial and boundary conditions:

at \( t = 0 : \)

\[
C_{O_2} = 0 \quad (0 \leq r \leq R_p) \tag{7.27}
\]

at \( t > 0 : \)

\[
\frac{\partial C_{O_2}}{\partial r} = 0 \quad \text{at} \ r = 0 \tag{7.28}
\]

\[
k_{LS}(C_L - C_S) = (-D_e \frac{d C_S}{d r}) \quad \text{at} \ r = R_p \tag{7.29}
\]
The rate of reaction of oxygen, \( R_{v,o_2} \), is dependent on the amount of oxygen present at the catalyst surface as well as on the activity of the catalyst. Therefore, from Equation (I) of Table 7.1,

\[
R_{v,o_2} = L_t \rho p k_1 \Theta^2 \Theta^2 C_{o_2} \quad (7.30)
\]

The rate of reaction can also be expressed in terms of the specific consumption of the reactant alcohol, as presented in Equation 7.15 as:

\[
R_{RC\text{H}_2OH} = L_t (k_3 + k_4 C_{OH}) \Theta_{RC\text{H}_2OH} \Theta^* \exp \left( \frac{EF}{RT} \right) \quad (7.31)
\]

### 7.3.2 Process design

The present process design is targeted for 1000 tons per year production capacity of 1-O-methyl \( \alpha \)-D-glucuronic acid (MG). This yearly production rate is chosen arbitrarily, since MG is at current not produced at a large scale. However, the production rate is nearly 1% of the yearly global production capacity of vitamin C (110,000 tons), which can be the possible application of this process. In order to make this process viable, high catalyst activity and selectivity have to be maintained. The focus is given on the appropriate reactor design and the possible economic constraints involved are not subject of this study and hence a cost estimation will not be considered.

The determination of the reactor size and the catalyst loading is an iterative procedure, for which the mass transfer rate of reactants and the MG production rate have to be optimised, respectively. The important process variables and catalyst properties, such as the oxygen partial pressure, the MGP concentration, pH, and the Pt crystallite size, the Pt metal distribution, and the type of support, respectively, were determined for maximization of the alcohol consumption rate. The reaction conditions are selected in relation to the experimental conditions for which the kinetic model presented in the previous section is valid.

According to the results in Chapter 3 (Figure 3.4a), a maximum reaction rate is obtained at a 40 kPa of oxygen partial pressure. However, the difference between the reaction rates at 40 kPa and 20 kPa is not that significant, which means air can be a better choice, because of reduced costs and improved safety. A temperature of 323 K and a relative mild pH of 8.0 is chosen in order to avoid catalyst deactivation by (side) product adsorption. According to the results in Chapter 5 (Figure 5.4a), the rate of reaction increases with an increase in pH, however the rate of catalyst deactivation due to over-oxidation also increases (Figure 5.4c). In addition, adsorption of mono- and dicarboxylic acids will take place at low pH, and side product formation increases with increasing pH as discussed in Chapter 5. The concentration of methyl \( \alpha \)-D-glucopyranoside (MGP) is taken as 1000 mol m\(^{-3}\), because the rate of reaction increases
with increasing MGP concentration, as presented in Chapter 2 (Figure 2.3a), and Chapter 5 (Figure 5.1a). At a higher concentration the viscosity of the feed will be too high and the feed will be difficult to handle. In order to achieve high catalytic activity, a 5 wt%, egg shell type, platinum on carbon catalyst is chosen, properties of which are presented in Table 7.3. This follows from the results obtained in Chapters 2, 4 and 5, that show that below a liquid oxygen concentration of 0.3 \( mol \, m^{-3} \), the egg shell catalyst distribution with carbon support gives the highest reaction rates.

