Oxidative dehydrogenation of aqueous ethanol on a carbon supported platinum catalyst

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Abstract

The kinetics of the selective oxidative dehydrogenation of ethanol to ethanal over a platinum on graphite catalyst with oxygen in water was investigated in a three-phase continuous stirred tank reactor by variation of temperature, pH and reactant concentrations. No effect of the pH on the disappearance rate of ethanol was observed. The oxidation proceeds by a sequence in which ethanal and ethanoate are formed successively. The reaction kinetics of the oxidative dehydrogenation of ethanol to ethanal can be described adequately by a relatively simple rate equation based on an irreversible dissociative adsorption of oxygen and an equilibrated dissociative adsorption of ethanol on the same type of sites. The dissociative adsorption of ethanol proceeds by abstraction of the hydroxyl hydrogen. These steps are followed by an irreversible surface reaction between the ethoxy and the oxygen surface species. At typical conditions, i.e. a temperature of 324 K, an ethanol concentration of 500 mol m$^{-3}$, a pH of 8, and an oxygen partial pressure of 50 kPa, the fractional surface coverages amount to 0.25 for oxygen and 0.11 for both ethoxy species and hydrogen.

Keywords: Ethanol; Ethanal; Kinetics; Oxidation; Oxydehydrogenation; Platinum

1. Introduction

The selective catalytic oxidation of alcohols and aldehydes with oxygen over highly dispersed noble metal catalysts in aqueous media has recently been discussed by several authors. Gallezot et al. [1] reported on the catalytic oxidation of aqueous glyoxal to glyoxylic acid, Mallat and Baiker [2,3] and Mallat et al. [4] investigated the oxidation of 1-methoxy-2-propanol, Schuurman et al. [5-7] studied the oxidation of methyl α-D-glucoside and Vinke et al. [8] oxidized 5-hydroxymethyl-
furfural. Reviews on this topic have been written by Van Bekkum [9] and Mallat and Baiker [10]. To obtain further insight into mechanism, kinetics and catalyst deactivation concerning these oxidation reactions this work reports on the oxidative dehydrogenation of ethanol over a platinum on graphite catalyst.

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

\[
\text{CH}_3\text{CH}_2\text{OH} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{CH}_3\text{CHO} + \text{OH}^- + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \quad (2)
\]

The first stoichiometric equation corresponds to an oxidative dehydrogenation reaction while the second equation corresponds to a selective oxidation. The equilibria for both reactions are far to the right. The above equations are not only stoichiometric equations for the oxidation of ethanol to ethanoate but are also generally believed to correspond to two separate consecutive reaction paths. The present paper focuses on the oxidative dehydrogenation (Eq. 1).

Much has been written on the mechanism of the oxidation of alcohols and aldehydes with dioxygen over noble metal catalysts after the discovery of this catalytic reaction by Döbereiner [11–22]. As is illustrated in Fig. 1, no general consensus has been reached on the type of hydrogen involved in the initial dissociative adsorption of alcohols. The fact that during aqueous oxidation a strong isotope effect has been observed between α-carbon deuterated and non-deuterated alcohols suggests that the abstraction of an α-carbon hydrogen is involved in the rate-determining step [20–22]. Whether this rate-determining step is the initial adsorption of the alcohol or the subsequent surface reaction of the adsorbed dissociated alcohol is not yet clear.

This paper reports on a steady-state kinetic study of the global disappearance of ethanol.

![Fig. 1. Schematic representation of the mechanism of the direct oxidative dehydrogenation in water of alcohols to aldehydes according to: (A) Willsau and Heitbaum [20] for the electrochemical oxidation, (B) DiCosimo and Whitesides [21] for the oxidation with oxygen, and (C) Franaszczuk et al. [22] for the electrochemical oxidation. The rate-determining step is marked RDS.](image)
2. Experimental

2.1. Catalyst

A highly dispersed platinum on graphite catalyst was prepared following a method described by Richard and Gallezot [23]. High surface area graphite from Johnson Matthey (CH10213) was first activated by partial combustion in flowing air at 773 K for 5 h. Under these conditions 25 wt.-% of the graphite was burned off. Subsequently the graphite was suspended at ambient temperature for 24 h in a solution of concentrated sodium hypochlorite (13 wt.-% in active chlorine, Janssen p.a.). After this wet activation step the graphite was separated from the solution by filtration on a Millipore filter (HV 0.45 μm), carefully rinsed with Millipore water and dried in a vacuum oven at 373 K. Platinum was introduced on the activated support by a competitive cation exchange technique [24] in a mixture of a platinumtetramine hydroxide solution (16 wt.-% in platinum, Degussa) and a 1 M ammonia (Merck p.a.) solution which was stirred at ambient temperature for 24 h. The catalyst was separated from the suspension by filtration on a Millipore filter (HV 0.45 μm), washed with Millipore water and dried in a vacuum oven at 373 K. The dried catalyst was reduced in flowing hydrogen at 473 or 573 K for 2 h and cooled down before exposure to air.

