ELSEVIER

Catalysis Today 66 (2001) 191–197

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Platinum catalysed aqueous methyl α-D-glucopyranoside oxidation in a multiphase redox-cycle reactor

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

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

Abstract

Platinum catalyst deactivation during aqueous alcohol oxidation is discussed, using the selective oxidation of methyl α-D-glucopyranoside as an example. The most important causes of platinum deactivation are catalyst over-oxidation and catalyst poisoning. Deactivation by over-oxidation can be reversed by applying a redox-cycle, i.e. cyclic exposure to oxidative and reductive circumstances. A kinetic model for methyl α-D-glucopyranoside oxidation, platinum deactivation, and reactivation, based on electrochemistry is presented and implemented into a three-phase stirred slurry reactor model, showing the advantages of applying redox cycles. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Alcohol oxidation; Redox cycle; Methyl α-D-glucopyranoside

1. Introduction

Platinum catalysed selective oxidation of alcohols provide useful products and intermediates for various applications in fine chemistry. A promising field of application is the selective oxidation of renewable feedstock (carbohydrates) towards valuable sugar acids. Two industrial scale examples are the manufacturing processes leading to D-gluconic acid and L-ascorbic acid (vitamin C), starting from D-glucose. The platinum catalysed alcohol oxidation process is characterised by low environmental impact, high selectivity, and mild reaction conditions.

Fast deactivation of the catalyst hinders large scale use of this type of alcohol oxidation in fine chemistry processes. Several mechanisms for the deactivation of platinum have been proposed, e.g. formation of strongly adsorbing by-products, coke deposition, oxidation of the platinum surface (over-oxidation), leaching, and Ostwald ripening of the platinum particles [1]. A recent study on platinum catalysed carbohydrate oxidation showed that platinum over-oxidation is the predominant cause of deactivation under oxygen rich conditions [2]. This has been confirmed by in situ EXAFS spectroscopy [3].

As stated by Horányi [4] and Mallat and Baiker [5], noble metal catalysed oxidations can be considered as electrochemical reactions. Alcohol oxidation takes place in two half reactions: alcohol dehydrogenation (producing electrons) and oxygen reduction (consuming electrons). The open-circuit potential of the catalyst is determined by the kinetics of these half reactions. The potential of the platinum particles determines the type of reactions taking place on the catalyst surface. At low potentials (<0.4 V vs. RHE), the surface is covered with hydrogen adatoms. At high potentials (>0.8 V vs. RHE) the surface is

---

* Corresponding author.
E-mail addresses: peter.markusse@dsm-group.com (A.P. Markusse), b.f.m.kuster@tue.nl (B.F.M. Kuster), j.c.schouten@tue.nl (J.C. Schouten).

PII: S0920-5861(00)00648-9

Nomenclature

A_0	pre-exponential Arrhenius factor (s^{-1})
c	concentration ($mol\,m^{-3}$)
E	potential (V)
E_a	energy of activation ($J\,mol^{-1}$)
F	Faraday's constant ($C\,mol^{-1}$)
k_i	reaction rate coefficient (var.)
L_t	weight specific catalyst surface ($mol\,Pt_s\,kg_{cat}{}^{-1}$)
p	pressure (Pa)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
R_i	surface specific reaction rate ($mol\,(mol\,Pt_s)^{-1}\,s^{-1}$)
R_w	weight specific reaction rate ($mol\,kg_{cat}{}^{-1}\,s^{-1}$)
T	absolute temperature (K)
θ	surface coverage

Subscripts

cat	catalyst
MAGP	methyl α-D-6-aldehydoglucopyranoside
MGP	methyl α-D-glucopyranoside
NaMG	sodium 1-*O*-methyl α-D-glucuronate
O_2	oxygen
RHE	reversible hydrogen electrode
SHE	standard hydrogen electrode

covered with oxygen species, and platinum oxide is formed. The most favourable potential range for alcohol oxidation is between 0.4 and 0.8 V (vs. RHE). However, poisoning by carbonaceous alcohol degradation products may occur in this region [6,7].