For the targeted production capacity, if 350 production days per year are assumed, a production rate of 0.16 \( mol \, s^{-1} \) can be obtained. In order to obtain a high catalytic productivity, the oxidation and the reduction period of the periodic cycle have been optimized, the detailed description of which is presented in the next section. At an oxidation period of 1000 s, a maximum average production rate of 4.4 \( mmol \, kg^{-1} \, s^{-1} \) is obtained, as shown in Figure 7.4. The amount of catalyst needed to achieve the targeted capacity is approximately 40 \( kg \). The reactor configuration is primarily determined by the mass transfer properties of the reactants. Because the solubility of oxygen in aqueous solution is very low (typically 1 \( mol \, m^{-3} \)), the oxygen mass transport from the gas phase towards the catalyst is most critical. A liquid oxygen concentration of 0.1 \( mol \, m^{-3} \) is desired to obtain a sufficiently high MGP oxidation rate and to safeguard against catalyst poisoning, as mentioned in Chapter 6. A gas-to-liquid mass transport coefficient \( k_{GLaGL} \) of 0.3 \( s^{-1} \) is considered, which is a typical estimate for industrial slurry reactors [38], especially for carbon slurries where enhancement factors of up to 3 have been observed due to particle to bubble adhesion [39]. In order to maintain the desired liquid oxygen concentration, around 0.1 \( mol \, m^{-3} \), while using approximately 5 times air surplus, resulting in a saturation concentration of 0.16 \( mol \, m^{-3} \), i.e. a driving force of 0.06 \( mol \, m^{-3} \), a liquid volume of 10 \( m^3 \) is required. This means that a catalyst loading of approximately 4 \( kg \, m^{-3} \) is required to achieve the production capacity. A standard tank configuration is chosen which implies that the reactor diameter is equal to the liquid height and a Rushton impeller with a diameter of 1/3 of the reactor diameter is chosen [38]. The liquid volume is realized by a reactor diameter of 2.34 m and a liquid height of 2.34 m. The specifications of the reactor are presented in Table 7.2.

As discussed in the previous section and due to possible formation of side products, for the selective production of MG, a conversion of 10 % per pass is considered. For the desired conversion level the reactor feed flow rate of methyl \( \alpha \)-D-glucopyranoside (MGP) amounts to 1.6 \( mol \, s^{-1} \) (\( F_{m,L} \)). A conversion of 10 % corresponds to a MGP concentration of 900 \( mol \, m^{-3} \) and a MG concentration of 100 \( mol \, m^{-3} \). The volumetric reactor feed flow rate of the reactant MGP (\( F_{v,L} \)) feed equals to \( F_{m,L}/C_{MGP} \) which amounts to 1.6 \( 10^{-3} \, m^3 \, s^{-1} \). The resulting average residence time of liquid amounts to approximately 6000 s. As mentioned before, in order to maintain the desired liquid oxygen concentration, the air feed rate is chosen higher than the
stoichiometric amount, which amounts to 0.12 $m^3s^{-1}$ (0.02 m/s superficial gas velocity). Since the average production rate benefits from a decrease of the reduction period a relative small gas volume in the reactor is chosen (3 $m^3$ for gas hold up and an additional 2 $m^3$ for gas head space), resulting in a total reactor volume of 15 $m^3$. The reaction is performed at atmospheric pressure and a relatively high gas feed flow rate is used. The liquid-to-solid mass transport coefficient, $k_{LS}$, is calculated from the correlation of Sano et al. [37], Equation 7.23, and amounts to 1.2 $10^{-3} ms^{-1}$. The volumetric liquid-to-solid interface surface area, $a_{LS}$, is calculated from Equation 7.25 and equals to 2.7 $10^3 m^{-1}$. These values have been used to optimise the periodic cycle.