This procedure yielded a catalyst with a platinum content of 4.5 wt.-%. The surface area averaged platinum particle size was determined from TEM micrograph analysis [7] to be 1.95 nm. The fraction exposed platinum atoms amounts to 0.66 corresponding to a specific amount of surface platinum atoms, $L_u$, of 0.15 mol kg$^{-1}$. The catalyst powder size distribution as determined with a Malvern 2600 particle sizer showed that less than 2 wt.-% of the particles is larger than 20 μm.

2.2. Experimental set-up

The reactor which was used for this work is a continuous stirred three-phase slurry reactor, CSTR, in which the catalyst was retained by a filter (see Fig. 2). This type of reactor offers good contacting of the three phases and assures thus a stable temperature, and, when using sufficiently fine catalyst powder, absence of mass transfer limitations.

Solutions of ethanol and NaOH were simultaneously added in a constant ratio. The NaOH was added to neutralize the acids produced in order to maintain a set pH. The concentration of NaOH in the feeding mixture is such that NaOH is the stoichiometric limiting reactant for the overall reaction given by Eq. (1) and (2). A typical feed mixture consists of 400 mol m$^{-3}$ ethanol (Merck p.a.) and 20 mol m$^{-3}$ NaOH (Merck p.a.). As the feed rate of the NaOH in this mixture is determined by the pH control, the concentrations will be kept constant in the reactor as long as no selectivity changes occur in time. The oxygen concentration in the liquid is kept
constant by maintaining the partial oxygen pressure in the reactor constant.

The gas-phase composition was determined with an on-line gas chromatograph (GC, HP 5890A Series II) equipped with a 10 µl sample loop injection, a 10 m molsieve 5A wide bore column (Chrompack), a 25 m poraplot Q wide bore column (Chrompack), and a thermal conductivity detector. The liquid phase composition was determined with a HPLC set-up (Spectra Physics). The separation of the components was achieved on a 280 mm long × 4.6 mm I.D. Lichroma SS column slurry packed with a Benson type of cation-exchange resin (BC-X8, 7–10 µm) brought into the H⁺-form by pumping overnight with a 0.025 M H₂SO₄ solution in water.

2.3. Starting procedure

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

2.4. Reaction conditions

The reaction conditions were varied between the limits given in Table 1. Most of the experiments however resulted in ethanal and ethanoate concentrations around 20 mol m\(^{-3}\). The total pressure was 600 kPa and the amount of catalyst used 350 mg in all experiments. Ultrapure Millipore water (18 \(\cdot\) 10\(^4\) \(\Omega\) m) was used for all experimental work. It was established that under these reaction conditions the obtained production rates were free of any mass or heat transfer limitations and represented thus the intrinsic kinetics.

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

\[
C - \text{balance} (\%) = \left( \frac{\sum C_i n_{C,i}}{\sum C_i n_{C,i}} \right) \times 100\%
\]  

in which \(n_{C,i}\) is the number of carbon atoms in a molecule \(i\). Eq. (3) can be used as mass balance only if the flow of liquid in and out of the reactor are equal and if

<table>
<thead>
<tr>
<th>Condition</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration ethanol</td>
<td>38–762 mol m(^{-3})</td>
</tr>
<tr>
<td>Concentration ethanal</td>
<td>5–40 mol m(^{-3})</td>
</tr>
<tr>
<td>Concentration ethanoate</td>
<td>5–51 mol m(^{-3})</td>
</tr>
<tr>
<td>Oxygen partial pressure</td>
<td>8–96 kPa</td>
</tr>
<tr>
<td>pH</td>
<td>7–10</td>
</tr>
<tr>
<td>Temperature</td>
<td>293–344 K</td>
</tr>
<tr>
<td>Conversion of ethanol</td>
<td>0.05–0.28</td>
</tr>
<tr>
<td>Feed flow-rate</td>
<td>1–10 ml min(^{-1})</td>
</tr>
</tbody>
</table>
the carbon containing components are not significantly present in the gas phase. These conditions are fulfilled during the experiments reported here.

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

2.5. Data analysis

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

$$R_{\text{F}} = F_{\text{V,L}} \left( \frac{C_0^{\text{CH}_3\text{CH}_2\text{OH}} - C^{\text{CH}_3\text{CH}_2\text{OH}}}{W} \right)$$  \hspace{1cm} (4)

The aqueous oxygen concentration was calculated using a semi-empirical correlation [25], the hydroxyl concentration in the reactor was calculated from the pH and the dissociation constant of water, $K_w$, at the reactor temperature.