The purpose of this paper is to provide a kinetic model for platinum catalysed selective methyl α-D-glucopyranoside oxidation towards 1-*O*-methyl glucuronic acid, based on electrochemistry, and to demonstrate the applicability of redox-cycles in multiphase reactors. This model will include deactivation and reactivation of the catalyst. Catalyst reactivation involves in situ reduction of oxidised platinum by the reactant alcohol in the absence of oxygen. As Vleeming et al. [2] found in their investigation of methyl α-D-glucopyranoside oxidation at 30–60°C, this reactivation takes less than 1000 s. The model is based on kinetic measurements in a three-phase continuous flow stirred tank reactor (CSTR), and electrochemical experiments that were discussed in our previous paper [7].

2. Experimental

The kinetics of platinum catalysed aqueous alcohol oxidations were determined by reaction rate measurements in a stirred slurry reactor, using graphite supported platinum catalysts. The reaction studied was the selective oxidation of methyl α-D-glucopyranoside towards 1-*O*-methyl glucuronic acid. Most of the reaction rate data used were provided by Vleeming et al. [2]. Additional reaction rate measurements and reactivation experiments were performed using a similar reactor set-up and catalyst. The catalyst used in this study had a higher platinum load (4.7 vs. 3.3 wt.%) and a smaller specific catalyst surface (37 vs. 73 mmol $Pt_s\,kg_{cat}{}^{-1}$). The diameter of 95% of the graphite particles were smaller than 15 μm. As in the Vleeming et al. experiments, the concentrations of reactants and products in the reactor were kept constant by adjusting the reactant feed rate to the sodium hydroxide consumption rate at constant pH.

Since the purpose of this work is to study the intrinsic kinetics of the reaction, the absence of mass transfer limitations was verified for all experiments. Reactivation of the catalyst was performed by replacing the oxygen feed by nitrogen. The electrochemical potential of the catalyst was measured using a bright platinum wire and a Ag/AgCl (0.139 V vs. SHE) reference electrode. The platinum wire adapts to the average open-circuit potential of the platinum catalyst particles [5]. Catalyst reactivation can be monitored using this potential, since the potential of reduced platinum is typically 0.5 V lower than the potential of oxidised platinum. The time assumed necessary for complete reactivation was the time at which the potential had dropped 80% of the total potential difference before and after reactivation.

3. Kinetic model

A kinetic model was constructed for the selective oxidation of methyl α-D-glucopyranoside (MGP) towards sodium 1-*O*-methyl α-D-glucuronate (NaMG), using oxygen as the oxidant. This model is partially based on a model we presented at the Eighth International Symposium Catalyst Deactivation in Brugge [8]. The most important modification is that the description of the alcohol oxidation step has two electrochemical half reactions: alcohol dehydrogenation (Eqs. (1a) and (1b))

$$\mathrm{MGP}^{*}\mathrm{p} + {}^{*} \xrightarrow{k_4} \mathrm{MAGP}^{*}\mathrm{p} + 2\mathrm{H}^{+} + 2\mathrm{e}^{-} + {}^{*},$$
$$R_4 = k_4 \theta_{\mathrm{MGP}} \theta^{*} \exp\left(\frac{EF}{RT}\right) \tag{1a}$$

$$\mathrm{MAGP}^{*}\mathrm{p} + \mathrm{H_2O} + {}^{*} \rightarrow \mathrm{NaMG}^{*}\mathrm{p} + 2\mathrm{H}^{+} + 2\mathrm{e}^{-} + {}^{*} \quad \text{fast} \tag{1b}$$

and oxygen reduction (Eq. (2))

$$\mathrm{O}^{*} + \mathrm{H}^{+} + 2\mathrm{e}^{-} \xrightarrow{k_7} \mathrm{OH}^{-} + {}^{*},$$
$$R_7 = k_7 \theta_{\mathrm{O}} \exp\left(-\frac{EF}{RT}\right) \tag{2}$$

The main features of the model are discussed below.

As proposed by Vleeming et al. [2], it is assumed that the reactants, oxygen and MGP, can adsorb independently. Adsorption of organic reactants and products is assumed to take place through physisorption (Eqs. (3) and (4))

$$\mathrm{MGP} + {}^{*}\mathrm{p} \overset{K_2}{\leftrightarrow} \mathrm{MGP}^{*}\mathrm{p}, \quad \theta_{\mathrm{MGP}} = K_2 c_{\mathrm{MGP}} \theta_{\mathrm{p}}^{*} \tag{3}$$