| T $[K]$ | 323 | $V_G$ $[m^3]$ | 5.0 |
| pH $[-]$ | 8.0 | $F_{v,L}$ $[m^3s^{-1}]$ | 1.6 $10^{-3}$ |
| $C_{MGP}$ $[mol m^{-3}]$ | 1000 | $F_{v,G}$ $[m^3s^{-1}]$ | 0.12 |
| $C_{cat}$ $[kg m^{-3}]$ | 4 | $d_R$ $[m]$ | 2.34 |
| $P_{tot}$ $[kPa]$ | 100 | $h_L$ $[m]$ | 2.34 |
| $P_{O_2}(air)$ $[kPa]$ | 20 | $d_I$ $[m]$ | 0.78 |
| $V_L$ $[m^3]$ | 10 | $N_I$ $[s^{-1}]$ | 2.3 |

| reactor | value | reference |
| impeller diameter $d_I$ | 0.78 [m] | |
| reactor diameter $d_R$ | 2.34 [m] | |
| impeller revolution speed $N_I$ | 2.5 [s$^{-1}$] | |
| impeller power number $N_p$ | 5 [-] | [32] |
| superficial gas velocity $u_G$ | $2 \times 10^{-3} [ms^{-1}]$ | |
| liquid volume $V_L$ | 10 [$m^3$] | |
| gas volume $V_G$ | 5 [$m^3$] | |

| thermodynamic and transport properties | value | reference |
| liquid volumetric mass $\rho_L$ | 1053 [$kg m^{-3}$] | |
| liquid dynamic viscosity $\mu_L$ | $7.6 \times 10^{-4} [kg m^{-1} s^{-1}]$ | |
| diffusion coefficient of oxygen in water $D_{O_2}$ | $3 \times 10^{-9} [m^2 s^{-1}]$ | [40] |
| liquid surface tension $\sigma_L$ | $7.1 \times 10^{-2} [N m^{-1}]$ | [40] |
| acceleration of gravity $g$ | 9.81 [$ms^{-2}$] | [40] |
7.3. Industrial scale process operation

**Periodic cycle optimisation**

Figure 7.3a shows that, during an oxidation period, the rate of production of 1-O-methyl α-D-glucuronate increases in 150 s to its maximum value of 7.35 mmol/kgs and then decreases due to catalyst deactivation by over-oxidation. As shown in Figure 7.3b, during the oxidation period the degree of coverage by the oxide increases from 0.15 for an oxidation period of 500 s to 0.27 for an oxidation period of 1000 s to 0.66 for an oxidation period of 10000 s (not shown). As shown in Figure 7.3c, for an oxidation period of 500 s the reduction period amounts to about 450 s of which 300 s are needed to remove oxygen from the aqueous phase, and 150 s to reduce the platinum surface. The electrochemical catalyst potential presented in Figure 7.3d and the oxygen coverage in Figure 7.3e coincide with the liquid oxygen concentration and give information on the oxidation (high potential)-reduction (low potential) state of the catalyst. Figure 7.3f shows that the oxygen concentration gradients inside the catalyst particle and at the liquid solid interface are negligible, indicating that the mass transport limitation lies at the gas liquid interface as designed for the process (driving force of 0.08 to 0.09 mol/m³).
Figure 7.3: Results for periodic feed oxygen operation: (a) MGP oxidation rate; (b) oxide coverage; (c) liquid oxygen concentration; (d) catalyst potential; (e) oxygen coverage as a function of time; and (f) oxygen concentration gradients inside particle. Continuous lines represent oxidation period of 1000 s and dashed lines represent oxidation period of 500 s. Conditions as described in the process design section 7.3.2.
Figure 7.4 shows the average rate of production as a function of the oxidation period. There is a clear maximum of 4.4 mmol/kgs corresponding to the oxidation period of 1000 s. At an oxidation period above 1000 s the production rate decreases due to relatively higher catalyst deactivation, while at an oxidation period below 1000 s, the rate decreases because the unproductive reduction period becomes relatively too long compared to the oxidation period.

![Graph showing average production rate vs. oxidation period]

Figure 7.4: Average rate of production of MG as a function of the oxidation period calculated according to Equations 7.2 to 7.27 and the model parameters in Tables 7.1, 7.2, 7.3, and 7.5.