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

The regression analysis was performed as outlined by Froment and Hosten [26] on the final data set of 42 points. The regression of the production rate data to the proposed rate equations, to obtain maximum likelihood estimates $b$ for the kinetic parameters $\beta$, was performed by minimization of the sum of squared residuals (least squares criterion) of the observed and calculated production rates:

$$SRS(b) = \sum_{i=1}^{n_{\text{obs}}} \left[ R_{W,i} - \hat{R}_W(x_i,b) \right]^2 \rightarrow \text{Min}$$  \hspace{1cm} (5)

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

This minimization was performed using the Marquardt algorithm [27].

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

$$F - \text{ratio} = \frac{(n_{\text{obs}} - n_{\text{par}}) \sum_{i=1}^{n_{\text{obs}}} \hat{R}_{W,i}^2}{n_{\text{par}} \sum_{i=1}^{n_{\text{obs}}} \left[ R_{W,i} - \hat{R}_W(x_i,b) \right]^2}$$  \hspace{1cm} (6)

in which $n_{\text{par}}$ is the number of parameters. A high value of this $F$-ratio, which is distributed according to the in statistics known $F$ distribution [28], indicates a high significance of the global regression.
The two sided $1-\alpha$ confidence intervals for the parameters were calculated from tabulated critical $t$-values as:

$$b_i - t_c(n_{\text{obs}} - n_{\text{par}}, 1 - \frac{1}{2} \alpha) s(b_i) < \beta < b_i + t_c(n_{\text{obs}} - n_{\text{par}}, 1 - \frac{1}{2} \alpha) s(b_i)$$  \hspace{1cm} (7)

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

$$k = A^0 \exp \left( -\frac{\Delta^aH^0}{RT} \right) = \frac{zR\tilde{T}}{2N_{av}h} \exp \left( \frac{\Delta^aS^0}{R} - \frac{\Delta^aH^0}{RT} \right) \exp \left( -\frac{\Delta^aH^0}{R} \left( \frac{1}{T} - \frac{1}{\tilde{T}} \right) \right)$$  \hspace{1cm} (8)

and

$$K = K^0 \exp \left( -\frac{\Delta H^0}{RT} \right) = \exp \left( \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \right) \exp \left( -\frac{\Delta H^0}{R} \left( \frac{1}{T} - \frac{1}{\tilde{T}} \right) \right)$$  \hspace{1cm} (9)

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

Standard conditions are for the liquid phase a concentration 1 mol dm$^{-3}$ and for the adsorbed phase a degree of coverage of 0.5 [29]. The form of the preexponential factor in Eq. (8) is derived from the transition state theory [30,31].

3. Results and discussion

3.1. Reaction network

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

To discern between these different reaction networks a concentration vs. space time ($W/\dot{F}^0$) curve was obtained and is shown in Fig. 3. From the initial slopes it is clear that ethanal is formed from ethanol before ethanoate is formed. Also it is clear that the ethanal concentration reaches a maximum while the ethanoate concentration continually increases. These observations are in agreement with a reaction network in which ethanal is formed from ethanol and ethanoate is successively formed from ethanol. Ethanal is thus an intermediate in the ethanol oxidation...
towards ethanoate. This conclusion is also supported by the observation that ethanal oxidation in the absence of ethanol yields ethanoate. As during the experiments no hydrogen was detected at the gas outlet, dehydrogenation of ethanol, leading to gaseous hydrogen rather than the final oxidation product water, could be eliminated as possible reaction path.

3.2. Effect of the reaction conditions on the rate of ethanol disappearance

The present kinetic analysis is limited to the ethanol disappearance rate. The latter can be accounted for completely by considering only the oxidative dehydrogenation towards ethanal because of the consecutive nature of the reaction network and because at the low ethanal and ethanoate concentrations investigated the surface coverages of species involved in the oxidation of ethanal to ethanoate can be neglected.

From Fig. 4 it is clear that the rate increases as both the ethanol concentration and the partial oxygen pressure increase but also that this increase levels off at higher concentrations. This indicates that both reactants are adsorbed on the surface. Most probably both reactants are in some way involved in the rate-determining step and occupy the same type of active sites, corresponding to a so-called dual-site mechanism as is depicted with step 3 in Table 2. Models in which only one adsorbed reactant is involved in the rate-determining step, a so-called single-site mechanism, cannot explain an increase of the ethanol disappearance rate for both an ethanol and an oxygen concentration increase.

