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Engineering aspects of the aqueous noble metal catalysed alcohol oxidation

J.H.J. Kluytmans [a], A.P. Markusse [a], B.F.M. Kuster [a,*], G.B. Marin [b], J.C. Schouten [a]

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

[b] *Laboratory of Petrochemical Engineering, University of Gent, Krijgslaan 281 S5, B-9000 Gent, Belgium*

Abstract

The aqueous noble metal catalysed alcohol oxidation is a reaction which can profitably be applied in fine-chemistry and for carbohydrate conversion. In this paper engineering aspects of this reaction are treated, i.e. the reaction kinetics, oxygen mass transfer restrictions, catalyst deactivation and reactivation, and implications for reactor design and operation.

First a reaction mechanism is proposed, which is very helpful for understanding the observed phenomena. Also a short summary is given on catalyst deactivation mechanisms.

Two different reaction regimes can clearly be distinguished: the oxygen mass transfer limited regime and the intrinsic kinetic regime, which are treated separately. Oxidations using noble metal catalysts promoted with less noble metals, like Pb, Bi, generally fall in the first regime, those using unpromoted noble metals in the second. Reaction rate data are evaluated for the Pd/Bi catalysed oxidation of glucose and the Pt catalysed oxidation of methyl-glucoside, respectively, illustrating the typical kinetic behaviour in both regimes.

From oxidation kinetics in the mass transfer limited regime, it is concluded that adherence of catalyst particles to the gas–liquid interface, is a major factor determining reaction kinetics. Oxygen transfer, direct from the gas to the catalyst particle, is likely. For the Pt catalysed oxidation, a kinetic model is presented for catalyst deactivation by over-oxidation and for catalyst reactivation.

Finally specific reactor options and suggestions for future engineering research are given: slurry catalyst versus fixed bed catalyst operation, avoidance of explosion risks, redox cycle reactors, electrochemical reactors, and multi-functional reactors.

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Nomenclature

a	gas–liquid interfacial area $\left(\mathrm{m}^2/\mathrm{m}_\mathrm{L}^3\right)$
a_S	external, specific, catalyst surface area (m^2/kg)
C_cat	catalyst concentration $\left(\mathrm{kg}/\mathrm{m}_\mathrm{L}^3\right)$
C_i	oxygen, liquid side, interface concentration $\left(mol/\mathrm{m}_\mathrm{L}^3\right)$
D	diffusion coefficient (m^2/s)
D_e	effective diffusion coefficient (m^2/s)
d_p	catalyst particle diameter (m)
E	gas–liquid mass transfer enhancement factor (–)
k_L	gas–liquid mass transfer coefficient (m/s)
k_S	liquid–solid mass transfer coefficient (m/s)

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[*] Corresponding author.

E-mail address: tgtcbk2@chem.tue.nl (B.F.M. Kuster).

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k_w	first-order, specific, reaction rate coefficient (m^3/kg/s)
R_v	volumetric reaction rate $\left(mol/\mathrm{m}_\mathrm{L}^3/\mathrm{s}\right)$
R_w	weight specific reaction rate (mol/kg/s)
η	effectiveness factor (–)
ϕ	Thiele number (–)
θ	fractional surface coverage (–)
ρ	density (kg/m^3)

Abbreviations

MGP	methyl-glucopyranoside
NaMG	sodium methyl-glucuronide

Subscripts

G	gas phase
L	liquid phase
O	oxygen
*	free site

1. Introduction

The aqueous noble metal catalysed alcohol oxidation, resulting in ketonic, aldehydic and carboxylic acid groups, is a very useful reaction for carbohydrate conversion and for application in fine-chemistry. The reaction has been reviewed in 1994 by Mallat and Baiker [1]. This review will be used as a start for the present publication.

Within our laboratory the reaction has been the subject of kinetic studies since 1967, when van der Baan and de Wilt started exploring catalytic conversion of sugars as renewable, chemical raw materials. The platinum catalysed oxidation of glucose to gluconic acid was the first reaction studied [2,3], followed by its further oxidation to glucaric acid [4–7]. Using lead promoted platinum, the selectivity for further oxidation of sugars changed from aldaric to 2-keto carboxylic acids [8,9]. Developing new routes for vitamin C synthesis and applications of carbohydrates in detergents, the platinum catalysed oxidation of glucosides was undertaken [10–15]. Ethanol was used as model reactant for in depth kinetic studies with in situ catalyst characterisation [16–20]. Bismuth promoted palladium was used for lactose oxidation [21] and bismuth, lead and tin promoted platinum for propylene glycol oxidation [22]. Finally, the platinum catalysed oxidation also has been explored for wastewater treatment up to 200°C [23,24].

In order to give a proper treatment of the kinetic aspects of this reaction, it is useful to discern two extreme regimes, which will be treated separately. The first one is the so-called *intrinsic kinetic regime*, i.e. the reaction rate is *only* determined by the chemistry at the catalytic site and not limited by mass transfer and diffusion effects, and the second one is the full *oxygen mass transfer limited regime*, i.e. the reaction rate *only* depends on oxygen mass transfer and diffusion. Generally, the reactions using unpromoted platinum fall in the first category [4–7,10–20], whereas those using promoted platinum [8,9,22] and palladium [21] fall in the second category. Literature data from other authors ([1], references cited therein) always concern batchwise oxidations, where the mixing characteristics of the laboratory reactor used are rather unspecified. Generally these data fall in a mixed regime, where the reaction rate is partly limited by oxygen mass transfer at the start of the reaction with a fresh, active catalyst, and finally, when the reactivity of the mixture is diminished or the catalyst becomes partly deactivated, one ends up in the kinetic regime.

It is the goal of the present paper to give a short, quantitative treatment of the kinetics of the reaction for both regimes in a generalised way, based on data from our laboratory. The kinetics, catalyst deactivation characteristics and safety restrictions, will result in suggestions for future reactor options and engineering research, which will be given at the end of the paper.

