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Published in:
Chemical Engineering Science

DOI:
10.1016/0009-2509%2896%2900035-8
10.1016/0009-2509(96)00035-8

Published: 01/01/1996

Citation for published version (APA):
KINETIC MODELLING OF MULTIPLE STEADY-STATES FOR THE OXIDATION OF AQUEOUS ETHANOL WITH OXYGEN ON A CARBON SUPPORTED PLATINUM CATALYST

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Abstract - Multiple steady-states data were used for the construction of a kinetic model for the oxidation of aqueous ethanol with oxygen on a carbon supported platinum catalyst. A model, incorporating reversible creation of oxygen adatoms on the catalyst surface from surface hydroxyl as well as reversible formation of subsurface oxygen from oxygen adatoms, could describe quantitatively all the observations. It was essential that the reaction rate coefficients for the formation of atomic and subsurface oxygen strongly depend on the corresponding degrees of coverage introducing positive and negative feedback features.

INTRODUCTION

The selective catalytic oxidation of alcohols and carbohydrates with dioxygen has received considerable attention in the recent past (Mallat and Baiker, 1994). Supported noble metals are the favourite catalysts. The reaction can be performed selectively at relatively mild conditions i.e. in aqueous media at a pH around 7 and at temperatures around 300 K.

The major bottleneck for the commercial application consists in so-called catalyst deactivation. Several causes have been put forward for the latter (Schuurman et al., 1992b; Mallat and Baiker, 1994; Vleeming et al., 1994). There is evidence for well known deactivation mechanisms such as metal dissolution and/or sintering (Schuurman et al., 1992b) and coverage of active sites by side or intermediate products of the desired reaction (Mallat and Baiker, 1994). A phenomenon more specific to the considered type of reactions has also been suggested. It is referred to as overoxidation of the metal surface. The term stems from the observation that the loss in activity occurs in parallel with an increase of the catalyst potential (Vleeming et al., 1994).

Recently steady-state multiplicity of the selective oxidation rate of aqueous ethanol over a platinum on carbon catalyst has been reported (Jelemensky et al., 1995). Up to three stable steady-state rates could be established over a feed ethanol concentration range from 300 to 400 mol m$^{-3}$ in a continuous flow stirred tank reactor. The upper steady-state was reached by a reductive start-up procedure while the two lower steady-states required an oxidative start-up. The existence of steady-state multiplicity is believed to be rather common for selective oxidations and hydrogenations by noble metals in the liquid phase.

Bifurcation phenomena, such as multiple steady-states (Rázon and Schmitz, 1987; Zhdanov and Kasemo, 1994), autonomous oscillations (Gray and Scott, 1990) or chaos (Scott, 1991) are well documented for heterogeneous catalytic reactions. In the absence of heat and/or mass transport limitations such phenomena have to be caused by purely chemical feedback features such as autocatalysis. The observations of Jelemensky et al. (1995) were free of transport limitations.

The present paper concerns the development of an intrinsic kinetic model for the platinum catalyzed selective oxidation of ethanol which allows a quantitative description of the complete set of data reported by Jelemensky et al. (1995).

The scope of such a model is not limited to a mere description of steady-state multiplicity. It provides a better understanding of the chemistry involved, not only of the selective oxidation itself but also of the so-called overoxidation mentioned earlier.

EXPERIMENTAL PROCEDURES

A continuous flow stirred slurry reactor was used. Experiments were performed in the absence of mass or heat transport limitations at a total pressure of 600 kPa, a temperature of 323 K and a pH of 8.4 within an ethanol feed concentration range from 100 to 2500 mol m$^{-3}$ and an oxygen partial pressure range from 8 to 20 atm.
120 kPa. The oxygen concentration in the liquid was kept constant by maintaining the oxygen partial pressure in the reactor constant using a PID control for the oxygen and nitrogen feed flow rate. The corresponding oxygen concentration in the liquid phase is the equilibrium oxygen concentration.

Multiple steady-states are obtained by systematic changes in the start-up procedure and variation of the feed concentration of ethanol and oxygen partial pressure in the reactor. Two and sometimes even three sets of steady-states, so-called branches, of the net disappearance rate of ethanol are observed. The steady-states were maintained during several hours.