No strong dependence of the rate on the pH, as was reported by Schuurman et al. [5] for the oxidation of methyl α-D-glucoside, could be found. This pH dependence was attributed by Schuurman et al. to the existence of a reaction path starting from the methyl α-D-glucoside anion. The lack of pH dependence for the oxidation rate of ethanol is consistent with the fact that the acidity of ethanol, $pK_a \approx 16$ [32], is much lower than the acidity of methyl α-D-glucoside, $pK_a = 13.7$ [5].
Fig. 4. Net specific disappearance rate of ethanol vs. (A) ethanol concentration at an oxygen partial pressure of 65 kPa; (B) oxygen partial pressure at an ethanol concentration of 353 mol m$^{-3}$. Full lines: regression results of model DI (Eq. 13 and Table 5) at temperatures of 324, 309, 304, 300 and 294 K. Symbols: experimental data.

<table>
<thead>
<tr>
<th>$\sigma_A$</th>
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<tbody>
<tr>
<td>1</td>
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<td>2</td>
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<td>2</td>
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</table>

3.3. Reaction sequences and rate equations

Taking the above observations into account, several reaction sequences were considered in which the isotherm of adsorption equilibria was assumed to be of the Langmuir type.

Only reaction sequences in which the ethanol adsorption was quasi-equilibrated could describe the data adequately. Hence, the ethanol adsorption cannot be the rate-determining step of the oxidative dehydrogenation. As it is generally accepted that the rate-determining step during the oxidation of an alcohol involves breaking
the α-carbon to hydrogen bond [21,22], the adsorption of ethanol cannot involve breaking the α-carbon to hydrogen bond. Therefore, if ethanol adsorbs dissociatively only the O–H bond can be involved.

A sequence in which ethanol is adsorbed associatively is given in Table 2. The stoichiometric numbers, σ, indicate the multiplicity of the corresponding elementary reaction which is required to obtain a closed sequence leading to the global reaction [33].

Applying the steady-state approximation to the reactive surface intermediates and assuming that the affinity of the reversible reactions is almost zero, i.e. that these reactions are virtually in equilibrium, the following rate equation is obtained:

\[
\hat{R}_{W,AE} = \frac{k_3 \sqrt{K_1 C_{O_2} K_2 C_{\text{ethanol}}}}{(1 + \sqrt{K_1 C_{O_2} + K_2 C_{\text{ethanol}}})^2} L_t
\]

(10)

in the case of quasi-equilibrated oxygen adsorption, and:

\[
\hat{R}_{W,Al} = \frac{2k_1 C_{O_2}}{(1 + \frac{2k_1 C_{O_2}}{k_3 K_2 C_{\text{ethanol}}}}) \frac{1}{2} L_t
\]

(11)

in the case of irreversible oxygen adsorption.

It should be noted that at the steady state the rate of disappearance of ethanol amounts to twice the rate of the chemisorption of oxygen and equals the rate of the surface reaction between the adsorbed species as can be seen from the closed reaction sequences in Tables 2 and 4. It should also be noted that in these rate equations \( L_t \) rather than \( L_t^2 \) is used in contrast to Schuurman et al. [5–7] as this is formally more correct and leads to rate and equilibrium coefficients which are independent from the specific amount of surface atoms. Also, the reported estimates for the standard activation entropy are based on the assumption that an active site consists of a single surface atom.

The regression results for these two models can be found in Table 3. It can be seen clearly from the F-ratio's that both models with associative adsorption of

<table>
<thead>
<tr>
<th>Table 3</th>
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<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>( \Delta S_r^0 / \Delta S_r^0 ) [J mol(^{-1}) K(^{-1})]</td>
</tr>
<tr>
<td>( \Delta S_x^0 ) [J mol(^{-1}) K(^{-1})]</td>
</tr>
<tr>
<td>( \Delta S_x^0 ) [J mol(^{-1}) K(^{-1})]</td>
</tr>
<tr>
<td>( \Delta H_r^0 / \Delta H_r^0 ) [kJ mol(^{-1})]</td>
</tr>
<tr>
<td>( \Delta H_x^0 ) [kJ mol(^{-1})]</td>
</tr>
<tr>
<td>( \Delta H_x^0 ) [kJ mol(^{-1})]</td>
</tr>
<tr>
<td>F-ratio</td>
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</tbody>
</table>
ethanol can describe the experimental data adequately. One of the parameter estimates in model AI, \( \Delta^\circ H_0 \), is not significantly different from zero, however, as can be seen from the 95% confidence limit. All other parameter estimates are significantly different from zero.

The sequences involving dissociatively adsorbed ethanol are given in Table 4. These sequences start all with the dissociative adsorption of oxygen, reaction (1), which is taken to be quasi-equilibrated, DE and DE', or irreversible, DI and DI'. The dissociation of ethanol, reaction (2), is assumed to proceed by abstraction of the hydroxyl hydrogen rather than the \( \alpha \)-carbon hydrogen as explained earlier. This choice does however not influence the corresponding rate equation.

