Multiple steady-states for the oxidation of aqueous ethanol with oxygen on a carbon supported platinum catalyst

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The selective oxidation of aqueous ethanol by dioxygen over a platinum on carbon catalyst was investigated in a three-phase continuously stirred tank reactor at a total pressure of 600 kPa, a temperature of 323 K, a pH of 8.4, and a catalyst concentration of 2.3 kg m^{-3}. Multiple steady-states were obtained by systematic changes in the start-up procedure and variation of the feed concentration of ethanol and partial oxygen pressure in the reactor. The ethanol feed concentration was varied from 100 to 2500 mol m^{-3} and the partial oxygen pressure from 8 to 120 kPa. On the time scale of the experiments, i.e. 21 ks, two steady-states of the net disappearance rate of ethanol are observed in the ethanol feed concentration range from 500 to 2500 mol m^{-3} at a partial oxygen pressure of 58 kPa and in the range of partial pressure of oxygen from 8 to 120 kPa at an ethanol feed concentration of 500 mol m^{-3}. Three steady-states are observed in the feed ethanol concentration range from 200 to 400 mol m^{-3} and a partial oxygen pressure of 58 kPa.

Keywords: aqueous ethanol; multiple steady-state; oxidation; platinum

1. Introduction

Several heterogeneous catalytic reactions show features typical for nonlinear systems such as multiple steady-states [1], autonomous oscillations [2] and chaos [3]. Qualitative changes in behaviour, such as a transition between different steady-states or an onset of oscillations, upon changing a control variable, such as a feed concentration, are known as bifurcations.

These bifurcations form a challenge for the modelling of many industrially important reactors. Also, the use of bifurcation data for validation and discrimination between different plausible reaction mechanisms has been recommended by
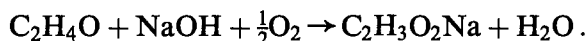
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Sheintuch and Luss [4–6], Graham and Lynch [7], Aluko and Chang [8], even for reactors which would normally be operated at conditions where bifurcations do not occur, as bifurcations are extremely sensitive to the details of the mechanism and the value of the corresponding rate coefficients. On the other hand, the steady-state rate equations for heterogeneously catalyzed reactions based on a Langmuir–Hinshelwood mechanism are characterized by a large number of often highly correlated kinetic parameters.

The heterogeneous catalytic oxidation of alcohols on supported catalyst provides an example. Several mechanisms for the oxidation of aqueous alcohol were reported by Gallezot et al. [9], Mallat and Baiker [10–12], Schuurman et al. [13,14], but a lot of important aspects of the reaction mechanisms are still under discussion. This reaction occurs in two stages – the oxidative dehydrogenation of ethanol:

$$C_2H_5OH + \tfrac{1}{2}O_2 \rightarrow C_2H_4O + H_2O \,,$$
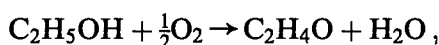
followed by the oxidation of acetaldehyde:

$$C_2H_4O + NaOH + \tfrac{1}{2}O_2 \rightarrow C_2H_3O_2Na + H_2O \,.$$

The possibility of multiple steady-states during the oxidation of aqueous ethanol was, to the best of our knowledge, first mentioned by van den Tillaart [15]. Bifurcation behaviour is often observed during electrochemical oxidations [16,17]. In the case of gaseous ethanol oxidation autonomous oscillations were reported by Jaeger et al. [18] and Engel-Herbert et al. [19].

This paper presents experimental evidence for the existence of multiple steady-state behaviour of the selective oxidation of aqueous ethanol with molecular oxygen on a carbon-supported platinum catalyst.

2. Experimental

2.1. SET-UP

A continuous stirred three-phase slurry reactor, CSTR, in which the catalyst was retained by a membrane filter was used. This type of reactor offers good contacting of the three phases, ensures good isothermality, and, when using sufficiently fine catalyst powder, absence of mass transfer and transport limitations.

Solutions of aqueous ethanol and NaOH were separately fed to the reactor. The NaOH was added to neutralize the acetic acid produced in order to maintain a set pH. The flow rate of NaOH is a function of the production rate of acetic acid and the difference between the feed hydroxide concentration and the set hydroxide concentration in the reactor. The feed hydroxide concentration was 200 mol m^{-3} ∼ pH = 13.3. The volumetric flow rate of hydroxide in the steady-state condition was maximal 3% of the volumetric flow rate of feed ethanol solution.

The oxygen concentration in the liquid was kept constant by maintaining the

partial oxygen pressure in the reactor constant using a PID control of the oxygen and nitrogen feed flow rate. The flow rate of the aqueous ethanol feed to the reactor was maintained by a HPLC pump (LKB 2150). Further experimental details are described by van den Tillaart [15].