Figure 1 shows the steady-state disappearance rate of ethanol as a function of the feed ethanol concentration at a given temperature, pH and oxygen partial pressure as obtained after different start-up procedures. The upper steady-state branch is reached by a reductive start-up and the lower branches by an oxidative start-up. Two steady-states are observed in the feed ethanol concentration range from 400 to 2500 tool m$^{-3}$ and three steady-states in the feed ethanol concentration range from 300 to 400 mol m$^{-3}$. Whether the middle (*) or the lowest (■) steady-state in Figure 1 is reached depends on the duration of the oxidative start-up. With an oxidative start-up of around 45 minutes, the lowest steady-state was systematically reached. For a start-up lasting only around 25 minutes it was difficult to predict which of the two lower steady-states would be reached. The probability that the middle steady-state is reached increases with decreasing start-up duration. A more extensive description of the experimental procedures and results has been given by Jelemensky et al. (1995).

The steady-state specific disappearance rate of ethanol is obtained from:

$$ R_w = \frac{(F_w^° + F_w^{°\text{OH}})}{W} (C_{\text{AI}} + C_{\text{Ac}}) $$

(1)

with $F_w^{°\text{OH}}$ the volumetric flow rate of sodium hydroxide which is added to neutralize the acetic acid produced in order to maintain a set pH. The experimental disappearance rates follow from eq.(1) after substitution of the observed concentrations $C_{\text{AI}}$ and $C_{\text{Ac}}$ whereas the disappearance rates calculated with the model equations follow from the substitution of the calculated concentrations $C_{\text{AI}}$ and $C_{\text{Ac}}$.

MATHEMATICAL PROCEDURES

For complex reactions in a continuous stirred tank reactor involving $n$ species the continuity equations for the $n$ species can be written as:

$$ \frac{dy}{dt} = f(y, \mu, K) $$

(2)

where $f$ is a vector of nonlinear functions, $y$ a vector of the concentrations, $\mu$ a bifurcation parameter and $K$ a vector of model parameters. If only the bifurcation parameter $\mu$ is varied equation (2) becomes at the steady-state:

$$ 0 = f(y, \mu) $$

(3)

Depending upon $\mu$ equation (3) yields one or more solutions $y^*$, i.e. a single or multiple steady-states. The graph of $y^*$ vs $\mu$ for a fixed $K$ is called a bifurcation diagram.

A steady-state solution is stable if all the real parts of the eigenvalues of the corresponding Jacobian are negative. It is unstable if at least one eigenvalue of the Jacobian has a positive real part. A branching point is a solution $(y_p, \mu_p)$ of eq.(3) where the number or the nature of the solutions changes when $\mu$ passes $\mu_p$. A branching point where the stability of the steady-state solution changes is called a turning point or a saddle node bifurcation point. Locally there are no solutions on one side of the turning point and two on the other side.

The global bifurcation diagram can be obtained numerically by a continuation method where the first solution of equation (3) for a given value of the bifurcation parameter is conveniently obtained by integration of equation (2) with physically reasonable initial conditions for $y$. The solution then follows from the asymptotic values obtained from the integration of equation (2) up to times sufficiently large to satisfy equation (3). Continuation from the first solution occurs with predictor-corrector steps. Continuation methods differ in the choice of predictor and corrector algorithm, in the parameterization strategy and in the control of the step length. In the present work the continuation program CONT (Marek and Schreiber, 1991) was used.

In the next section solutions for a set of model equations were obtained for different feed ethanol concentrations or oxygen concentrations in the liquid phase, i.e. considering these as bifurcation parameters. The model equations consist of the mass balances for ethanol, acetaldehyde and sodium acetate in the liquid phase and for the species involved on the catalyst. The number of the latter depends on the considered reaction mechanism.
MODEL CONSTRUCTION

The investigated oxidation can be thought of as consisting of two global reactions: an oxidative dehydrogenation into an aldehyde reaction I in Table 1, followed by further oxidation of the aldehyde, reaction II in Table 1.