$$\mathrm{NaMG} + {}^{*}\mathrm{p} \overset{K_3}{\leftrightarrow} \mathrm{NaMG}^{*}\mathrm{p}, \quad \theta_{\mathrm{NaMG}} = K_3 c_{\mathrm{NaMG}} \theta_{\mathrm{p}}^{*} \tag{4}$$

and two separate site balances are used. Oxygen chemisorption (Eq. (5))

$$\mathrm{O_2} + 2^{*} \xrightarrow{k_1} 2\mathrm{O}^{*}, \quad R_1 = k_1 c_{\mathrm{O_2}} \theta^{*2} \tag{5}$$

is believed to be dissociative and irreversible. The oxidation of MGP takes place in two steps (Eqs. (1a) and (1b)) via the intermediate product, methyl α-D-6-aldehydoglucopyranoside (MAGP). This aldehyde has been found only in very small amounts in the reaction mixture. It is assumed to react much faster than MGP, and as a reactive intermediate it will have a very low surface coverage.

The two electrochemical reaction steps determining the MGP oxidation rate are given in Eqs. (1a) and (2). The surface specific MGP oxidation rate R_4 increases with increasing potential E, and decreases with increasing oxygen coverage θ_{O}. The potential is determined by the reaction rates R_4 and R_7, and to a minor extent by R_6, according to the current balance $4R_4 = 2R_7 + 2R_6$. This results in Eq. (6):

$$E = \frac{RT}{2F} \ln\left(\frac{k_7 \theta_{\mathrm{O}} + k_6 \theta_{\mathrm{ox}} \theta^{*}}{2k_4 \theta_{\mathrm{MGP}} \theta^{*}}\right) \tag{6}$$

Catalyst deactivation is described with platinum surface oxide formation (Eq. (7)):

$$\mathrm{O}^{*} + {}^{*}{}_{\mathrm{s}} \xrightarrow{k_5} \mathrm{ox}^{*} + {}^{*}{}_{\mathrm{i}}, \quad R_5 = \theta_{\mathrm{O}}(1 - \theta_{\mathrm{ox}}) \tag{7}$$

which is potential independent. The platinum surface oxide reduction rate (Eq. (8))

$$\mathrm{ox}^{*} + \mathrm{H}^{+} + 2\mathrm{e}^{-} + {}^{*} \xrightarrow{k_6} \mathrm{OH}^{-} + 2^{*},$$
$$R_6 = k_6 \theta_{\mathrm{ox}} \theta^{*} \exp\left(-\frac{EF}{RT}\right) \tag{8}$$

is assumed to decrease with increasing potential. Since the potential increases with oxygen coverage θ_{O}, adsorbed oxygen will inhibit platinum oxide reduction. This accounts for the very different time scales for catalyst deactivation and reactivation.

The kinetic model equations were implemented in a reactor model with four independent differential equations regarding the variables $p_{\mathrm{O_2}}$ (partial oxygen pressure), $c_{\mathrm{O_2}}$ (bulk liquid oxygen concentration), θ_{O} (platinum surface oxygen coverage), and θ_{ox} (platinum surface oxide coverage). The reactant MGP and product NaMG concentrations are constant. In the absence of mass transfer limitations, the oxygen concentration inside the catalyst particles can be assumed to be equal to the bulk liquid oxygen concentration. The catalyst potential, which follows from Eq. (6), is uniform over the catalyst particles. The weight specific MGP oxidation rate $R_{\mathrm{w,MGP}}$ equals R_4 (Eq. (1a)) multiplied by the weight specific catalyst surface L_t.

This reaction model has been validated using MGP oxidation data from Vleeming et al. [2] and new reactivation data. All data were measured in a stirred slurry reactor at 30–60°C using platinum on graphite catalysts at pH 8. The catalyst concentration was 2–10 $\mathrm{kg\,m^{-3}}$. Mass transfer calculations showed that all experiments were carried out under intrinsic conditions. A typical result of a reactivation experiment