Starting from the review of Mallat and Baiker [1], we will first present a simplified reaction mechanism and a short summary on catalyst deactivation [12]. The first main part will give details on oxygen mass transfer and diffusion, and on oxygen mass transfer enhancement by catalytic particles, adsorbing to the gas bubbles. In the second main part, the intrinsic kinetics of the oxidation reaction, of the catalyst deactivation by “over-oxidation”, and of catalyst reactivation will be treated.

Although it certainly is an engineering aspect, heat transfer will not be addressed due to the limited size of this paper. The treatment of experimental data is generally restricted to Pt and Pd catalysts on carbon carriers: active carbon, carbon fibrils and graphite.

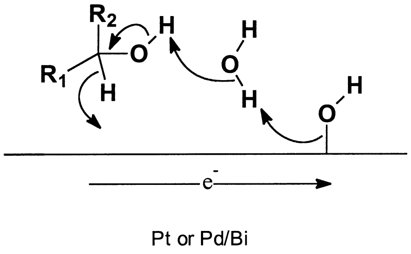

Fig. 1. Proposed mechanism for the oxidation reaction, featuring hydride transfer to a metallic site, electron transfer through the catalyst, (remote) reduction of surface hydroxyl and proton migration by hydrogen bond shifts.

2. Oxidation mechanism

For an easy understanding of our treatment of kinetic data and oxygen mass transfer effects, we propose for the oxidation mechanism, a hydride transfer from the alcohol to a free, metallic site, simultaneous with a reduction of a surface hydroxyl (or oxygen) group, as depicted in Fig. 1. This proposal allows for a kinetic formula, properly fitting our experimental data, and can also help to explain mass transfer limited kinetics, as will be made clear in the following sections.

Essential features of this mechanism are: the product R_1R_2CO is formed in one single step by simultaneous deprotonation and hydride transfer, the rate of this step is likely to increase at higher pH and at higher potential of the catalyst, i.e. at electron deficient free metallic sites, this step is immediately followed by desorption of H^+ and OH^- from surface H and OH, the catalyst acts as a short-circuited electrochemical cell, i.e. the alcohol dehydrogenation and the oxygen reduction may be locally separated, while electrons are transferred through the metal and the carrier and protons through the catalyst pores. In the overall reaction 2 surface-OH will be used, which is equivalent to 1 surface-O.

In accordance with the mechanism, hydrogen can be formed during the reaction. This “spontaneous” dehydrogenation can occur at high pH, but also at low pH under the influence of oxygen adsorption. Therefore, explosion risks exist for special situations. This will be further treated in Section 6.

The catalyst potential, reflecting the balance between alcohol oxidation and oxygen reduction, can take values between 0 V (relative to the reversible hydrogen electrode, RHE) for a reduced surface and about 1 V for an oxidised surface. This catalyst potential can be measured during an oxidation reaction (1), it will be high during an intrinsic kinetic experiment and low for oxygen mass transfer limited conditions.

3. Catalyst deactivation

A short overview on catalyst deactivation is presented, based on Mallat and Baiker’s review [1] and our recent work [12]. We treat the phenomena in the order of increasing catalyst potential. As stated already in the introduction, we mainly refer to carbon carried catalysts.

3.1. Crystallite agglomeration

In a strongly reducing environment noble metal crystallites become mobile on the carbon support, probably due to destruction of the anchoring sites. The result is agglomeration of metal crystallites and a reduction of available active surface. The effect is especially pronounced at high pH. These circumstances should be avoided [12].

3.2. Inhibition (poisoning, coking, product inhibition)

This type of deactivation may occur at any potential, but is generally more pronounced in the lower potential range. Poisoning can be due to impurities in the reactor feed, to too much promoter metal [21], and to strongly adsorbing intermediates or side products, e.g. CO, which are especially formed in the low potential range. Polymer or tar formation (coking) from reactive intermediates results in pore filling and loss of activity. Finally, an adsorbing main product, e.g. carboxylic acids at low pH, will prevent the starting reactant from reaching the catalytic site. This can be avoided by working at pH > 7 [25] or by removing the product by e.g. ion-exchange or electrodialysis.

3.3. Over-oxidation (corrosion)

Working under kinetic control, the catalyst potential will be close to 1 V immediately after the start of a reaction, and deactivation is caused by “over-oxidation”, i.e. an inactive oxidised, corroded surface is slowly formed and catalyst activity drops typically by a factor 5 within 2 h [14]. This type of deactivation is reversible.

It was found that promoted catalysts are more sensitive to over-oxidation, i.e. if there is no mass transfer limitation of oxygen, these catalysts show no activity at all from the start of reaction [8,9,21,22]. These catalysts probably only work well below the potential, where the promoter metal is oxidised to a too high oxidation state.

In their review, Mallat and Baiker [1] suggest a causal sequence: chemical poisoning → over-oxidation → corrosion. This might hold for many literature data for batchwise oxidations, as mentioned already in the introduction, but in fact over-oxidation is an independent phenomenon for which poisoning is no prerequisite [14]. Furthermore, it should be noted, that our experimental data point to the conclusion that promotion improves catalyst activity, by an apparent increased dehydrogenation activity, possibly caused by prevention of poisoning [1]. The most likely result will be that over-oxidation does not occur, due to oxygen mass transfer limitation. Therefore, also the causal sequence given by Gallezot [26], that "promotion improves catalyst activity by preventing over-oxidation", better can be reverted to "promotion prevents over-oxidation by improving catalyst activity".

3.4. Crystallite growth, leaching

After prolonged over-oxidation, especially in the presence of chelating substances or high pH, metal crystallites inside the catalyst pores are growing (Ostwald ripening) due to dissolution and redeposition, i.e. large crystallites are formed at the expense of the small ones. This generally results in permanent loss of catalyst activity [10,12]. If such conditions persist, the active metal may leach from the catalyst and get lost. Obviously such conditions should be avoided.