**Table 1.** Sequences of proposed steps for the selective oxidation of aqueous ethanol with dioxygen.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>( \sigma_{\text{STO}} )</th>
<th>( \sigma_{\text{STO}}^* )</th>
<th>( \sigma_{\text{OH}} )</th>
<th>( \sigma_{\text{O}} )</th>
<th>( \sigma_{\text{SO}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1')</td>
<td>( \text{O}_2 + 2^* \rightarrow 2O^* )</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(1)</td>
<td>( \text{O}_2 + 2\text{H}_2\text{O} + 4^* \rightarrow 4\text{OH}^* )</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(2)</td>
<td>( \text{OH}^* + \text{OH}^* \rightarrow \text{O}^* + ^* + \text{H}_2\text{O} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(3)</td>
<td>( \text{O}^* + ^* \rightarrow \text{O}_{\text{ads}}^* + ^* )</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>(4)</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{OH}^* )</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(5)</td>
<td>( \text{CH}_3\text{CH}_2\text{OH}^* + 2\text{OH}^* \rightarrow \text{CH}_3\text{CHO}^* + 2\text{H}_2\text{O} + 3^* )</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(6)</td>
<td>( \text{CH}_3\text{CHO}^* + 2\text{OH}^* + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + 2\text{H}_2\text{O} + 3^* )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(7)</td>
<td>( \text{CH}_3\text{CHO}^* \rightarrow \text{CH}_3\text{CHO} + ^* )</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(8)</td>
<td>( \text{CH}_3\text{CHO}^* + \text{O}^* \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2^* )</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>(9)</td>
<td>( \text{CH}_3\text{CHO}^* + \text{O}^* + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} + 2^* )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(10)</td>
<td>( \text{CH}<em>3\text{CHO}^* + \text{O}</em>{\text{ads}}^* + \text{NaOH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2^* )</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>(11)</td>
<td>( \text{CH}<em>3\text{CHO}^* + \text{O}</em>{\text{ads}}^* + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} + 2^* )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>( 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} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>( 2\text{CH}_3\text{CHO} + \text{O}_2 + 2\text{NaOH} \rightarrow 2\text{CH}_3\text{COONa} + 2\text{H}_2\text{O} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The different reaction steps which were considered during the construction of a kinetic model describing the observed phenomena are also shown in Table 1. The stoichiometric numbers, \( \sigma \), indicate the multiplication of the corresponding elementary step which is required to obtain a closed sequence leading to the global reaction (Horiuti, 1957; Temkin, 1971). Each set of stoichiometric numbers leads to elimination of the intermediate species and defines a reaction path. In Table 1 the columns of stoichiometric numbers, \( \sigma \), each define a different path for the global reaction I. Similar combinations of elementary steps lead to global reaction II, which, however, are not given in the Table 1.

The first mechanism used to describe the rate multiplicity was based on the work of Schuurman et al. (1992a) and van den Tillaart et al. (1994) and assumed Langmuir-Hinshelwood kinetics. It corresponds to reaction path STO in Table 1.

*Figure 1 shows that this model (--- line) describes only the high branch of steady-state reaction rates. Although a large range of values for the rate coefficients was investigated no multiplicity could be calculated. Actually, the data which were regressed by Schuurman et al. (1992a) and van den Tillaart et al. (1994) have been obtained after a reductive start-up and, hence are limited to these high reaction rates.*

Modification of this model by considering one active site only for adsorption of ethanol and oxygen does reveal multiplicity as could be expected (Yablonskii et al., 1991) but the calculated reaction rates are far away from the experimental data. In particular the low stable branch is very low compared with the experimental low branch.

Modification more close to a pure dehydrogenation mechanism, i.e figuring free sites rather than oxygen adatoms in the irreversible surface step(8), the reaction path STO in Table 1 also allows only to simulate the high experimental branch and cannot even reveal steady-state multiplicity.

The main reason why these models do not sufficiently predict multiple steady-states is the absence of a strong positive feedback. Langmuir - Hinshelwood reactions can provide positive feedback if they are accompanied by the creation of additional free active sites, e.g. (McKarnin et al. 1988):

\[ \text{A}^* + \text{B}^* + 2^* \rightarrow \text{products} + 4^* \]

a typical example of autocatalysis. This kind of positive feedback was introduced in step (8) of the reaction path STO in Table 1. Only in some cases could multiplicity be calculated and wherever this occurred, the calculated
low branch was again much too low when compared with the experimental data.

Strongly positive feedback features can also be introduced by considering that the adsorption and desorption rate coefficients of oxygen and ethanol depend on the degree of coverage with these species according to the Frumkin formalism:

\[
\begin{align*}
    k_{\text{adsorption}} &= k_{\text{adsorption}}^o e^{-\Delta g_o} \\
    k_{\text{desorption}} &= k_{\text{desorption}}^o e^{\Delta g_o}
\end{align*}
\]

In the Frumkin formalism \( g \) determines the attractive or repulsive interactions between the adsorbed species. Depending upon the sign of \( g \) positive feedback is either introduced via the adsorption or via the desorption.