The outlet liquid phase composition was analyzed by a HPLC on-line set-up (Spectra Physics) consisting of a HPLC pump (TSP P100), a Valco injector, a heated column, a refractive index detector (Refractor Monitor IV) and an integrator Data Jet combined with TSP PC Winner on Windows. The separation of ethanol, acetaldehyde and sodium acetate was achieved on a 280×4.6 i.d. mm Lichroma SS column slurry packed with a Benson type of cation-exchange resin (H^+). Elution was performed with a flow of 0.7 ml/min 0.025 M H_2SO_4 at a temperature of 343 K. The injection volume of the sample valve was 20 μl. No components other than oxygen and nitrogen were detected in the gas outlet stream.

2.2. CONDITIONS

For all experiments a total pressure of 600 kPa, a temperature of 323 K, a pH of 8.4 and 0.347 g (dry weight) catalyst ESCAT 211 (Engelhard de Meern, NL)–0.8% Pt supported on carbon powder (supplied with 55.5% of H_2O) was used. The specific concentration of surface platinum atoms, L_t, for the dry catalyst was 0.024 mol kg_{cat}^{-1} as determined with CO-pulse chemisorption, taking 1 : 1 stoichiometry. The volume mean diameter of the catalyst powder particles amounts to 23 μm. The feed concentration of ethanol was changed from 100 to 2500 mol m^{-3} and the feed flow rate of the ethanol solution was kept constant at 3 ml min^{-1}. The partial pressure of oxygen in the reactor was varied between 8 and 120 kPa.

2.3. START-UP PROCEDURES

Heterogeneous catalytic reactions, which show bifurcation behaviour such as multiple steady-states, are of course very sensitive to the initial state of the catalyst. Depending upon the initial coverage of the catalyst by reactants, the reaction can approach different steady-states [1,2,3,20]. This idea is applied to obtain multiple steady-states during the oxidation of ethanol.

At the start of an experiment the reactor is filled with the catalyst and 350 ml water. After closure the reactor is purged with nitrogen at atmospheric pressure to remove the oxygen. During this procedure the stirring speed is maintained at 18 s^{-1} and the reactor temperature is brought to 363 K. As soon as the oxygen concentration at the reactor outlet is lower than 1000 ppm the nitrogen is replaced with hydrogen for half an hour to reduce the catalyst in situ. During this procedure the pH in the reactor equals 5. Thereafter the reactor is again purged with nitrogen and the reactor temperature is brought to 323 K. The above procedure is common to every experiment.

2.3.1. Reductive start-up procedure

In the so-called reductive start-up procedure the reactor pressure is increased to 600 kPa and 175 ml water is removed via the liquid outlet. This amount is replaced by a concentrated ethanol solution via the liquid inlet in order to obtain a concentration of ethanol in the reactor which is identical to the feed concentration. After this pretreatment the catalyst surface is occupied with dehydrogenated ethanol and free of oxygen [14,21]. Then the stirring speed is reduced to 4 s^{-1}. Thereafter, oxygen and aqueous ethanol are continuously fed to the reactor. The reaction is started as soon as the outlet oxygen concentration is close to the desired reactor oxygen concentration by increasing the stirring speed to 18 s^{-1} and by starting the pH-controller.

2.3.2. Oxidative start-up procedure

In the so-called oxidative start-up procedure the nitrogen purge at 323 K is followed by a flow of 4.3×10^{-5} mol s^{-1} of oxygen for half an hour at atmospheric pressure. After this pretreatment procedure the catalyst surface is occupied with oxygen [14,21]. Next, the reactor pressure is increased to 600 kPa and 175 ml of water is replaced by a concentrated ethanol solution while maintaining the flow of oxygen and the stirring speed to avoid mass transfer limitation for oxygen. Finally, the ethanol solution is continuously fed to the reactor and the desired pH and partial pressure of oxygen are set.

2.4. DATA ANALYSIS

The C-balance was calculated from the inlet and outlet flow rates of reactants and products. The experimental error during the analysis of solutions with high concentration of ethanol caused the C-balance to close typically up to 96–100%. For this reason the so-called normalization method was used. This method assumes a 100% carbon balance, which allows to calculate the outlet flow rate from the measured inlet flow rates and the composition of the liquid outlet stream. Vaporization of ethanol and acetaldehyde could be neglected.