In sequence D the \( \alpha \)-carbon hydrogen is irreversibly abstracted from the adsorbed ethanol by adsorbed oxygen to form an adsorbed hydroxyl species and ethanal, step 3. The adsorbed hydroxyl species reacts potentially very fast with adsorbed hydrogen to yield water, step 4. Alternatively, the reaction could also proceed as is depicted in sequence D'. An adsorbed hydroxyl species is formed by the irreversible combination of oxygen and hydrogen adatoms, step 3'. This hydroxyl species reacts with adsorbed ethanol to yield ethanal and water, step 4'. Both sequences D and D' result in the same equation for the ethanol disappearance rate but the former sequence is considered more likely in view of the reported isotope effect between \( \alpha \)-carbon deuterated and non-deuterated alcohols [20–22]. Both sequences can of course occur in parallel. This would, however, not result in a mathematically different form of the rate equation.

The rate equations which can be derived from these sequences, assuming that step 4 or 4' is potentially very fast, i.e. that the surface coverage of species OH* can be neglected compared to the surface coverages of the other surface species in the reaction sequence, are:

\[
\hat{R}_{W,DE} = \frac{k_3 \sqrt{K_1 C_{O_2}} \sqrt{K_2 C_{ethanol}}}{(1 + \sqrt{K_1 C_{O_2} + 2 \sqrt{K_2 C_{ethanol}}})^2} L_t
\]  

(12)

when the adsorption of oxygen, reaction (1), is considered equilibrated, and:

<table>
<thead>
<tr>
<th></th>
<th>( \sigma_D )</th>
<th>( \sigma_D' )</th>
</tr>
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<tbody>
<tr>
<td>(1)</td>
<td>( \text{O}_2 + 2^* \rightarrow 2\text{O}^* )</td>
<td>1</td>
</tr>
<tr>
<td>(2)</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{O}^* + \text{H}^* )</td>
<td>2</td>
</tr>
<tr>
<td>(3)</td>
<td>( \text{CH}_3\text{CH}_2\text{O}^* + \text{O}^* \rightarrow \text{CH}_3\text{CHO} + \text{OH}^* + ^* )</td>
<td>2</td>
</tr>
<tr>
<td>(3')</td>
<td>( \text{H}^* + \text{O}^* \rightarrow \text{OH}^* + ^* )</td>
<td>0</td>
</tr>
<tr>
<td>(4)</td>
<td>( \text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O} + 2^* )</td>
<td>2</td>
</tr>
<tr>
<td>(4')</td>
<td>( \text{CH}_3\text{CH}_2\text{O}^* + \text{OH}^* \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2^* )</td>
<td>0</td>
</tr>
</tbody>
</table>

2\( \text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 \rightarrow 2\text{CH}_3\text{CHO} + 2\text{H}_2\text{O} \)
\[
\hat{R}_{W,\text{DI}} = \frac{2k_1C_\text{O}_2}{\left(1 + \frac{2k_1C_\text{O}_2}{k_3\sqrt{K_2C_\text{ethanol}}} + 2\sqrt{K_2C_\text{ethanol}}\right)2L_1}
\] (13)

when the adsorption of oxygen, reaction (1), is considered irreversible.

The terms in the denominator of the rate equations correspond to the amounts of the different surface species related to the amount of vacant sites. Some of these terms are expressed as an adsorption equilibrium, others are expressed as a ratio of production to disappearance rates. For instance the first term in the denominator of the rate equation for model DI (Eq. 13) represents the relative fraction of vacant sites, obviously being 1. The second term is the relative fraction of \(O^*\) given as the ratio of the rate of step 1 to that of step 3. The last term represents the species \(\text{CH}_3\text{CH}_2\text{O}^*\) and \(\text{H}^*\) which are in equilibrium with the ethanol concentration in the liquid phase. As they are both formed in equilibrium 2 and both disappear at the same rate, i.e. the rate of step 3, the coverages of these two species will be equal, hence the factor 2. Indeed, the \(\text{OH}^*\) produced in step 3 will be immediately converted into water by reaction 4. Hence, for each \(\text{CH}_3\text{CH}_2\text{O}^*\) converted by reaction (3), one \(\text{H}^*\) will be converted by reaction (4).

The regression results of models DE and DI can be found in Table 5. It can be seen from the relative high \(F\)-ratio in Table 5 that model DI describes the experimental data much better than any other of the proposed models. Also all parameter estimates are significant, as can be seen from the 95% confidence limits. Fig. 4 illustrates the capability of Eq. (13) to describe the experimental data.

Fig. 5 shows the residual vs. reaction condition diagrams and the calculated rate vs. observed rate diagram. The residuals are evenly distributed indicating the lack of any bias, i.e. any systematic deviation between the experimental data and the rate equation. The sequence of elementary steps of model DI can thus adequately describe the kinetics of the ethanol oxidative dehydrogenation in the investigated range of conditions.