From Figure 1 it follows that a model (--- line) with this type of positive feedback introduced for the adsorption of ethanol and oxygen, in this example \( g_6 = -1 \) and \( g_9 = -2 \), can predict multiplicity but still the calculated low rates of ethanol disappearance are very low compared with the experimental results.

It is known that for sequences of steps of the type:

\[
A \xrightarrow{k_1} X \xrightarrow{k_2} B
\]

steady-state multiplicity in the rate of disappearance of \( A \) can be caused by an inhibiting effect of \( X \) on the rate coefficient \( k_2 \). The sequences (1') and (8) or (1') and (9), of the reaction path STO in Table 1, belong to this category with \( O^* \) as \( X \). Based on this and on the parallelism between the decrease in oxidation activity and the potential of the catalyst (Eng et al., 1987; Schuurman et al., 1992b; Vleeming et al., 1994) an exponential decrease of the rate coefficients for the irreversible surface reactions (8) and (9) with the degree of surface coverage of oxygen was considered:

\[
\begin{align*}
    k_3 &= k_3^o e^{-D_3O} \\
    k_{-3} &= k_{-3}^o e^{D_3O}
\end{align*}
\]

This modification was also motivated by the work of Slinko and Slinko (1978) where this feedback mechanism was introduced into the mechanism of hydrogen oxidation with dioxygen on polycrystalline metals. Results similar to those using the Frumkin formalism were obtained for \( D = 5 \) (--- line) - see Figure 1.

From the above, it is clear that the mechanism based on the work of Schuurman et al. (1992a) and van den Tillaart et al. (1994) lacks an essential feature. Therefore this mechanism is extended with the slow formation of relatively inactive oxygen, step (3) of the reaction path STSO in Table 1. This could correspond to an oxidation of the metal surface layer, e.g. by formation of subsurface oxygen as was suggested by Sales et al. (1982). This step is not assumed to be a pure buffer step because a reaction of subsurface oxygen with adsorbed ethanol and acetaldehyde, steps (10) and (11) in the reaction path STSO in Table 1, is also allowed. This possibility seems to be realistic because Lauterbach et al. (1994) observed a reaction of subsurface oxygen with CO and hydrogen and there is some experimental evidence for the crucial role of subsurface oxygen during autonomous oscillations (Bassett and Imbihl, 1990; Schüth et al., 1993). It is assumed of course that the activity decreases in the order \( O^* > O_{3o}^* \).

As with the original mechanism, the model corresponding to the paths STO and STSO in parallel could not predict steady-state multiplicity as long as Langmuir-Hinshelwood kinetics were considered. When the rate coefficients for step (3) in Table 1 are considered to depend exponentially on the degree of coverage with oxygen adatoms and subsurface oxygen:

\[
\begin{align*}
    k_3 &= k_3^o e^{D_{3o}O} \\
    k_{-3} &= k_{-3}^o e^{-D_{3o}O}
\end{align*}
\]

a qualitative improvement in the agreement with the experimental data is obtained, however. From Figure 1 it is clear that this model (--- line), with in this example \( D_{3o} = 30 \), allows to describe more adequately both the high and low experimental branches where the positive feedback consists in the backward activation of \( k_3 \) by subsurface oxygen and the negative feedback consists in the backward inhibition of \( k_{-3} \) by oxygen adatoms.

This causes abrupt switching of the surface oxygen to subsurface oxygen or vice versa. The higher and lower branches shown in Figure 1 correspond to a different type of oxygen which is dominant. Oxygen adatoms are
Kinetic modelling of multiple steady-states

The most abundant species on the surface at the higher branch. The corresponding fraction of subsurface oxygen is very low. At the low stable branch subsurface oxygen is the most abundant species. The region of bistability strongly depends on the value $D_{SO}$ and the rate coefficients $k_{O.3}$ and $k_{O.3}$. If the value of $D_{SO}$ is close to zero the model simulates only the high branch adequately. The model also predicts bistability when subsurface oxygen does not react at all with adsorbed ethanol and acetaldehyde but then the low stable branch is again very low compared with the experimental data. Although the agreement between the calculations and the experimental data shown in Figure 1 has improved drastically, no satisfactory description of the complete set of data reported by Jellemensky et al. (1995) was possible by considering only two types of oxygen interacting with the catalyst. This is why further modelling was based on the assumption that three different forms of adsorbed oxygen can coexist on platinum: hydroxyl, oxygen adatoms and subsurface oxygen. Three different types of surface oxygen were indeed reported by Vishnevskii and Savchenko (1990) and Kislyuk et al. (1981) for platinum in contact with gas and by Burke and Lyons (1986) for platinum in contact with oxygen dissolved in water.