The net specific disappearance rate of ethanol follows from the mass balance for ethanol:

$$R_{w,E} = \frac{F_{V,E}^0 + F_{V,OH}^0}{W}(C_{Al} + C_{Ac}) + \frac{V_R}{W}\frac{d(C_{Al} + C_{Ac})}{dt}, \qquad (1)$$

where $R_{w,E}$ is the net specific disappearance rate of ethanol in mol kg$_{cat}^{-1}$ s^{-1}, $F_{V,E}^0$ is a feed volumetric flow rate of ethanol solution in m^3 s^{-1}, $F_{V,OH}^0$ is a feed volumetric flow rate of NaOH solution in m^3 s^{-1}, V_R is the volume of the liquid phase in the reactor in m^3, W is the mass of wet catalyst in kg$_{cat}$, C_{Al} is the acetaldehyde concentration in mol m^{-3} and C_{Ac} is the sodium acetate concentration in mol m^{-3} in the liquid phase in the reactor.

3. Results and discussion

Multiple steady-state behaviour during the oxidation of ethanol on carbon supported platinum was observed in a large region of ethanol and oxygen concentrations. Fig. 1 shows the dependence of the steady-state net specific disappearance rate of ethanol on the feed concentration of ethanol at a partial pressure of oxygen of 58 kPa in the reactor. It is clear that two different activity levels can be distinguished between 500 and 2500 mol m^{-3} feed concentration of ethanol. Between 200 and 400 mol m^{-3} feed concentration of ethanol there are indications for the existence of three steady-states. Fig. 2 shows the net specific disappearance rates of ethanol as a function of time for the two start-up procedures using a feed ethanol concentration of 300 mol m^{-3}. The different activity levels are quite reproducible as illustrated in fig. 2d. The highest steady-state reaction rate was reached when the reductive start-up procedure was followed. The middle and the lowest steady-state were reached when the oxidative start-up procedure was followed. Whether the middle or the lowest steady-state is reached depends on the oxygen concentration established on the catalyst surface during the oxidative start-up procedure. After each oxidative start-up procedure the surface concentration of oxygen is apparently not exactly the same and for this situation, depending on the feed ethanol con-
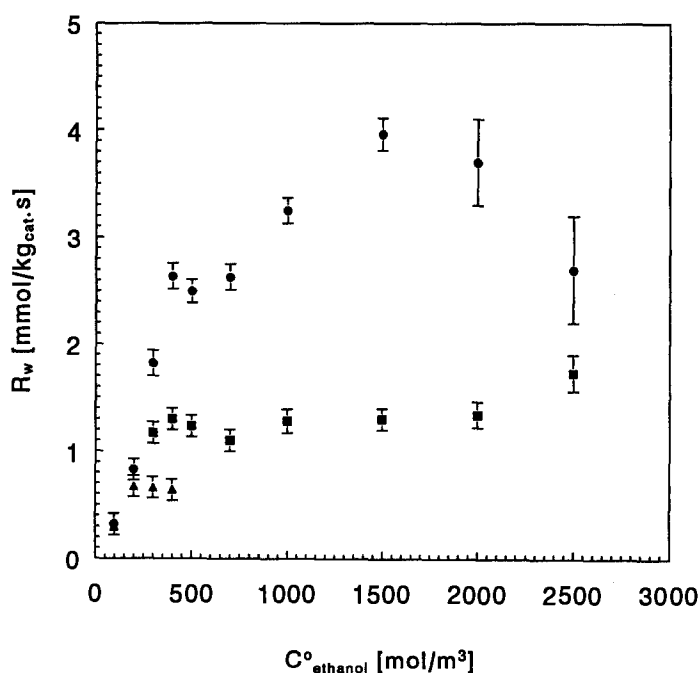