Table 5
Parameter estimates with 95% confidence limits for the model with dissociative adsorption of ethanol, adsorbed oxygen in the rate determining step with equilibrated dissociative adsorption of oxygen, model DE (rate equation 12), and with irreversible dissociative adsorption of oxygen, model DI (rate equation 13)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model DE</th>
<th>Model DI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta S_f^\text{R}/\Delta S_f^\text{R}) [J mol(^{-1}) K(^{-1})]</td>
<td>(-154 \pm 255)</td>
<td>(-203 \pm 29)</td>
</tr>
<tr>
<td>(\Delta S_f^\text{R}) [J mol(^{-1}) K(^{-1})]</td>
<td>(-262 \pm 133)</td>
<td>(-320 \pm 60)</td>
</tr>
<tr>
<td>(\Delta S_f^\text{R}) [J mol(^{-1}) K(^{-1})]</td>
<td>(-57 \pm 80)</td>
<td>(-80 \pm 22)</td>
</tr>
<tr>
<td>(\Delta H_f^\text{R}/\Delta H_f^\text{R}) [kJ mol(^{-1})]</td>
<td>(-62 \pm 81)</td>
<td>(2.1 \pm 1.0)</td>
</tr>
<tr>
<td>(\Delta H_f^\text{R}) [kJ mol(^{-1})]</td>
<td>(-81 \pm 43)</td>
<td>(-99 \pm 30)</td>
</tr>
<tr>
<td>(\Delta H_f^\text{R}) [kJ mol(^{-1})]</td>
<td>(61 \pm 25)</td>
<td>(55 \pm 6.9)</td>
</tr>
<tr>
<td>(F)-ratio</td>
<td>725</td>
<td>1893</td>
</tr>
</tbody>
</table>
Fig. 5. Purity and residual diagrams for the regression with model DI (Eq. 13 and Table 5).
In aqueous alkaline solutions adsorbed hydroxyl, OH\(^*\), rather than oxygen adatoms are often considered as the most abundant oxidizing species during electrochemical oxidations [34]. X-ray absorption spectroscopy on supported platinum catalysts also indicated the presence of such species [35,36]. Regression of sequences with adsorbed hydroxyl, OH\(^*\), in the irreversible surface reaction step rather than with adsorbed oxygen, O\(^*\), step 3 Table 4, was however not successful.

3.4. Assessment of the Langmuir parameter estimates

Having shown the statistical soundness of rate equation (13), the underlying assumptions still have to be verified to be physico-chemically meaningful. This will be done by confronting the values of the parameter estimates for model DI reported in Table 5 with those to be expected from the theory of Langmuir chemisorption or of the transition state.

The value of the estimated standard adsorption enthalpy of ethanol on platinum, \(\Delta H_a\), indicates a strong chemisorption of ethanol as would be expected for a dissociative adsorption.

A strict rule for the value of the standard adsorption entropy for adsorption from the gas phase has been put forward by Boudart et al. [37] and Vannice et al. [38] for both associative and dissociative adsorption. This rule can be directly translated to the aqueous phase as:

\[
0 < - \Delta S_{\text{ads}}^0 < S_{\text{aq}}^0
\]

Eq. (14) expresses the necessary loss of standard entropy upon adsorption and the fact that a molecule cannot lose more entropy than it possesses. The estimated standard entropy loss upon adsorption of ethanol, \(\Delta S_{\text{ads}}^0\), is larger than the standard entropy of aqueous ethanol, \(S_{\text{aq}}^0\), of 158 J mol\(^{-1}\) K\(^{-1}\) and even larger than the standard entropy of gaseous ethanol at 324 K which amounts to 288 J mol\(^{-1}\) K\(^{-1}\) [39]. This would mean that ethanol loses more entropy than it possesses. However, if the interaction between ethanol and the platinum surface is very strong, then platinum surface atoms could also lose some entropy upon ethanol adsorption. The standard entropy of crystalline platinum amounts to 44 J mol\(^{-1}\) K\(^{-1}\) and the standard entropy of gaseous platinum amounts to 194 J mol\(^{-1}\) K\(^{-1}\) at 324 K [39]. The standard entropy of a surface platinum atom in a small particle would thus be somewhere in between these two limits. As at least two platinum surface atoms are involved in dissociatively bonding one ethanol molecule, the total entropy content of one ethanol molecule and two platinum surface atoms is much higher than the entropy content of one ethanol molecule only. Another possible explanation could be that the adsorption of ethanol induces also changes in the hydration of the surface and the hydration of ethanol. Moreover, as ethanol adsorbs dissociatively two surface species will have to be hydrated instead of one. Hydration will obviously contribute to a more negative adsorption entropy.
3.5. Assessment of the Arrhenius parameter estimates