In this final model the dissolved oxygen is considered to adsorb on the surface in the hydroxyl form as is generally accepted in electrochemistry. Step (1) in Table 1 describes the above process. It corresponds to the transfer of four electrons which occurs in several steps. Thereafter the adsorbed hydroxyl species slowly and reversibly react to adsorbed oxygen step (2) and finally a slow reversible oxidation of the metal surface layer by formation of subsurface oxygen occurs step (3). Furthermore, the adsorption rate of oxygen, step (1), decreases exponentially with increasing degree of coverage by subsurface oxygen as was suggested by Bassett and Imbihl 1990. The reactivities of these forms of oxygen with respect to ethanol and acetaldehyde are assumed to decrease in the order hydroxyl, atomic oxygen and subsurface oxygen.

The complete mechanism now consists of the reaction paths OH, O and SO shown in Table 1. The balances for the active sites on the surface and in the subsurface layer are given by:
where \( \theta_{\text{tr}} = 1 - 2\theta_{\text{o}} - \theta_{\text{OH}} - \theta_{\text{Al}} - \theta_{\text{o}} \) and \( \theta_{\text{SL}} = 1 - \theta_{\text{so}} \) (7).

Steps (2) and (3) play a key role and the rate coefficients obey relations similar to expression (6). These relations now cause abrupt switching between the hydroxyl species and the oxygen adatoms on one hand and between the oxygen adatoms and subsurface oxygen on the other hand. The rate coefficients of steps (2) and (3) are considered to be low compared to the adsorption and Langmuir-Hinshelwood reactions and higher for step (2) than for step (3). Also the rate coefficients for Langmuir-Hinshelwood steps (8) and (9) are assumed lower than for steps (5) and (6) but higher than for steps (10) and (11).

The final model equations consist of the steady-state balances, equations (3), for the five surface species and three liquid components corresponding to the complete mechanism presented above, see the Appendix.

It should be noted that predicting steady-state multiplicity is possible without considering the mass balances for the liquid species, i.e. without introducing feedback linked to the CSTR. However, these equations are of course required to allow a comparison with the experimental data obtained in the CSTR as shown in the Figures 2, 4 and 5. The final model is mainly sensitive to the values of the rate coefficients for steps (2) and (3) and the corresponding parameters \( D_{\text{o}} \), \( D_{\text{so}} \). If \( D_{\text{o}} = D_{\text{so}} = 0 \), the model has only one steady-state. The values of the parameters in the final model are given in the Appendix. All estimates presented in the Appendix are within the range of physically realistic values (Zhdanov et al. 1988 and Dumesic et al. 1993) expected for rate coefficients corresponding to the elementary steps (1) to (11) in Table 1.

The possibility, that subsurface oxygen does not react with adsorbed ethanol and acetaldehyde was also considered. In this case subsurface oxygen only plays the role of a buffer. Such a model yields qualitatively and quantitatively the same results as shown in Figures 2, 4 and 5.

RESULTS AND DISCUSSION

From Figure 2 it is clear that the agreement between experimental and calculation is satisfactory. Four turning points were identified during the continuation. There exists a region of feed ethanol concentrations with five steady-states: three stable and two unstable. Every branch of steady-state solutions is characterised by a different coverage of the surface, see Figure 3.

A comparison of the corresponding calculated steady-state concentration of acetaldehyde and acetic acid with experimentally measured concentrations in the reactor for different feed ethanol concentrations follows from Figure 4. From Figure 4 B it is clear that the calculated middle branch does not yet describe very well the experimental results for sodium acetate.