Fig. 1. Steady-state net specific disappearance rates of ethanol versus the feed concentration of ethanol for $T = 323$ K, $P_{O_2} = 58$ kPa, pH = 8.4. (●) Reductive start-up procedure; (▲, ■) oxidative start-up procedure.
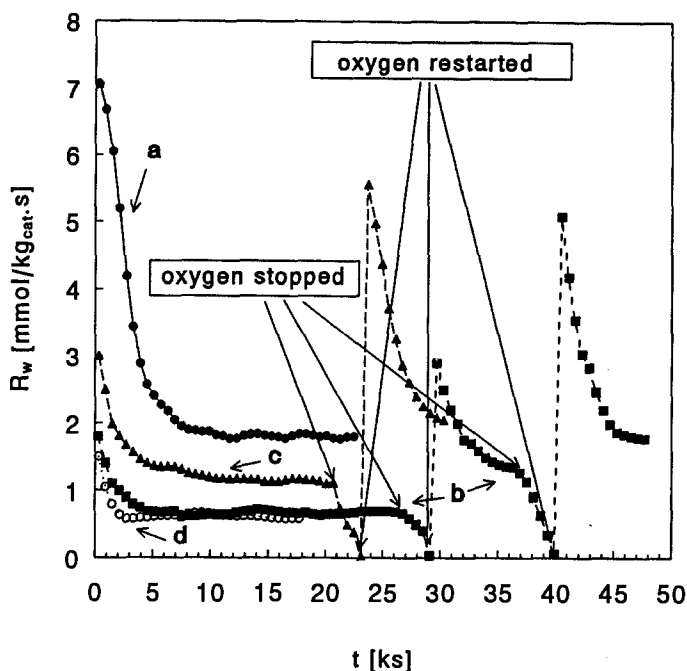
Fig. 2. Net specific disappearance rates of ethanol versus time for a feed concentration of ethanol of 300 mol m^{-3}, $T = 323$ K, $P_{O_2} = 58$ kPa, pH = 8.4. (●) Reductive start-up procedure, (■) oxidative start-up procedure and reaction alternated with two reduction periods, (▲) oxidative start-up procedure and reaction alternated with one reduction period, (○) oxidative start-up procedure.

centration, two different steady-states may result. This could be caused by the sensitivity of the reaction system to the initial conditions. Furthermore, it follows from fig. 2c that the middle steady-state jumped to the highest steady-state after a reduction period consisting of feeding the ethanol solution together with nitrogen without oxygen during 45 min [13,14,22]. During this reduction period the feed flow rate of ethanol solution was kept constant and the stirring speed was reduced to 4 s^{-1}.

The three steady-states could be reached starting from the oxidative start-up procedure by discontinuing the oxygen feed flow, see fig. 2b. The lowest steady-state jumped to the middle steady-state after the first reduction period by ethanol solution and the middle steady-state jumped to the highest state after the second reduction period by ethanol solution. Curve 2b between 30 and 37 ks is comparable to curve 2c between 0 and 7 ks. The initial rate as well as the approach of the final rate are very similar. Three steady-states could not be reached starting from the reductive start-up procedure while maintaining the ethanol feed flow. Apparently it is very difficult to oxidise the catalyst surface sufficiently in the presence of ethanol during a relatively short period.

The pH control, as mentioned in the experimental part, created an external feedback. Zimmermann et al. [23] showed that an external feedback can stabilize

unstable states or create an oscillation behaviour. The possibility exists that the middle steady-state is stabilized by this external feedback, although van den Tillaart [15] showed that the specific disappearance rate of ethanol does not strongly depend on pH in the region of pH from 7 to 9. Future modelling work will have to clear this question.

Fig. 3 shows the net specific disappearance rates of ethanol as a function of time for different start-up procedures at a feed ethanol concentration of 700 mol m^{-3}. Only two steady-states were observed. Apparently the two steady-states obtained after the oxidative start-up procedure at lower feed ethanol concentrations have merged. Again, the low steady-state jumped to the high steady-state after a reduction period by ethanol solution.

Multiple steady-states were also observed for different oxygen concentrations. Fig. 4 shows the dependence of the net specific disappearance rates of ethanol on the partial pressure of oxygen in the reactor at a feed ethanol concentration of 500 mol m^{-3}. Two steady-states were clearly observed. For partial pressures higher than 85 kPa the upper steady-state rates show a large standard deviation. From fig. 1 it can be seen that the last two values of the upper steady-state rate show also a large standard deviation. These large standard deviations could indicate that the steady-state was not truly reached within the experimental time scale of 21 ks, when the reductive start-up procedure was followed. The latter amounts
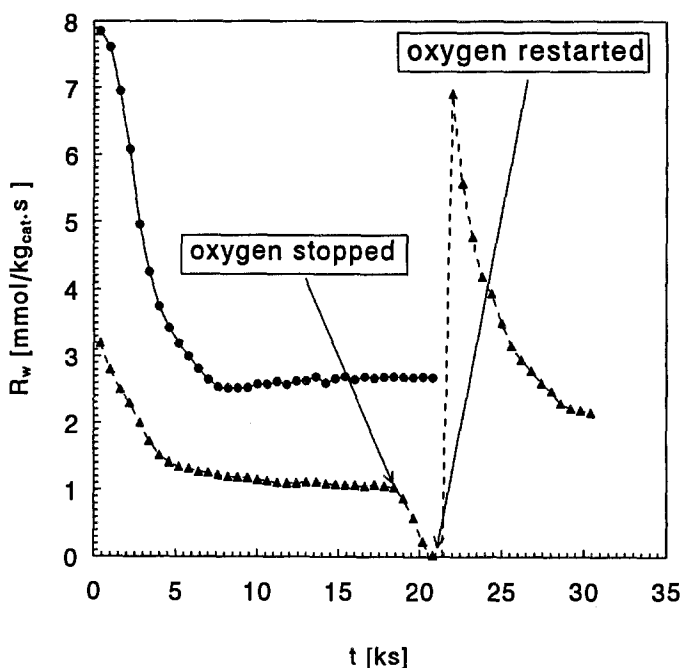