3.5. Promoter leaching

As the promoters used, e.g. Pb, Sn, Bi, are less noble than Pt and Pd, they are most susceptible to leaching. In fact, it can be stated that the location of the promoter is a rather dynamical one, where it can be present on the noble metal crystallite, on the catalyst support [8,9,22] or in solution [26–28]. Oxidative conditions and chelating agents will lead to excessive promoter leaching, which is detrimental for industrial application. However, this problem can be largely overcome by a short reductive treatment of the product solution in the presence of the catalyst, where virtually all promoter is readsorbed from solution by the catalyst [27,28]. Low promoter loadings generally result in insignificant leaching [26].

From the overview, given above, it might be clear what the pitfalls are for industrial application of the noble metal catalysed alcohol oxidation. Conditions which favour crystallite growth and agglomeration, leaching of metals, and tar (coke) formation, must be avoided. How to cope with the problems of over-oxidation will be further treated in Section 5. Consequences of poisoning and product inhibition for reactor design and operation, will be treated in Section 6.

4. Oxygen mass transfer

For the oxidative dehydrogenation of an alcohol to proceed, oxygen has to be transferred from the gas phase to the liquid phase, to the catalyst particle and, finally, has to diffuse to the catalytic site inside the particle. A typical concentration profile is shown in Fig. 2.

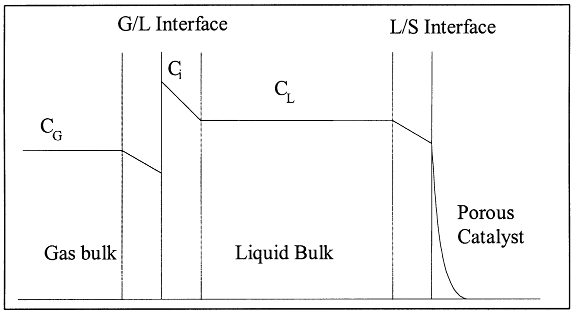

Fig. 2. Mass transfer and reaction in series for a porous catalyst. Concentration profile for a dissolving gas, transferred to the catalyst surface and reacting inside the catalyst, C_i being the interface, equilibrium concentration. For oxygen dissolving in water, C_G is not to scale, actually $C_G \sim 50\,C_L$.

Since the solubility of oxygen in water is very low, typically 1 mol/m^3 at ambient conditions using 100% oxygen gas and pure water, and the alcohol concentration generally is in the range of 1000 mol/m^3, it is allowed to only consider oxygen transfer and diffusion as being the limiting factor for the reaction rate. In the following we will give a short treatment of the implications of general accepted mass transfer theories for our reaction. Detailed information can be found in the comprehensive review of Beenackers and van Swaaij [29] on mass transfer in gas–liquid slurry reactors.

Neglecting mass transfer resistance in the gas phase, and assuming a first-order disappearance reaction for oxygen at the catalytic site, which is not unlikely for oxygen reduction at low potential, the following equation can be used to estimate the volumetric reaction rate, R_v

$$\frac{C_i}{R_v} = \frac{1}{k_L a E} + \frac{1}{k_s a_s C_{cat}} + \frac{1}{\eta k_w C_{cat}}, \tag{1}$$

where C_i is the oxygen, liquid side saturation, interface concentration, C_{cat} the catalyst concentration, k_L the gas to liquid mass transfer coefficient, a the specific gas–liquid contact area, k_s the liquid to solid mass transfer coefficient, a_s the specific solid interfacial area, k_w the specific reaction rate constant, η the catalyst efficiency, and E the enhancement factor for gas–liquid mass transfer.

The catalyst efficiency, η, is given by

$$\dot{\eta} = 3/\phi^2(\phi/\tanh\phi - 1), \tag{2}$$

where ϕ is the Thiele modulus, given by

$$\phi = d_p/6(\rho_{cat} k_w / D_e)^{1/2} \tag{3}$$

with d_p the particle diameter, ρ_{cat} the catalyst density, and D_e the effective diffusion coefficient.

Oxygen mass transfer and diffusion, set certain limits to the attainable reaction rates, which will be dealt with in the following sections. Rate data for the glucose oxidation, using Pd/Bi catalyst [30], will be used as illustration.

4.1. Internal diffusion

Supposing $k_L a$ and $k_S a_S$ high, Eq. (1) reduces to

$$R_v = \eta k_w C_{cat} C_i \quad \text{or} \quad R_w = \eta k_w C_i, \tag{4}$$

where R_w being the weight specific reaction rate.

Substituting experimental data for glucose oxidation, $R_w = 0.04$ mol O$_2$/kg/s and $C_i = 0.1$ mol/m^3 (when using 10% oxygen in the gas phase), results in a minimum value for $\eta k_w = 0.4$ m^3/kg/s. Substituting $D_e = 4 \times 10^{-10}$ m^2 s^{-1}, $\rho_{cat} = 700$ kg m^{-3}(dry cat), $d_p = 30 \times 10^{-6}$ m results in $\phi/\tanh\phi \sim 7$, and the Thiele modulus, $\phi = 7$. This means that the effectiveness factor will be lower than 0.3 [31], or that oxygen is only present in the outer layer of the catalyst particle. However, if transfer resistances in the gas–liquid and the liquid–solid boundary layers cannot be neglected, the oxygen concentration at the catalyst outer surface is much lower than the saturation concentration. Consequently, probably $\eta k_w > 0.4$ m^3/kg/s, $\phi > 7$, and $\eta < 0.3$.

4.2. Liquid–solid mass transfer

To estimate the limitations set by liquid–solid mass transfer, it is appropriate to use correlations for k_S [29] of the form

$$Sh = \frac{d_p k_s}{D} = 2 + 0.4 Re^{0.25} Sc^{0.33}, \tag{5}$$

where *Sh*, *Re*, and *Sc* are the Sherwood, Reynolds, and Schmidt number, respectively. The lowest value for *Sh* will be 2, and the highest estimated value 5.5, substituting the physical data, $Sc \sim 200$ and taking into account dissipation of mixing energy, 4 kW/m^3, giving $Re \sim 3.8$. This leads to a range for k_S between 2×10^{-4} and 6×10^{-4} m/s. Taking $k_S = 5 \times 10^{-4}$ m/s and the values for ρ_{cat} and d_p mentioned before, results in $k_S a_S = 0.15$ m^3/kg/s.