The steady-state solution on the catalyst surface at very high feed ethanol concentrations is characterized by the absence of any subsurface oxygen, Figure 3D, as well as of any oxygen adatoms, Figure 3B. One third of the surface is covered by hydroxyl species, Figure 3A, and sixty percent by the reducing ethanol and acetaldehyde, the balance being made up of free active sites, Figure 3C. At very low feed ethanol concentrations the situation is symmetrical: the surface is fully covered by oxygen adatoms and the sublayer is completely saturated with oxygen. It is reasonable to expect that the former situation corresponds to a reductive start-up and the latter to an oxidative start-up. Depending upon the initial coverage of the catalyst by reactants a different steady-state was indeed calculated by the final model at feed ethanol concentrations between 500 and 2500 mol m\(^{-3}\). If the ethanol is initially predominant on the surface then the solution approaches the higher stable branch. If oxygen adatoms
Kinetic modelling of multiple steady-states

Figure 5 Steady-state net specific disappearance rates of ethanol vs. the oxygen partial pressure for a feed ethanol concentration of 500 mol m\(^{-3}\), \(T = 323\) K and \(pH = 8.4\). Experimental data: \(\ast\) reductive start-up procedure; \(\bigstar\) oxidative start-up procedure. Lines: calculated with final model --- stable steady-state; \(---\) unstable steady-state.

Figure 6 Fraction of A) the hydroxyl form of oxygen, B) oxygen adatoms, C) free active sites and D) subsurface oxygen on the catalyst surface vs. the oxygen partial pressure calculated for the same condition as in Figure 4. \(\ast\) corresponds to a reductive start-up; \(\bigstar\) corresponds to an oxidative start-up.

The situation is not so clear in the region with three steady-states. In order to be able to predict unambiguously to which of the two lower branches an oxidative start-up leads, the separatrices in the five dimensional state space for the catalyst surface would have to be determined (Yablonskii et al. (1991)).

An oxidative as well as a reductive start-up lead to a unique stable steady-state at the middle branch up to an ethanol feed concentration of 290 mol m\(^{-3}\) i.e. up to the turning point T.P.4. Further increasing the ethanol feed concentration leads to a stable steady-state at the middle branch up to an ethanol feed concentration of 500 mol m\(^{-3}\) where the turning point T.P.1 is reached. The disappearance rate of ethanol jumps at the turning point T.P.1 to the low stable branch. The corresponding degree of coverage of subsurface oxygen abruptly decreases to a low value as shown in Figure 3 D and the degree of coverage with oxygen adatoms jumps from 0.6 to 0.85, Figure 3 B, while the amount of hydroxyl species on the surface, Figure 3 A, remains vanishingly small.

Further increasing the ethanol feed concentration leads to a reactor operation along the lower stable branch in Figure 2. At the turning point T.P.2 the disappearance rate increases up to a value which would have been obtained directly by a reductive start-up. The degree of coverage with oxygen adatoms and subsurface oxygen abruptly becomes vanishingly small. The degree of coverage with hydroxyl jumps from 0.1 to 0.4, see Figure 3 A. As expected, the model predicts hysteresis. When decreasing the ethanol feed concentration the degrees of coverage with oxygen adatoms and subsurface oxygen remain small and the degree of coverage with hydroxyl is increasing. The corresponding disappearance rate...
reductive start-up and the low experimental points by the oxidative start-up. The calculated high branch is higher than the experimental results. That the high unstable branch fits the latter is fortuitous.

It was shown that the lower steady-state relaxes to the higher steady-state after a reduction period consisting of feeding the ethanol solution without oxygen (Vleeming et al., 1994; Jelemensky et al., 1995). From Figures 5 and 6 it follows that decreasing the oxygen partial pressure between the turning points T.P.4 and T.P.3 leads to a decrease of coverage by oxygen adatoms from 0.9 to 0.4, the balance of the surface being free. The corresponding fraction of subsurface oxygen decreases from 0.2 to 0.01. At turning point T.P.3, the reaction rate jumps to a high value because the degree of coverage with oxygen adatoms jumps to a low value and the degree of coverage with hydroxyl to a high value. The degree of coverage with subsurface oxygen becomes vanishingly small. Clearly the platinum surface can be reduced in the liquid phase by ethanol even in the presence of dioxygen. This is important from the practical point of view because if the stable steady-state is low a relaxation towards a higher stable steady-state can be reached without discontinuing the oxygen feed, but by limiting the oxygen supply temporarily e.g. by decreasing the stirring rate.

CONCLUSIONS

A single set of model equations and kinetic parameter values have been found which can describe at least qualitatively the observed bifurcation behaviour of a complex oxidation network. Three types of oxygen species, at least two of them being active for the oxidations, have to be considered. It is essential that both the interconversion of these species and their reactivity towards the adsorbed ethanol and acetaldehyde is strongly dependent on the state of the catalyst i.e. deviations from the assumptions underlying Langmuir-Hinshelwood kinetics have to be pronounced.