### 7.4 Concluding remarks

A periodically operated process for the platinum catalysed selective oxidation of methyl α-D-glucopyranoside to 1-O-methyl α-D-glucuronate has been presented. Deactivation by over-oxidation of the catalyst, resulting in a low catalyst activity, is overcome by feeding air and nitrogen periodically. The selectivity is improved by continuous removal of the main product, avoiding secondary reactions. In this way a high average production rate and high catalyst life span can be maintained. The annual targeted production of 1000 ton of 1-O-methyl α-D-glucuronate can be achieved in a 15 m$^3$ reactor with 4 kg m$^{-3}$ of catalyst loading.
Bibliography

Chapter 8

Conclusions and outlook

In this research work, platinum catalysed alcohol oxidation has been investigated. The oxidation of methyl α-D-glucopyranoside (MGP), a polyol, to 1-O-methyl α-D-glucuronic acid (MG), was considered as a model reaction. Experiments were performed in a semi-batch reactor with oxygen as the oxidant in a continuous mode, and the liquid reactant methyl α-D-glucopyranoside in a batch mode. Two types of catalysts with different metal dispersion were used, viz., Pt on active carbon support and Pt on graphite support. The in-situ measurement of the electrochemical catalyst potential gave useful information on the oxidation state of the catalyst. Emphasis was given in understanding the influence of catalyst properties (active metal distribution, metal dispersion, and support type) and reaction conditions (alcohol concentration, oxygen concentration, pH, and start-up procedure) on the catalyst activity and deactivation.

It was found that the alcohol oxidation exhibits a maximum in the reaction rate as a function of oxygen concentration, which shifts from high oxygen concentration in the liquid to relatively low oxygen concentration with increasing oxygen mass transport rate. This maximum rate is fully determined by the catalytic kinetic constants, and is independent of the oxygen mass transfer coefficient, oxygen effective diffusivity, catalyst particle size and geometry, and active site distribution profile.

The reaction rate of MGP oxidation at oxygen partial pressures below 40 kPa, was found to be higher for the egg shell activity distribution than for the uniform catalyst activity distribution. Also, the catalyst deactivation rate due to over-oxidation increased dramatically with increasing oxygen partial pressure from 10 to 40 kPa, for both catalysts. The pitfalls in obtaining proper kinetic parameters for negative order reactions were presented. For negative order reactions, kinetic parameters obtained with intrinsic data only, result in erroneous model predictions. This was demonstrated for simple Langmuir-Hinshelwood kinetics and for MGP oxidation. A new parameter estimation from a combination of intrinsic and mass transport limited data greatly improved the prediction capability of both models. Consequently, for negative order reactions,
kinetic parameters have to be obtained from a combination of intrinsic data as well mass transport limited data.

A dynamic electrochemical kinetic model has been developed, which accurately describes the observed pH effect and catalyst deactivation due to over-oxidation. The rate determining steps and the model parameters have been deduced from previous reaction rate measurements in a CSTR, with graphite supported Pt catalyst (former work), and from stirred slurry semi-batch reaction rate data, with carbon and graphite supported Pt catalyst (this work). The effect of pH was incorporated by considering parallel reaction steps depending on the acidity or the alkalinity of the medium. Hydroxyl ions were mainly responsible for strong deactivation of the catalyst in the alkaline medium, whereas in neutral or acidic medium the deactivation was due to strong adsorption of oxygen atoms only. In both cases, the formation of inactive platinum oxide was responsible for the catalyst deactivation. Both types of catalyst showed the same degree of vulnerability to deactivation due to over-oxidation. However, the carbon supported Pt catalyst gave higher initial reaction rates compared to the graphite supported catalyst. The modelling results confirm that the intermediate aldehyde was present at low pH and the selectivity towards the aldehyde decreases with increase in pH.