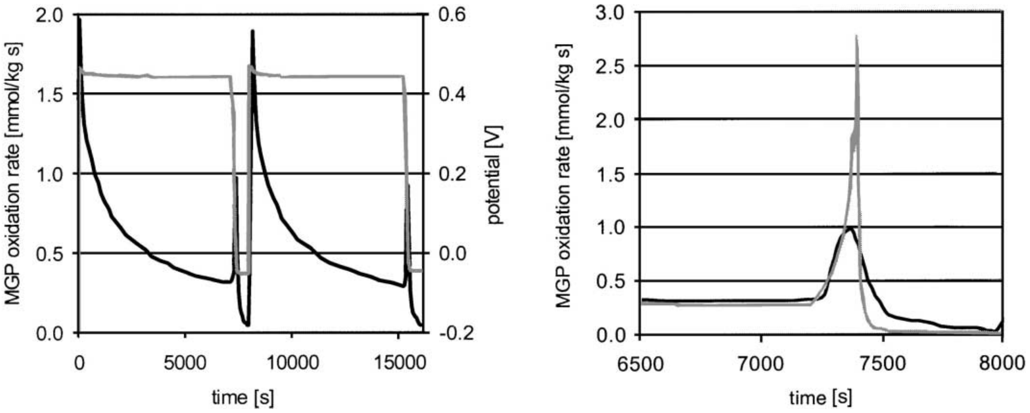

Fig. 1. Redox-cycle experiment with alternating oxygen (MGP oxidation and catalyst deactivation) and nitrogen (catalyst reactivation) feed. In the left side figure the black line indicates MGP oxidation rates (left axis), and the grey line indicates the catalyst potential vs. SHE (right axis). The right side figure shows the response of the experimental (black line) and simulated (grey line) MGP oxidation rates to the change from oxygen feed to nitrogen feed after 7200 s.

is displayed in Fig. 1. In this experiment at 50°C and MGP concentration 50 mol m^{-3}, the time necessary for reactivation after 7200 s of oxidation was 198 s. An interesting feature is the initial increase in MGP oxidation rate during reactivation, which is caused by the negative reaction order in oxygen under the given circumstances.

Regression was performed to find the best set of parameters to describe 14 reaction rate profiles from 0 to 10 000 s (40 data points each), as measured by Vleeming et al. [2], and nine reactivation data points. The temperature range studied was 30–60°C; the MGP concentration range was 5.6–420 mol m^{-3}; the oxygen partial pressure range was 20–100 kPa; the pH was 8.

The optimal parameter set is presented in Table 1. The parameters k_4 and k_5 are calculated according to the Arrhenius equation $k_i = A_{0,i}\exp(-E_{a,i}/RT)$. The parameters $A_{0,4}$, k_6 and k_7 are valid for potentials referred to the SHE. The RHE equals SHE, corrected for pH according to $E_{\mathrm{RHE}} = E_{\mathrm{SHE}} - (RT/F)\ln_{10}$ pH. At pH 8 and 50°C the potential difference between RHE and SHE is 0.513 V.

Table 1
Kinetic parameter set for the model

Parameter	Value
k_1 (m^3 mol^{-1} s^{-1})	6.5×10^3
K_2 (m^3 mol^{-1})	1.26×10^{-2}
K_3 (m^3 mol^{-1})	1.77×10^{-1}
$A_{0,4}$ (s^{-1})	2.76×10^5
$E_{a,4}$ (J mol^{-1})	6.71×10^4
$A_{0,5}$ (s^{-1})	5.80×10^1
$E_{a,5}$ (J mol^{-1})	2.89×10^4
k_6 (s^{-1})	1.61×10^4
k_7 (s^{-1})	3.53×10^5

The regression results are shown in Figs. 2–7. For convenience of comparison, experimental and calculated MGP consumption rates are displayed at only

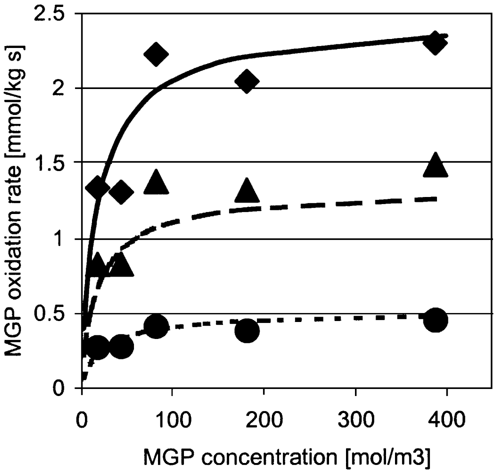

Fig. 2. Experimental and calculated MGP consumption rates at $t = 0$ (diamonds and drawn lines), $t = 1000$ s (triangles and dashed lines), and $t = 10\,000$ s (circles and dotted lines).