The estimated standard activation enthalpy for the adsorption of oxygen on platinum, $\Delta_{ads}^\circ H^0$, is close to zero which is not unusual. The activation enthalpy for the surface reaction, $\Delta_{reaction}^\circ H^0$, is also low. One should, however, keep in mind that the steps reported here are not necessarily elementary steps. If an equilibrium is preceding an elementary step the apparent rate coefficient equals the product of the equilibrium coefficient and the real rate coefficient and, hence [30]:

$$\Delta_{app}^\circ H^0 = \Delta_{reaction}^\circ H^0 + R\dot{T} + \Delta H^0$$ (15)

If this preceding equilibrium is exothermic the apparent activation enthalpy will be lower than the activation enthalpy expected for an elementary reaction step.

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

$$\Delta_{app}^\circ S^0 = \Delta_{reaction}^\circ S^0 + \Delta S^0$$ (16)

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

3.6. Comparison between ethanol and methyl $\alpha$-D-glucoside

When the results of the kinetic analysis of the steady-state rate of ethanol oxidative dehydrogenation are compared with the results of the kinetic analysis of the oxidation of methyl $\alpha$-D-glucoside as reported by Schuurman et al. [5,6] there are some differences in the reaction sequence. Where the ethanol oxidative dehydrogenation seems to proceed by a mechanism involving a dissociatively adsorbed ethanol species and irreversible dissociatively adsorbed oxygen, the oxidation of methyl $\alpha$-D-glucoside was reported to proceed by a mechanism involving an associatively adsorbed glucoside species and reversible dissociatively adsorbed oxygen. However, both oxidation reactions are proceeding via the same rate-determining step: the abstraction of a hydrogen atom from the chemisorbed alcohol by an oxygen surface species. The activation enthalpies for this surface step, 55 kJ mol$^{-1}$ for the ethanol oxidation and 51 kJ mol$^{-1}$ for the methyl $\alpha$-D-glucoside oxidation, are quite comparable.

At 303 K the rate coefficient for the surface reaction amounts to 0.47 s$^{-1}$ for the ethanol oxidation and to 0.16 s$^{-1}$ for the oxidation of methyl $\alpha$-D-glucoside. It seems that the higher potential rate of oxidation of ethanol and the presence of
adsorbed hydrogen, resulting from the dissociative adsorption of ethanol, are keeping the surface relatively free of oxygen. If the oxygen coverage is far from the equilibrium coverage the oxygen adsorption can be described very well by an irreversible step, whereas close to equilibrium the adsorption of oxygen can of course be better described as being reversible. This could be an explanation for the different description of the oxygen adsorption during the ethanol and the methyl α-D-glucoside oxidation.

The fractional surface coverages calculated using Eq. (13) at typical conditions at which the oxidative dehydrogenation of ethanol was investigated, i.e. a temperature of 324 K, an ethanol concentration of 500 mol m\(^{-3}\), a pH of 8, and an oxygen partial pressure of 50 kPa, amount to a fractional coverage of 0.25 of oxygen, a coverage of 0.11 for both ethanol and hydrogen and a fraction of free surface sites of 0.52. When the temperature is decreased to 303 K the fractional coverages amount to 0.20 for oxygen, 0.26 for both ethanol and hydrogen and 0.28 for the vacant sites. Schuurman et al. \[5,6\] found, at a pH of 8, fractional surface coverages changing from 0.6 to 0.8 for oxygen and changing from 0.13 to 0.08 for methyl α-D-glucoside when the temperature was decreased from 333 to 303 K.

At a pH of 8, a concentration of 200 mol m\(^{-3}\), a partial oxygen pressure of 26 kPa and a temperature of 303 K, the turnover frequency of methyl α-D-glucoside amounts to \(1.3 \times 10^{-2} \text{ s}^{-1}\), while the turnover frequency of ethanol amounts to \(2.0 \times 10^{-2} \text{ s}^{-1}\). In a dual-site reaction the rate of the surface reaction is given by the product of the coverages of the two surface species involved in the reaction and the rate coefficient for the surface reaction. Although the rate coefficient for the surface reaction of ethanol is much larger than that of methyl α-D-glucoside, the effect on the turnover frequency is countered by the larger product of the coverages of both surface species involved in the surface reaction of methyl α-D-glucoside. This is mainly due to the equilibrated nature of the oxygen chemisorption in the latter case.