It has been demonstrated, with the help of experiments and the recently developed electrochemical reaction model, that independent of the reaction start-up procedure, over-oxidation was the main cause of catalyst deactivation. These results can be generalised for the oxidation of weakly reducing compounds, under oxygen rich conditions in a weakly alkaline medium. A periodically operated process for the selective oxidation of methyl α-D-glucopyranoside to 1-O-methyl α-D-glucuronate has been presented. Catalyst deactivation by over-oxidation of the catalyst, resulting in a low catalyst activity, is overcome by feeding air and nitrogen periodically. The annual production that can be achieved in a 15 m³ reactor with 4 kg m⁻³ is 1000 ton of 1-O-methyl α-D-glucuronate.

**Outlook**

The developed electrochemical kinetic model combines knowledge from heterogeneous catalysis and electrochemistry. The results show that above 0.7 V RHE catalyst potential, at oxygen rich conditions, the model can adequately describe the observed experimental data. The catalyst potential measurement and its subsequent modelling are proven to be accurate for low reducing alcohol compounds. However, for high reducing compounds, in the presence of pure oxygen gas, potential measurement is instable and the measuring technique needs to be improved. Also, the electrochemical kinetic model has to be improved by taking into account adsorbed hydrogen species and an additional catalyst potential dependent reaction of proton formation. In addition,
an interesting development can be inclusion of the formation of CO or carbonaceous species in the kinetic model, which has been widely observed at oxygen deficient conditions, for strong reducing compounds. This means that alcohol oxidation experimental data have to be available at low catalyst potential (below 0.7 V RHE). The CO formation kinetic step can be envisaged through decomposition of intermediate species.

Working at oxygen mass transport limited conditions necessitates use of promoters. It has been experimentally observed that promoters have a strong influence on alcohol oxidation. Their addition to noble metal catalysts can greatly increase the oxidation rate, selectivity and catalyst activity, especially for strong reducing agents like D-glucose but for low reducing agents like MGP, they have little (mass transport limited conditions) or negative influence (intrinsic conditions) on the rate of oxidation. However, the role of promoters is still unclear and it rather depends on the type of reaction and operating conditions. The results sofar suggest that promoters enhance the oxygen coverage at the catalyst surface, which has influence on the alcohol dehydrogenation rate and catalyst deactivation. Extension of the developed model, in order to understand and describe the effect and role of promoters on alcohol oxidation, can be of special interest.

The modelling results show that the Pt particle size (dispersion) has a strong effect for a weakly reducing compound like MGP. However, this effect needs to be scrutinized via experiments, using catalysts with different dispersion. Also, the effect of the catalyst support needs to be investigated, along with possible limitations for the active sites accessibility for the alcohol molecule. The model can be further improved by taking into consideration diffusion limitation for the alcohol molecule, which can be crucial at higher conversion. It was also found that glucose (strongly reducing compound) oxidation can only be modelled by considering that the reaction is taking place at the gas-liquid interface and is influenced by particle-bubble adhesion. For proper modelling, good estimates for the effective diffusivity and partition coefficient should be obtained, and the effect of particle to bubble adhesion on mass transfer enhancement should be assessed.
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List of publications


Vikrant Gangwal was born on 30th June 1976 in Chapaner-Aurangabad, India. He started his PhD work at the Eindhoven University of Technology (TU/e) in October 2000. The PhD work was done under the supervision of Prof.dr.ir. J.C. Schouten and Dr.ir. B.F.M. Kuster at the Laboratory of Chemical Reactor Engineering. Before joining TU/e, he was working at the Indian Institute of Technology Bombay, as a project engineer in the CAD centre. He has obtained his master degree (M.Tech.) in chemical engineering from the Indian Institute of Technology Madras. He did his master thesis work in the field of ”Nonlinear Data Reconciliation”, under the guidance of Prof. S. Narasimhan. Starting from 1st April 2005, he will start postdoctoral work on ”Kinetic modeling of NOx reduction in automotive converters” at the Laboratory of Chemical Reactor Engineering, TU/e.