If liquid–solid mass transfer would be the only rate determining factor, Eq. (1) reduces to

$$R_v = k_s a_s C_{at} C_i \quad \text{or} \quad R_w = k_s a_s C_i. \tag{6}$$

It now appears that the maximum $R_w = 0.015$ mol O$_2$/kg/s, which is almost lower by a factor of 3 than the experimental value! Apparently, the standard procedure, assessing transfer limitation, fails. The most logical explanation for this exceptional result is, that the main route for oxygen mass transfer to the catalyst, bypasses the bulk liquid and is taken place directly from the gas phase to the, liquid filled, catalyst particle.

4.3. Gas–liquid mass transfer

It is generally supposed, that gas–liquid mass transfer is the most limiting factor for the glucose oxidation, which would be proven experimentally by measuring the dissolved oxygen concentration in the bulk solution, being almost 0 (zero) [21]. For this extreme situation, Eq. (1) reduces to

$$R_v = k_L a E C_i. \tag{7}$$

Many correlations can be found in literature [29], to estimate $k_L a$ for different gas–liquid contactors. The value for $k_L a$ mostly is in the range 0.05–0.5 1/s, depending on superficial gas velocity and stirring rate. For our glucose oxidation reactor, using a stirring rate of 1500 rpm, we estimated $k_L a \sim 0.46$ 1/s. At a catalyst load of $C_{cat} = 1$ kg/m^3, the experimental value for R_v/C_i was 0.57 1/s, as can be seen in Fig. 3. This would result in an apparent enhancement factor, $E \sim 1.2$, which is a reasonable value [29].

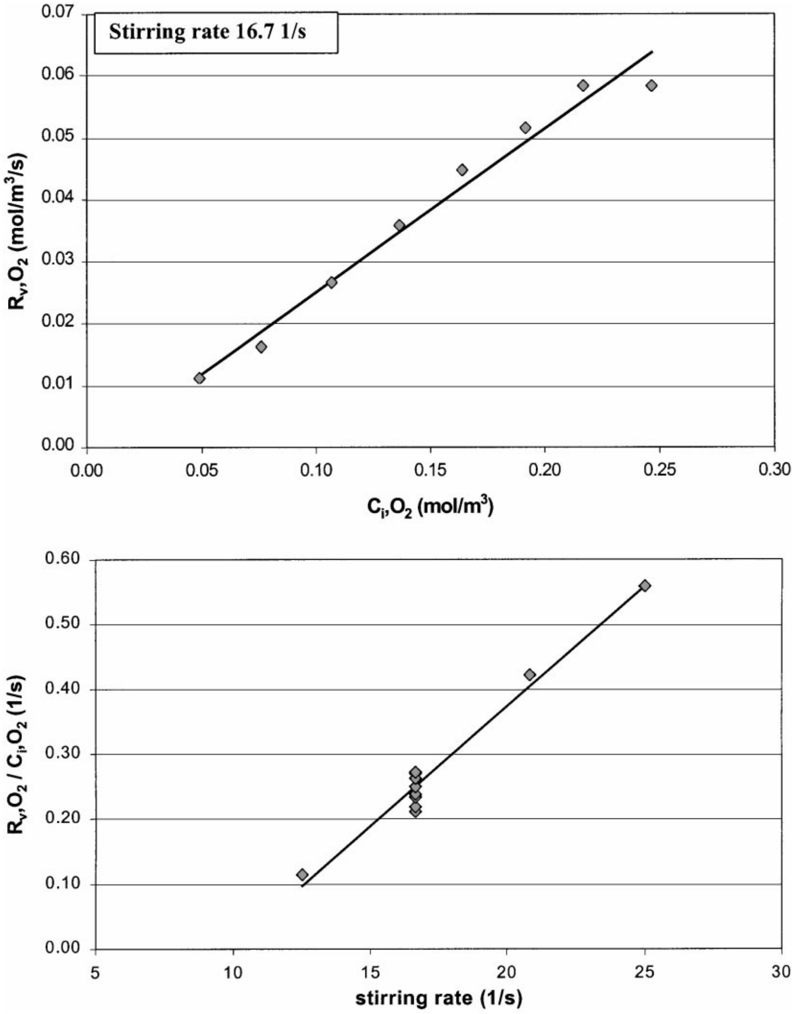

Fig. 3. Reaction rate data for batchwise glucose oxidation over a 5% Pd on active carbon catalyst, Pd/Bi = 5 mol/mol. Initial $C_{gluc} = 500$ mol/m^3, conversion 0–90%, $C_{cat} = 1$ kg/m^3, 50 C, pH 9. The stoichiometric ratio glucose/O_2 = 2.

Enhancement of gas–liquid mass transfer, accounted for by the factor E, can be caused by fine catalyst particles, which are present in the diffusion layer around the gas bubbles. The effect is especially important for carbon particles, which have the tendency to bind to the gas–liquid interface. This effect is reasonably documented and attempts have been made to quantify it [29]. Most recent quantitative descriptions are given by Van der Zon et al. [32]. Up to now however, it is not possible to give reliable, quantitative predictions for the enhancement factor, E. The reason is that solid–gas adhesion is strongly dependent on the physical properties of the catalyst, like hydrophobicity, iso-electric point and catalyst potential, which are generally unknown and, if already known for the fresh catalyst, probably will change during reaction due to adsorption of reactants and products, due to a changing potential and due to slow changes of carbon surface characteristics.

So far, the generally accepted supposition, that the reaction rate is determined by gas–liquid mass transfer, looks reasonable. However, there are some good reasons to doubt it, as will be made clear in the sections below.