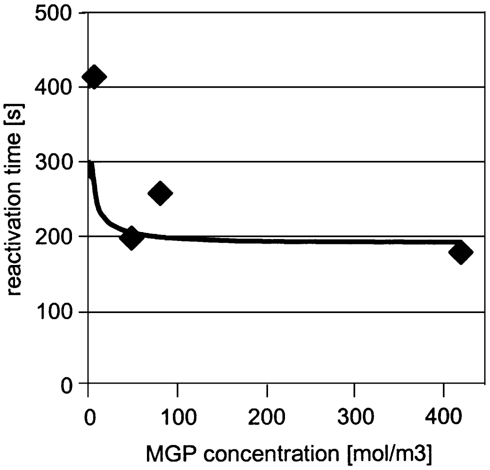

Fig. 3. Experimental and calculated reactivation time (diamonds and drawn lines).

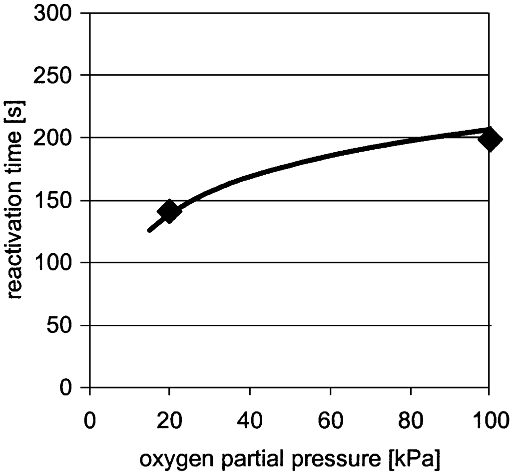

Fig. 5. Experimental and calculated reactivation time (diamonds and drawn lines).

three points in time: 0, 1000 and 10 000 s. An interesting phenomenon is the increase in MGP oxidation rate with decreasing oxygen partial pressure, which was also observed in the initial stage of reactivation (Fig. 1). Under the reaction conditions studied, the catalyst coverage with oxygen species as calculated with the present model exceeds 98%. Since free catalyst sites are necessary for MGP dehydrogenation to proceed (Eq. (1a)), a lower oxygen and oxide coverage increases the MGP oxidation rate. However, the oxygen coverage increases the catalyst potential and hence the activity of the catalytic sites. The MGP oxidation rate will decrease below 50% oxygen coverage ($\theta_O < 0.5$), a situation that will occur at low oxygen partial pressure and in the case of oxygen transfer limitation.

Fig. 8 shows the simulated catalyst potential, surface coverages, and oxygen concentration against time for a typical reactivation situation. Apparently,

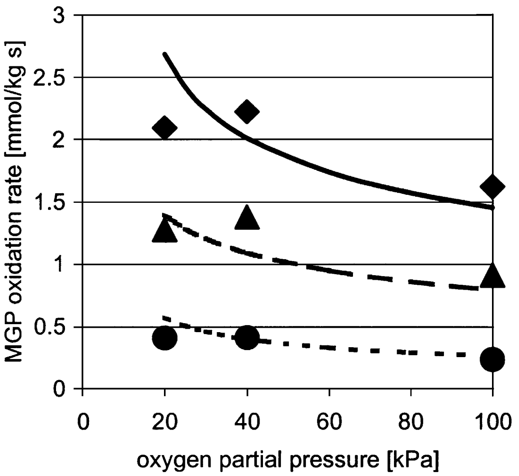

Fig. 4. Experimental and calculated MGP consumption rates at $t = 0$ (diamonds and drawn lines), $t = 1000$ s (triangles and dashed lines), and $t = 10\,000$ s (circles and dotted lines).

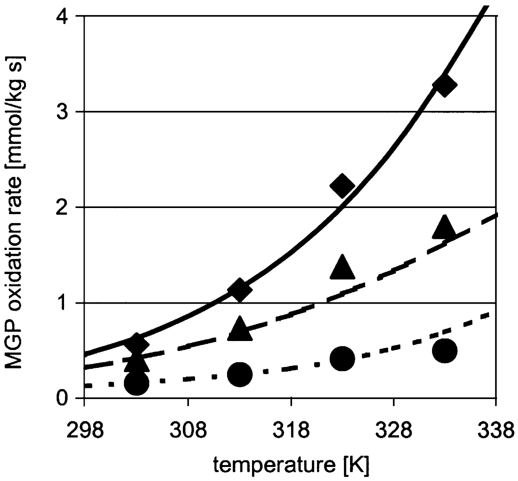

Fig. 6. Experimental and calculated MGP consumption rates at $t = 0$ (diamonds and drawn lines), $t = 1000$ s (triangles and dashed lines), and $t = 10\,000$ s (circles and dotted lines).