Fig. 3. Net specific disappearance rates of ethanol versus time for the feed concentration of ethanol 700 mol m^{-3}, $T = 323$ K, $P_{O_2} = 58$ kPa, pH $= 8.4$. (●) Reductive start-up procedure; (▲) oxidative start-up procedure and reaction alternated with one reduction period.
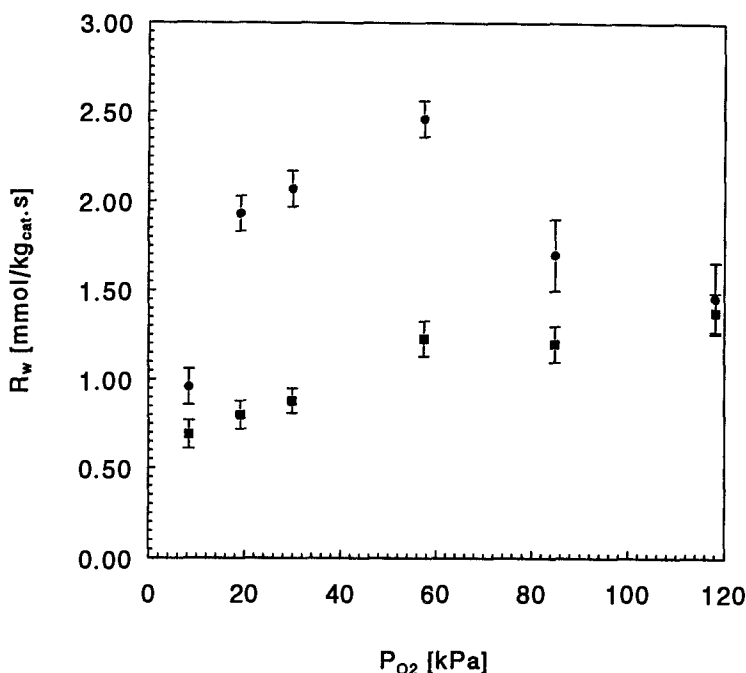
Fig. 4. Steady-state net specific disappearance rates of ethanol versus the partial oxygen pressure for the feed ethanol concentration 500 mol m^{-3}, $T = 323$ K, pH = 8.4. ($\bullet$) Reductive start-up procedure; ($\blacksquare$) oxidative start-up procedure.

to three times the residence time of the liquid in the reactor calculated from $t_r = V_R/(F_{V,E}^0 + F_{V,OH}^0)$, i.e. to three times the time scale on which the set-up responds to changes in conditions in the absence of reaction.

It can be seen from fig. 2 that with the oxidative start-up procedure a steady-state is reached on this time scale in the presence of reaction. With the reductive start-up procedure, however, the relaxation takes much longer in the presence of reaction. For linear kinetics the intrinsic chemical relaxation time, i.e. the relaxation time related exclusively to change in the degree of coverage of the reaction intermediates on the catalyst surface, is close to the reciprocal of the turnover frequency [24]. The steady-state turnover frequency of the oxidation is in the order of 0.05 s^{-1}. Hence, the steady-state oxidation rate is expected after 20 s if extrinsic chemical relaxation caused by "side" processes, e.g. reconstruction of a catalyst surface layer caused by reaction can be excluded.

Slow relaxation can also be a result of the nonlinearity of chemical kinetics [20]. Vleeming et al. [22] observed an increase of the open circuit potential of a platinized platinum electrode upon admitting oxygen to a continuous flow reactor for the oxidation of ethanol on a time scale of 1 ks. This increase was attributed to an increasing degree of coverage by oxygen or oxygen containing species. The same phenomena most probably explains the slow relaxation observed after a reductive start-up procedure.

4. Conclusions

There exists a region of process variables with up to three steady-states for the platinum catalyzed oxidation of aqueous ethanol at isothermal conditions and in the absence of mass transfer limitations. The upper steady-state is reached by a reductive route, either during the start-up or by discontinuing the oxygen feed. Reaching the lower steady-state requires an oxidative start-up procedure.

Acknowledgement

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