4.4. *Influence of catalyst load on the volumetric reaction rate*

For “intrinsic” chemical kinetic conditions, the volumetric reaction rate, R_{v}, generally is linear proportional to the catalyst load. The same holds if the rate is limited by internal diffusion or liquid–solid mass transfer, see Eqs. (4) and (6). However, if the rate would be fully determined by gas–liquid mass transfer, it would be independent of the catalyst load, see Eq. (7), provided there is no enhancement ($E=1$) due to catalyst particles adhering to the gas–liquid interface. If enhancement occurs, and the amount of catalyst present at the gas–liquid interface is proportional with the catalyst load, it can be proven that the volumetric reaction rate will be proportional with the square root of this load [22,29]. However, if the catalyst load is so high, that the gas–liquid interface is fully occupied with solid particles, it can be expected that the volumetric reaction rate will reach its high limit.

For our test reaction at hand, not yet sufficient data are available to fully assess the influence of catalyst load [30].

4.5. *Influence of concentrations and stirring rate*

In Fig. 3 data [30] are plotted, which we obtained for several batchwise glucose oxidations, using different stirring rates and different feed flows of oxygen. The reaction rate appeared to be fully independent of conversion up to 90%, and proportional to the *gas phase* oxygen concentration, or the calculated equilibrium interface oxygen concentration, C_{i}. Apparently, Eq. (1), or the special case Eqs. (4), (6) and (7), give an exact description of the reaction rate.

Furthermore it appears, that the reaction rate depends almost linearly on the stirring rate. The line cutting the x-axis at about 10 1/s, marking the onset of gas bubble formation in the reactor system used.

As is clear from the equations and Fig. 3, very high reaction rates can be realised using pure oxygen. This is in accordance with the high reaction rates obtained by Smits et al. [8,9] for the Pt/Pb catalysed oxidation of glucose and those obtained by Hendriks et al. [21] for the Pd/Bi catalysed oxidation of lactose. We discovered that for the Pd/Bi catalysed oxidation of glucose [27], and especially of galactose, the use of pure oxygen leads to explosive conditions. We will come back to this issue in Section 6.

4.6. *Final assessment of mass transfer limitations*

The limitations, set by liquid–solid mass transfer as pointed out before, are so restrictive, that we propose that oxygen diffusion through stagnant liquid boundary layers, as depicted in Fig. 2, is not the actual mechanism of mass transfer, and that a considerable portion of the catalyst will be in direct contact with the gas phase. Furthermore, Hendriks et al. [21] showed that the reaction rate is strongly dependent on the amount of promoter used. Reaction rates could differ by an order of magnitude. These large differences are very unlikely to be caused by a different enhancement factor, E, especially while the physical characteristics of the system did hardly change. Therefore, we propose a modification of Eq. (4)

$$R_{\mathrm{v}} = f_{\mathrm{cat}}\eta k_{\mathrm{w}} C_{\mathrm{cat}} C_{\mathrm{i}}, \tag{8}$$

where f_{cat} is the fraction of the outer catalyst particle surface in direct contact with gas.

This fraction is dependent on the available bubble surface, the amount of catalyst, and the solid–gas adhesion forces. For highly reactive systems it might be necessary to take into account additional mass transfer resistance in the gas phase. However, liquid mass transfer resistances, represented by k_L and k_S, are ruled out.

It is clear from the above, that the classical treatment of mass transfer resistances in series, fails for carbon carried catalysts, adhering to the gas bubbles. Nevertheless, often very simple rate equations can be derived, the reaction rate being independent of the conversion of the organic reactant, and first order in the *gas* phase oxygen concentration. The dissolved oxygen concentration, being almost zero, plays no role in the kinetics. The kinetic formulas derived, can be used to estimate reactor performance under circumstances where the reaction rate is determined by oxygen reduction on a catalyst at low potential.

5. Intrinsic oxidation kinetics, catalyst deactivation and reactivation

If the dehydrogenation activity of the catalyst for the alcohol is relatively low, one has to work at higher catalyst potential, i.e. without too much oxygen mass transfer limitation, in order to carry out the reaction at sufficient rate. Such conditions typically apply for the Pt-catalysed oxidation of primary alcohols to carboxylic acids via the intermediate aldehydes. The stoichiometric ratio alcohol/$O_2 = 1$ applies for the overall reaction. The reaction typically proceeds at rates 1–10 mmol/kg/s, which are an order of magnitude lower than the oxygen mass transfer limited rates, mentioned before. Under such conditions the Thiele number, ϕ, is low, <2.5, resulting in catalyst effectiveness >80%, i.e. hardly any concentration gradient exists inside the catalyst particle. Also liquid–solid and gas–liquid mass transfer are not limiting the reaction rate. The dissolved oxygen concentration is practically the same as its saturation concentration.

5.1. Catalyst over-oxidation and reactivation

From intrinsic kinetic studies, carried out in our laboratory in continuous stirred tank reactors, where the catalysts are subjected to an environment without any change, i.e. concentrations are constant during the run, it was clearly proven that deactivation occurs due to over-oxidation of the catalytic surface. Catalyst activity could be fully restored by interrupting the oxygen flow to the reactor for a sufficient long time in order to let the alcohol reduce the surface. An example of such behaviour is given in Fig. 4 for methyl-glucoside oxidation. The same behaviour also has been found for gluconic acid [4–7], ethanol [16–20], cyclohexanol [33] and ammonia [24] oxidation.

5.2. Kinetic modelling, rate determining step, non-linearity

Kinetic modelling of a reaction is useful for reactor design, for optimising reaction conditions, and it also may help in elucidating a reaction mechanism. However, often the same experimental results can be fitted with different models, a single mechanism may lead to different models, and even different mechanisms may lead to the same model. Therefore, it is not surprising that, based on limited sets of experimental data, several kinetic models, which might look mathematically rather different, have been presented in our previous publications. However, the basic element in most of the models was that the alcohol dehydrogenation rate could be given by $R_{\mathrm{dehyd}} = k\theta_{\mathrm{alc}}\theta_{\mathrm{O}}$, where θ_{alc} and θ_{O} are the fractional surface coverages by alcohol and oxygen [10,11,14,16–20]. This represented the simplest dual site reaction, which gave a proper fit of the experimental results. We now propose $R_{\mathrm{dehyd}} = k\theta_{\mathrm{alc}}\theta_{\mathrm{O}}\theta_{*}$, which appears to give an even better fit of previous data. This equation is also in accordance with the mechanism as shown in Fig. 1, where a free site, *, is needed for the reaction to proceed. The equation does not mean that this reaction step is a true triple site reaction, where the three different surface species must be located next to each other, but it apparently gives a good quantitative description for the enhancement of the dehydrogenation activity of the free metal surface, due to an increased potential caused by adsorbed oxygen species. Here, we will give a short discussion of the main features of our most recent kinetic model.