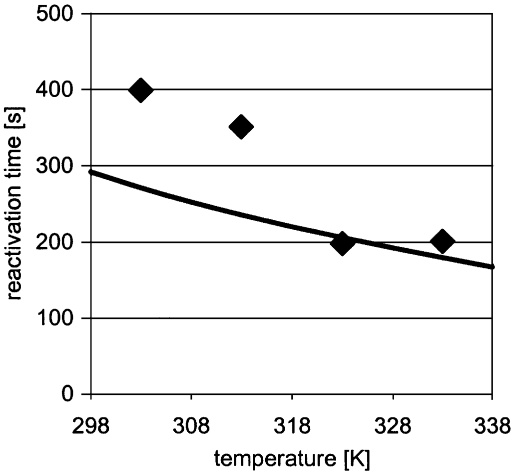

Fig. 7. Experimental and calculated reactivation time (diamonds and drawn lines).

oxide reduction takes place in three consecutive steps. In the first step (until $t = 145$ s), oxygen adsorption is fast enough to maintain an oxygen covered surface. As the dissolved oxygen concentration approaches zero, the adsorbed oxygen coverage and the potential decays rapidly. After a threshold oxygen coverage is reached ($t = 165$ s), the potential has dropped sufficiently for the actual platinum oxide reduction to begin. This oxide reduction is completed within 25 s.

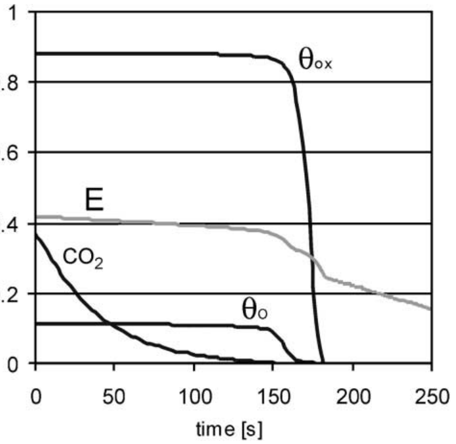

Fig. 8. Responses of dissolved oxygen concentration c_{O_2} (mol m^{-3}), adsorbed oxygen coverage θ_O (–), oxide coverage θ_{ox} (–), and potential E (V vs. SHE) to a step in gaseous oxygen feed from 40 to 0 kPa at $t = 0$ after 7200 s of reaction (same y-axis for all variables).

It should be noted that the present model has only been validated with intrinsic kinetic data, assuming no concentration gradients for oxygen and the organic reactants inside the catalyst particles. The model might hold under mass transfer limited conditions if concentration gradients inside the catalyst particles are considered.

4. Redox-cycle operation

Redox-cycle operation implies alternating exposure of the active phase (the catalyst) to oxidative and reductive circumstances. In view of the rapid catalyst deactivation observed, which exceeds 80% after 5000 s, the catalyst performance can be improved substantially by applying reactivation treatments. It was shown in the previous section that deactivation by over-oxidation can be reversed by interrupting the oxygen flow for a short period, typically 200 s. The reactivation can be monitored using the catalyst open-circuit potential [5].

As several organic reactants are likely to form poisoning degradation products on reduced platinum, the reductive period of the redox cycle should be minimised. The benefits of redox-cycle operation are demonstrated in Fig. 9, in which the MGP consumption per hour is plotted against the duration of the oxidative period of the redox cycle for three different reactivation times (240, 360, and 600 s). In the oxidative period 40 kPa oxygen and 60 kPa nitrogen are fed, and in the reductive period 100 kPa nitrogen is fed. It is obvious that the shortest reactivation period gives the highest MGP consumption in all cases, since the reductive part of the redox cycle is the least productive. It is surprising that the optimal oxidation period is extremely short, e.g. 100 s for the 360 s reduction period. Using this redox cycle, oxygen is fed during only 22% of the time. This clearly indicates the advantage of applying redox cycles during platinum catalysed aqueous alcohol oxidations. It should be noted that the model probably over-estimates the reaction rate under mass transfer limited circumstances. If the oxygen concentration is low, oxygen will not reach the inner part of the catalyst particles, and the catalyst effectivity will be low. This is likely to occur in the beginning of the oxidation period and in the end of the reactivation period.