It is believed that the proposed model not only allows to describe steady-state multiplicity and to understand in a qualitative way the effects of different start-up procedures but that it also provides the possibility to describe the observed changes in activity at constant conditions. The latter should be considered as relaxations from an initial state to a steady-state.

ACKNOWLEDGMENT

This work was supported by Shell Research Amsterdam.

NOTATION

\[ C \] concentrations [m³s⁻¹]
\[ C^{\text{OH}}_{\text{feed}} \] feed sodium hydroxide concentration - 200 mol m³
\[ F_{\text{V}} \] inlet volumetric flow rate - 5.0 \times 10⁴ m³s⁻¹
\[ g \] parameters in Frumkin formalism
\[ k \] reaction rate coefficient [s⁻¹] or [m³ mol⁻¹ s⁻¹]
\[ L \] specific amount of surface atoms - 0.024 mol kg⁻¹
\[ R_{\text{p}} \] disappearance rate [mol kg⁻¹ s⁻¹]
\[ t \] time [s]
\[ V_{\text{R}} \] liquid volume of reactor - 350.0 \times 10⁵ m³
\[ W \] mass of dry catalyst - 0.347 \times 10³ kg

GREEK SYMBOLS

\[ \Theta \] fraction of total number of available active sites occupied
\[ \sigma \] stoichiometric number

SUBSCRIPTS

1,2,3... number of reaction step
\[ E \] ethanol
\[ AI \] acetaldehyde
\[ Ac \] sodium acetate
\[ * \] free active site
\[ O \] atomic oxygen
\[ SO \] subsurface oxygen
\[ SL \] subsurface layer
\[ p \] branch point

SUPERSCRIPTS

\[ o \] for \[ \Theta = 1 \]
\[ s \] at steady-state
REFERENCES


APPENDIX FINAL MODEL EQUATIONS AND PARAMETER VALUES

In a continuous flow stirred slurry reactor, in the absence of inter- and intraparticle mass transport limitations, the mass balances for the various liquid and surface species lead to the following dimensionless equations at the steady state:

**Surface**

- hydroxyl form

\[ 0 = \mu_O \theta_O^e \left( k_{OH} \theta_O^{OH} - k_{SO} \theta_O^{SO} \right) - 2 \theta_O^{OH} - 2 k_{\theta} \theta_{Al}^{Al} \theta_O^{OH} - 2 k_{\theta} \theta_{SO}^{SO} \theta_O^{OH} + 2 k_{\theta} \theta_{SO}^{SO} \theta_O^{SO} (A.1) \]

- ethanol

\[ 0 = \mu_E \theta_E^{E} \left( k_{OE} \theta_E^{OE} - k_{OE} \theta_E^{OE} \right) - \theta_E^{OE} \theta_O^{OE} - \theta_E^{OE} \theta_O^{OE} + \theta_E^{OE} \theta_O^{OE} + \theta_E^{OE} \theta_O^{OE} \theta_O^{OE} (A.2) \]

- acetaldehyde

\[ 0 = \theta_{Al}^{Al} \theta_O^{Al} + k_A \theta_{Al}^{Al} \theta_O^{Al} + k_A \theta_{Al}^{Al} \theta_O^{Al} - k_A \theta_{Al}^{Al} \theta_O^{Al} - k_A \theta_{Al}^{Al} \theta_O^{Al} - k_A \theta_{Al}^{Al} \theta_O^{Al} (A.3) \]

- oxygen adatoms

\[ 0 = k_{O} \theta_O^{OH} \left( k_{OE} \theta_O^{OE} + k_{OE} \theta_O^{OE} \right) + k_{O} \theta_O^{OE} \theta_O^{OE} + k_{O} \theta_O^{OE} \theta_O^{OE} + k_{O} \theta_O^{OE} \theta_O^{OE} \theta_O^{OE} (A.4) \]
- subsurface oxygen

\[ 0 = k_{j3}O_2 \theta_{sL} e^{(D_{SO} \theta_{SO})} - k_{j4} \theta_{SO} \theta_{sL} e^{(-D_{SO} \theta_{SO})} - k_{j10} \theta_{E} \theta_{SO} - k_{j11} \theta_{Al} \theta_{SO} \]  

(A.5)