The surface composition of the catalyst is determined by: equilibrium adsorption of the alcohol and the products, a balance between dissociative oxygen

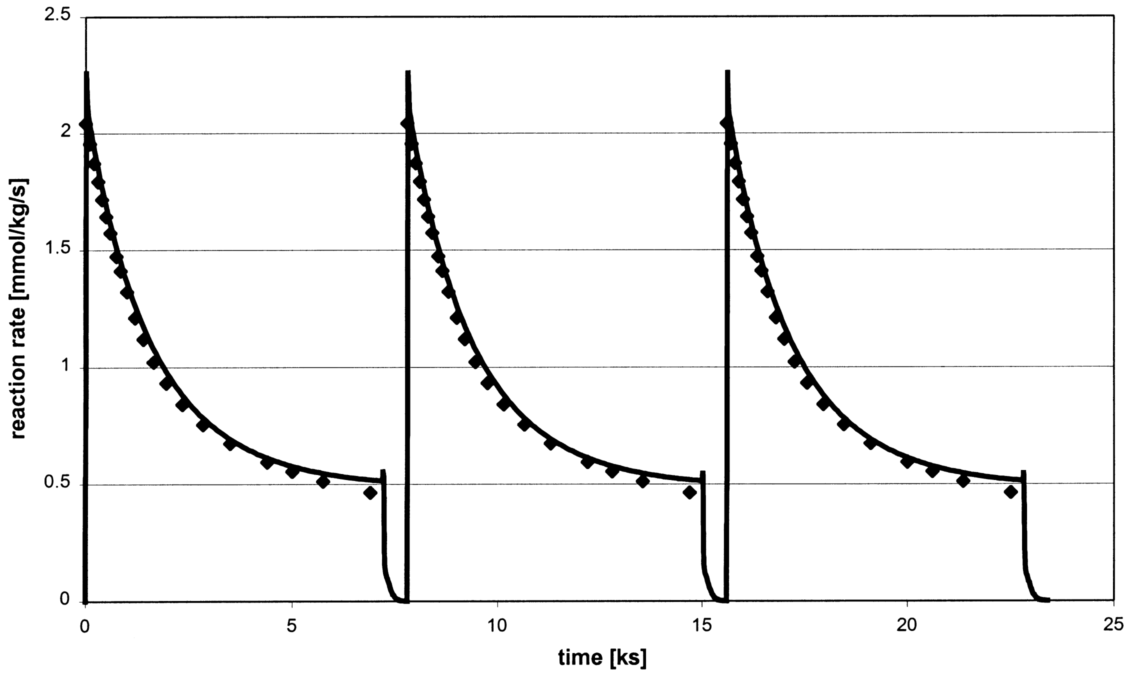

Fig. 4. Weight specific reaction rate for continuous methyl-glucoside oxidation over a 3.3% Pt on graphite catalyst as a function of time on stream, with interruption of the oxygen flow. $C_{\mathrm{MGP}} = 181\,\mathrm{mol/m^3}$, $C_{\mathrm{NaMG}} = 18.4\,\mathrm{mol/m^3}$, $C_{\mathrm{cat}} = 2\,\mathrm{kg/m^3}$, 50 C, pH 8. The stoichiometric ratio $\mathrm{MGP/O_2} = 1$. (◆) experimental data, lines calculated with the model from Table 1.

adsorption and alcohol dehydrogenation, and the degree of over-oxidation. The reaction rate follows from the surface composition. As an example the kinetic model for methyl-glucopyranoside, MGP, is given in Table 1 [34]. This model has been used to simulate the data given in Fig. 4. It excellently describes deactivation and reactivation of the catalyst.

Some essential features of the model are discussed below:

Table 1
Reaction scheme for MGP oxidation, with rate equations

$\mathrm{O_2} + 2* \xrightarrow{k_1} 2\mathrm{O}*$	$R_1 = k_1 c_{\mathrm{O_2}} \theta *^2$	(1)
$\mathrm{MGP} + *p \overset{k_2}{\rightleftarrows} \mathrm{MGP} * p$	$\theta_{\mathrm{MGP}} = K_2 c_{\mathrm{MGP}} \theta * p$	(2)
$\mathrm{NaMG} + *p \overset{k_3}{\rightleftarrows} \mathrm{NaMg} * p$	$\theta_{\mathrm{NaMG}} = K_3 c_{\mathrm{NaMG}} \theta * p$	(3)
$\mathrm{MGP}*p + 2\mathrm{O}* \xrightarrow{k_4} \mathrm{NaMG}*$ $p + \mathrm{H_2O} + 2*$	$R_4 = k_4 \theta_{\mathrm{MGP}} \theta_{\mathrm{O}} \theta *$	(4)
$\mathrm{O} * \xrightarrow{k_5} \mathrm{ox}*$	$R_5 = k_5 \theta_{\mathrm{O}}$	(5)
$\mathrm{ox} * \xrightarrow{k_6} \mathrm{O}*$	$R_6 = k_6 \theta_{\mathrm{ox}} \exp(-g\theta_{\mathrm{O}})$	(6)
$\mathrm{MGP} * p + 2\mathrm{ox} * \xrightarrow{k_4}$ $\mathrm{NaMG} * p + \mathrm{H_2O} + 2*$	$R_7 = k_7 \theta_{\mathrm{MGP}} \theta_{\mathrm{ox}}$	(7)

Step 1. Dissociative adsorption of oxygen is supposed to be far from equilibrium. However, for some data sets equilibrium adsorption fits equally well [14,16,17]. It also can be rather indifferent for the kinetic modelling if it is supposed that surface hydroxyl is formed from rapid hydration of dissociated oxygen in the first step, as was done by Jelemensky [18–20]. The step 1, presented in Table 1, just results in the simplest equation, which fits the experimental data.