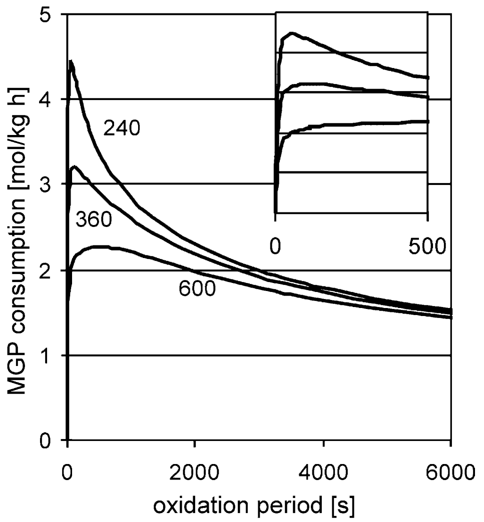

Fig. 9. Influence of the length of the oxidative period of the redox cycle on time-averaged MGP consumption for three different reactivation times (240, 360, and 600 s). The inset is a detail, showing the MGP consumption for oxidation periods up to 500 s.

The solubility of the reactant oxygen in water is low, typically 1 mol m^{-3}. Gas–liquid oxygen transfer is the most critical mass transfer step. Hence, attention has to be given to the influence of oxygen mass transfer on the oxygen concentration in the liquid during reaction and during reactivation. Gas–liquid mass transfer influences the removal of dissolved oxygen from the reactant solution, which is the first and slowest step in catalyst reactivation. This oxygen removal can be enhanced by faster gas phase replacement, and a larger gas–liquid interfacial area. If oxygen is not purged from the solution, it has to be removed completely by reaction, which will take longer time. As Kluytmans et al. [9] suggested, the redox cycle can be implemented into a bubble column, which operates as an air lift loop reactor. The catalyst travels through an aerobic zone (the riser), and an anaerobic zone (the downcomer), in which reactivation takes place.

5. Conclusions

Under aqueous alcohol oxidation circumstances, platinum catalyst deactivation can be caused either by over-oxidation (in the presence of oxygen) or by catalyst poisoning (in the absence of oxygen). Deactivation by platinum over-oxidation can be reversed by brief exposure (typically 4–10 min) of the catalyst to a reductive environment, e.g. oxygen-free reactant solution, which is called a redox cycle. The reaction, deactivation, and reactivation kinetics for a typical reactant, methyl α-D-glucopyranoside, are properly described by the kinetic model. In this model, the rate determining steps are electrochemical half reactions. The kinetic model was implemented into a three-phase stirred slurry reactor model and validated with methyl α-D-glucopyranoside oxidation experiments. The applicability and advantages of redox cycles for reactor operation were demonstrated, and further improvements were suggested.

References

[1] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.
[2] J.H. Vleeming, B.F.M. Kuster, G.B. Marin, Ind. Eng. Chem. Res. 36 (1997) 3541.
[3] A.P. Markusse, B.F.M. Kuster, D.C. Koningsberger, G.B. Marin, Catal. Lett. 55 (1998) 141.
[4] G. Horányi, Catal. Today 19 (1994) 285.
[5] T. Mallat, A. Baiker, Catal. Today 24 (1995) 143.
[6] J.F.E. Gootzen, A.H. Wonders, A.P. Cox, W. Visscher, J.A.R. van Veen, J. Mol. Catal. A 127 (1997) 113.
[7] A.P. Markusse, B.F.M. Kuster, J.C. Schouten, in: Proceedings of the International Memorial K.I. Zamaraev Conference, Novosibirsk, 1999, J. Mol. Catal. A 158 (2000) 215.
[8] A.P. Markusse, B.F.M. Kuster, J.C. Schouten, in: Proceedings of the Eighth International Symposium on the Catalyst Deactivation, Brugge, 1999, Stud. Surf. Sci. Catal. 126 (1999) 273.
[9] J.H.J. Kluytmans, A.P. Markusse, B.F.M. Kuster, G.B. Marin, J.C. Schouten, Catal. Today 57 (2000) 143.