Liquid phase
- ethanol

\[ 0 = (\tau_e + H_{OH} \xi_{Ac})(1 - X_e) - \gamma X_e \theta_{sL}^2 e^{(\Delta_{E} \theta_{E})} + \frac{k_{j4} \gamma \theta_{Al}^2 e^{(\Delta_{E} \theta_{E})}}{\mu_e} \]  

(A.6)

- acetaldehyde

\[ 0 = (\tau_e + H_{OH} \xi_{Ac})(X_{Ac}^O - X_{Ac}) + \frac{k_{j2} \gamma \theta_{Al}^2 \theta_{OH}}{\mu_e} - \phi X_{Al} \theta_{sL} \]  

(A.7)

- sodium acetate

\[ 0 = (\tau_e + H_{OH} \xi_{Ac})(X_{Ac}^O - X_{Ac}) + \frac{k_{j2} \gamma \theta_{Al}^2 \theta_{OH}}{\mu_e} + k_{j7} \frac{\gamma \theta_{Al}^2 \theta_{Al} \theta_{sL} \theta_{SO}}{\mu_e} + k_{j11} \frac{\gamma \theta_{Al} \theta_{Al} \theta_{SO}}{\mu_e} \]  

(A.8)

where

\[ \xi_{Ac} = \frac{k_{j4} \theta_{Al}^2 \theta_{OH}}{\mu_e} + \frac{k_{j7} \theta_{Al} \theta_{Al} \theta_{SO}}{\mu_e} \]  

(A.9)

corresponds to the dimensionless production rate of sodium acetate.

The dimensionless concentrations of oxygen and ethanol in the liquid phase are defined as:

\[ \mu_o = \frac{4 k_1}{k_5} C_{O_2} \quad \mu_e = \frac{k_4}{k_5} C_{E} \]

Other dimensionless parameters are defined as:

\[ \gamma = \frac{L_e W}{V_R k_3} \quad \phi = \frac{L_e W}{V_R k_5} \quad \tau_e = \frac{F_{V}^0}{V_R k_5} \quad H_{OH} = \frac{L_e W}{V_R (C_{OH}^O - C_{OH})} \]

\[ k_1 = \frac{k_{j1}}{k_5} \quad k_3 = \frac{k_{j2}}{k_5} \quad X_{Ac}^O = \frac{C_{Ac}^O}{C_{E}} \]

Table A.1 Set of values for the kinetic parameters corresponding to the final mechanism consisting of the reaction paths OH, O and SO in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{j1} ) [m(^3)mol(^{-1})s(^{-1})]</td>
<td>6.2465 ( \times 10^3 )</td>
<td>( k_{j4} ) [m(^3)mol(^{-1})s(^{-1})]</td>
<td>0.0067</td>
<td>( k_{j5} ) [m(^3)mol(^{-1})s(^{-1})]</td>
<td>0.1125</td>
<td>( \xi_{OH} )</td>
<td>0.500</td>
</tr>
<tr>
<td>( k_{j2} ) [s(^{-1})]</td>
<td>9.500 ( \times 10^4 )</td>
<td>( k_{j4} ) [s(^{-1})]</td>
<td>29.250</td>
<td>( k_3 ) [s(^{-1})]</td>
<td>2.025</td>
<td>( \xi_E )</td>
<td>- 0.500</td>
</tr>
<tr>
<td>( k_{j3} ) [s(^{-1})]</td>
<td>1.000 ( \times 10^3 )</td>
<td>( k_5 ) [s(^{-1})]</td>
<td>11.250</td>
<td>( k_6 ) [s(^{-1})]</td>
<td>0.4500</td>
<td>( \xi_{SO} )</td>
<td>2.000</td>
</tr>
<tr>
<td>( k_{j3} ) [s(^{-1})]</td>
<td>2.800 ( \times 10^3 )</td>
<td>( k_7 ) [s(^{-1})]</td>
<td>2.000</td>
<td>( k_{j10} ) [s(^{-1})]</td>
<td>0.010</td>
<td>( D_{SO} )</td>
<td>24.500</td>
</tr>
<tr>
<td>( k_{j3} ) [s(^{-1})]</td>
<td>1.000 ( \times 10^3 )</td>
<td>( k_7 ) [s(^{-1})]</td>
<td>4.500</td>
<td>( k_{j11} ) [s(^{-1})]</td>
<td>0.010</td>
<td>( D_{SO} )</td>
<td>7.300</td>
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</tbody>
</table>