Steps 2 and 3. Equilibrium adsorption of reactant, MGP, and product, NaMG, is supposed to occur in a “physisorption” layer. This fits considerably better than allowing for direct, one-to-one, competition with oxygen on the catalyst surface. It just may reflect the different space requirement of the larger organic molecules and oxygen.

Step 4. The reaction presented is the overall surface reaction, the oxidation of the alcohol to the carboxylic acid. The reaction proceeds via the intermediate aldehyde, which under the experimental circumstances is very quickly oxidised. Therefore this compound can be eliminated from the kinetic scheme. The rate of the overall reaction is determined by the first step, in accordance with the mechanism as presented in Fig. 1. Although, it looks like an unusual, triple site reaction, it appears to give a good quantitative description of the oxygen assisted, "electrochemical" dehydrogenation. This equation fits better than the, previously reported, binary reaction rate [14].

Steps 5 and 6. Surface oxygen causes surface corrosion resulting in catalyst deactivation. The deactivation–reactivation is strongly non-linear, which is reflected in the term, $\exp(-g\theta_O)$. Such terms also were needed to explain multiple steady state behaviour for the ethanol oxidation [18–20]. It is also a necessary factor to allow for the very different timescales of deactivation and reactivation. It apparently gives a good quantitative description of the effects of oxygen island formation, surface corrosion and surface reconstruction, which probably are the real causes of the behaviour observed.

Step 7. This step is needed for a proper description of the effect of the alcohol concentration on steady state activity and reactivation time.

5.3. *Start-up procedures and multiple steady-states*

As was already apparent from the work of Dirkx et al. [4,5], the way a reaction is started has a large influence on the course of the reaction, especially for compounds which are not capable of reducing an oxidised surface at a sufficient rate. Reaction rates as well as selectivities are affected. Starting with a reduced catalyst results in high activity, starting with an oxidised catalyst in low activity. Therefore, for poor reductants, the reaction can best be started by first adding the alcohol to the catalyst slurry, wait for the catalyst to become reduced, and thereafter start supplying oxygen. However, the procedure may fail if the reactants can easily form catalyst poisons at low catalyst potential. A short treatment of the catalyst with hydrogen or formic acid (formiate) before the start of a reaction, is then to be preferred.

The experiments, which results are shown in Fig. 4, were started with a reduced catalyst. The experimental data set could excellently be fitted with the model given in Table 1. Using oxidation of ethanol to acetate, via acetaldehyde, as a model reaction, Jelemensky et al. [18–20] proved the existence of three different steady states, which could be reached by starting with a catalyst that was reduced or oxidised to different extents. From his mathematical analysis, it appeared, that, in comparison with the model given in Table 1, an additional active surface oxygen species was needed: OH* being the most active, O* being less active and O_{sub}*(ox*) being inactive.

From the aforementioned it is clear, that the behaviour of a noble metal catalyst is rather complicated in the kinetic regime, i.e. at high catalyst potential, such behaviour probably being caused by the underlying mechanisms of oxygen island formation, surface reconstruction and corrosion. Nevertheless, relative simple quantitative models can be derived, which can be profitably be used for reactor design, as will be treated in next section.

6. Reactor options and future research

Most of the work done on the noble metal catalysed alcohol oxidation, has been performed in stirred slurry reactors, which are most suitable for screening new catalysts and new reactions on laboratory scale. The stirred reactor also is the workhorse for small scale operations in the fine chemical industry. Gas–liquid mass transfer in stirred reactors has been reviewed recently [35]. For larger scale operations slurry bubble columns might be used favourably [36]. Reactor systems using a fixed catalyst are applicable if a catalyst will stay sufficiently active for a few months. However, proper data on long term catalyst deactivation are not available up to now. Due to the many deactivation causes, as mentioned in Section 3, it is not likely that fixed catalyst systems will be profitable in the short term. In the following, however, possible reactor configurations are presented to maintain high catalyst activity. First we will deal with the explosion risks of the reaction.

6.1. *Explosion risks*

From the mechanism of the reaction it appears that hydrogen can be formed. Sugars are converted to sugar acids over noble metals, while hydrogen gas is evolved, in strongly alkaline medium [37]. In our laboratory it appeared that hydrogen gas also evolves at relatively low pH $\sim$ 8 under the influence of oxygen

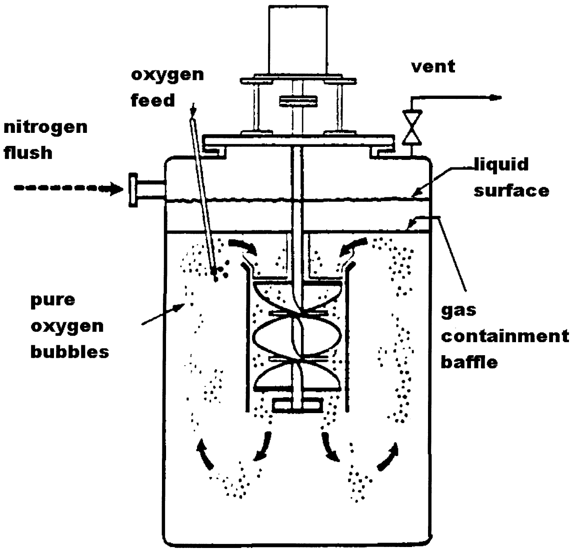

Fig. 5. “Liquid organic reactor” LOR after Praxair [38].

adsorption on the catalyst. This results in H_2/O_2 mixtures in the gas head of the reactor, which may exceed the explosion limits. The risks are especially high using the highly active, promoted catalysts and easily dehydrogenating substances. We have had some explosions during glucose [27] and galactose oxidations over Pd/Bi catalysts, using pure oxygen. The presence of hydrogen becomes visible in the glass reactor by glowing catalyst particles sticking to the glass wall in the gas head. Explosions could be avoided using a sufficient flow of inert N_2.