An important difference between ethanol and methyl α-D-glucoside is the much lower rate of catalyst deactivation with the former reactant. The catalyst deactivation which occurs in the case of methyl α-D-glucoside was attributed to oxygen surface coverages slowly increasing beyond the steady-state degree of coverage and platinum particle growth \[7\]. The latter was accompanied by the presence of platinum ions in the aqueous phase. The adsorption of methyl α-D-glucoside could be better described by an associative adsorption rather than a dissociative adsorption so no significant amount of hydrogen is expected on the surface during the oxidation of methyl α-D-glucoside. As the fractional surface coverage of oxygen is low and some hydrogen is present on the surface, oxidation of the platinum surface and formation of ionic platinum will not easily occur during the ethanol oxidation. Hence no significant deactivation is expected during the oxidation of ethanol at the investigated conditions.

4. Conclusions

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

The reaction kinetics of the oxidative dehydrogenation of ethanol to ethanal can be described adequately by a relatively simple rate equation:

\[
\dot{R}_W = \frac{2k_1C_{O_2}}{1 + \frac{2k_1C_{O_2}}{k_3\sqrt{K_2C_{ethanol}}} + 2\sqrt{K_2C_{ethanol}}} \]

This equation is based on an irreversible dissociative adsorption of oxygen and a quasi-equilibrated reversible dissociative adsorption of ethanol on the same type of sites. The dissociative adsorption of ethanol is assumed to proceed by abstraction of the hydroxyl hydrogen. These steps are followed by two irreversible surface reactions, one between the ethoxy species and the oxygen adatoms and one between the hydrogen adatoms and the hydroxyl species, the latter being potentially very fast:

\[
\begin{align*}
(1) & \quad \text{O}_2 + 2^* \rightarrow 2\text{O}^* \\
(2) & \quad \text{CH}_3\text{CH}_2\text{OH} + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{O}^* + \text{H}^* \\
(3) & \quad \text{CH}_3\text{CH}_2\text{O}^* + \text{O}^* \rightarrow \text{CH}_3\text{CHO} + \text{OH}^* + ^* \\
(4) & \quad \text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O} + 2^*
\end{align*}
\]

\[
2\text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 \rightarrow 2\text{CH}_3\text{CHO} + 2\text{H}_2\text{O}
\]

An assessment of the estimates of the kinetic parameters reveals that some of the steps in this reaction sequence are not true elementary reaction steps but are probably consisting of a reaction step preceded by an equilibrium reaction. Also, due to the ambiguity of steady-state kinetics, a similar rate equation could correspond to more than one reaction sequence.

A comparison with the selective oxidation of methyl α-D-glucoside shows that although the reaction sequences are quite similar, the differences in the rate coefficients of the corresponding elementary steps can have important macroscopic effects in particular with respect to catalyst deactivation.

5. Notation

**Roman symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A^0)</td>
<td>preexponential factor</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>vector of parameter estimates</td>
<td></td>
</tr>
<tr>
<td>(C)</td>
<td>concentration</td>
<td>mol m(^{-3})</td>
</tr>
<tr>
<td>(F)</td>
<td>molar flow-rate</td>
<td>mol s(^{-1})</td>
</tr>
<tr>
<td>(F_v)</td>
<td>volumetric flow-rate</td>
<td>m(^3) s(^{-1})</td>
</tr>
<tr>
<td>(h)</td>
<td>Planck constant ((= 6.6262 \cdot 10^{-34}))</td>
<td>J s</td>
</tr>
</tbody>
</table>
$H$ enthalpy \hspace{1cm} \text{kJ mol}^{-1} \\
$k$ reaction rate coefficient \\
$K$ equilibrium coefficient \\
$I_x$ specific amount of surface atoms \hspace{1cm} \text{mol kg cat}^{-1} \\
$n$ number \hspace{1cm} - \\
$N_{av}$ Avogadro constant ($= 6.0220 \cdot 10^{23}$) \hspace{1cm} \text{mol}^{-1} \\
$R$ gas constant ($= 8.3144$) \hspace{1cm} \text{J mol}^{-1} \text{K}^{-1} \\
$R_W$ specific production/disappearance rate \hspace{1cm} \text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1} \\
$s$ standard deviation \\
$S$ entropy \hspace{1cm} \text{J mol}^{-1} \text{K}^{-1} \\
$t$ $t$-value \\
$T$ temperature \hspace{1cm} \text{K} \\
\bar{T}$ average temperature for reparametrization \hspace{1cm} \text{K} \\
$W$ catalyst mass \hspace{1cm} kg_{\text{cat}} \\
$x$ vector of independent variables \\
$z$ number of neighbouring sites \hspace{1cm} - \\

Greek symbols \\

$\alpha$ probability of rejecting correct hypothesis \\
$\beta$ vector of parameters \\
$\sigma$ stoichiometric number \hspace{1cm} - \\

Subscripts \\

1 oxygen \\
2 ethanol \\
3 surface reaction \\
app apparent \\
c critical \\
C carbon atoms \\
cat catalyst \\
i of $i$th class \\
L liquid \\
obs observations \\
par parameters \\

Superscripts \\

0 at reactor inlet, standard
References