Working with pure oxygen, however, will strongly increase the volumetric reaction rate for the oxygen mass transfer limited reactions. Reactors, as being developed for oxidations in flammable organic liquids, as shown in Fig. 5, might be useful [38]. Coping with the possible explosion risks, will be a major prerequisite for reactor design.

6.2. Redox cycle reactors

From our intrinsic kinetic experiments in continuous stirred tank reactors [14,34], it appeared that a sufficient catalyst activity can be maintained by a regular interruption of the oxygen flow, as shown in Fig. 4. Oxygen flow interruption, however, might not be the most efficient way for catalyst reactivation on a larger scale. It can be envisaged that it would be more practical to cycle the slurry catalyst through aerobic and anaerobic zones inside a reactor. Such operation could be realised using interconnected, stirred reactors, an aerobic one and an small anaerobic one, through which the reaction mixture is slowly circulated. Another possibility would be to use slurry bubble columns with internal or external loops as depicted in Fig. 6. Slurry circulation rate and the ratio of the aerobic to the anaerobic volume should be such, that the proper timescales for reaction and reactivation are met. Also stirred air lift reactors [39] might be useful in this respect.

Diffusion stabilised catalyst have been proposed to overcome deactivation by over-oxidation [40]. As was mentioned before, noble metals will become poisoned if kept too long at too low potential, and, therefore, application of “diffusion stabilisation” most likely will result in deactivation by poisoning and pore filling (coking), albeit on a longer timescale than deactivation by over-oxidation. The same problem also may arise using catalysts in the oxygen mass transfer limited regime. The severity of the problem will be very much dependent of the type of reactants used. However, partly poisoned catalyst can probably be regenerated by oxidation [33]. It looks worthwhile to test the redox cycle concept also for mass transfer limited reactions, in order to overcome poisoning effects by CO and carbon fragments, and to prevent permanent loss of activity due to pore filling and coking. The catalyst then should be subjected to a short surplus of oxygen after a longer time of working in the mass transfer limited regime.

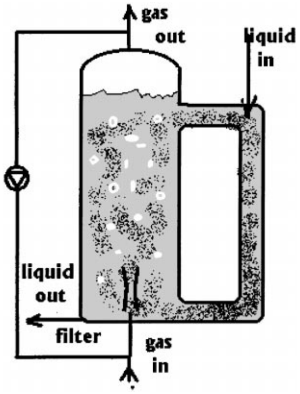

Fig. 6. Redox cycle bubble column loop reactor.

6.3. Electrochemical reactors

If sufficient life-time of the catalyst can be maintained, systems with a fixed catalyst become applicable. Also for these systems redox cycles can be applied. Carbon carriers are generally used for aqueous systems, and new materials as monoliths [41] and carbon cloths and carbon fibrils [42], open up possibilities for new catalytic reactor configurations. The use of a fixed catalyst on a conducting carrier, also opens up the possibility to apply the redox cycle to the catalyst by electrochemical means. It would be worthwhile to test such option, to see whether over-oxidation of the catalyst can be undone by applying a short low potential to the catalyst in the presence of oxygen, and to see whether poisoning and coking can be avoided by shortly applying high potentials.

It must be stressed that in the procedure, proposed above, electrical energy is only used to regenerate the catalyst, and not for oxidation or reduction of the reactants. Therefore, costs for electricity will be negligible.

Consulting the electrochemical literature will show the way to many new catalytic reactor concepts. As shown before, the catalytic oxidation of glucose probably proceeds in a very similar way as in a fuel cell. Therefore, it might be useful to apply fuel cell concepts for new catalytic reactors. Especially, literature on the direct methanol fuel cell is very relevant [43]. Such concepts also may result in safe reactors using pure oxygen, where the formation of explosive gas mixtures can be avoided.

Relations between heterogeneous catalysis and electrocatalysis have been treated by Horányi [44]. A comprehensive review on the electrocatalytic oxidation of oxygenated aliphatic organic compounds at noble metal electrodes is given by Beden et al. [45].

6.4. Multi-functional reactors

Multi-functional reactors also offer interesting possibilities for improvements for the catalytic oxidation reaction.

As mentioned before, inhibition of the reaction by adsorbing products often can be overcome by selective removal of these products e.g. carboxylic acids, simultaneously with reaction. Removal of the products also will lead to improvement of selectivity if these products are subject to further oxidation. Selective membranes, electrodialysis, selective extraction and crystallisation, and ion-exchange can be applied for this purpose.

The use of gas diffusion membranes in the reactor might enable safe operation, avoiding the occurrence of explosive gas mixtures. Furthermore, membranes could be used as a carrier for the catalyst. Finally, cross-flow membrane units also could be very efficient in retaining slurry catalysts inside the reactor, enabling continuous product removal.

7. Concluding remarks

The noble metal catalysed alcohol oxidation reaction appears to be an interesting reaction, not only due to its versatility for industrial application, but also because it raises so many engineering problems to be solved by unconventional, innovative reactor design. The major factors determining reactor configuration will be explosion risk and catalyst deactivation.

Modelling concepts have been presented which can be used to evaluate reactor performance, for the oxygen mass transfer limited, as well as for the kinetic regime. The classical treatment of mass transfer fails, and specific research, on gas–solid mass transfer for catalyst particles adhering to the gas–liquid interface, is needed to further quantify the effects.

The redox-cycle concept has been presented to overcome catalyst deactivation problems. It appeared to work well for the intrinsic kinetic regime. If it also can be used to overcome long term deactivation problems in the oxygen mass transfer limited regime, still has to be tested.

New and safe reactor concepts can possibly be derived from electrochemistry and fuel cell technology. The application of new carbon based catalyst carriers, also opens up possibilities for innovative reactor configurations. Finally, the use of membranes and in situ product removal also can lead to safe and profitable processes for the aqueous noble metal catalysed alcohol oxidation.

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