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Modelling Concentration Oscillations in the Oxidation of Carbon-Monoxide/Propene Mixtures over Supported Platinum Catalysts

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Modelling concentration oscillations in the oxidation of carbon-monoxide/propene mixtures over supported platinum catalysts

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A study is reported on the oscillatory effects observed in the oxidation of carbon-monoxide/propene mixtures over a supported platinum catalysts in a flow reactor. The oscillatory behaviour has been examined over a range of operating variables, together with catalyst site concentration. It is shown that the elementary step treatment developed for explaining the behaviour of CO/butene oxidation provides a largely satisfactory approach for this system also. The kinetic model accounts for the appearance and disappearance of oscillations as the reactor residence time is increased. A simpler asymptotic third-order model, soluble analytically, is useful in that it successfully predicts the appearance of the oscillations. For the reaction dynamics observed, it is not necessary to invoke temperature effects or the formation of surface oxides.

Nomenclature

C_{TOT}	total gas concentration in the reactor (mol cm^{-3})
k_1	reaction rate constant for step i (cm^3 mol^{-1} s^{-1} for k_{p1}, k_{p2}, k_{p4}; s^{-1} for all other k_1)
m	mass of catalyst (g)
N_{s}	number of active sites onto which one propene molecule adsorbs (dimensionless)
r_1	rate of mechanism step i (s^{-1}) ($= r_{p1} - r_{m1}$, $i = 1, 2, 4, 6, 7$)
s	active catalyst site
s′	support adsorption site
s_1	surface concentration of species i (mol g^{-1})
s_0	total concentration of active sites (mol g^{-1})
s'_1	support concentration of species i (mol g^{-1})
s_{sup}	total concentration of support adsorption sites (mol g^{-1})
V	reactor volume (cm^3)
x_1	gas phase mole fraction of species i
z_1	dimensionless surface concentration of species i ($= ms_1/Vc_{\mathrm{TOT}}$)
z_0	surface capacity factor ($= ms_0/Vc_{\mathrm{TOT}}$) (dimensionless)
z'_1	dimensionless support concentration of species i ($= ms'_1/Vc_{\mathrm{TOT}}$)
z_{sup}	support capacity factor ($= ms_{\mathrm{sup}}/Vc_{\mathrm{TOT}}$) (dimensionless)
Σ	volume change correction term defined by (31) (s^1)
τ	mean gas residence time in the reactor (s)

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Subscripts

F	feed
v	vacant

Species

1	CO
2	oxygen (molecular if gas phase, atomic if surface)
3	propene
4	CO_2

Reaction steps

$p1$	CO adsorption
$m1$	CO desorption
$p2$	oxygen adsorption
$m2$	oxygen desorption
3	CO (adsorption) oxidation
$p4$	propene adsorption on active catalyst
$m4$	propene desorption from active catalyst
5	adsorbed propene oxidation
$p6$	propene adsorption on support
$m6$	propene desorption from support
$p7$	CO_2 adsorption on support
$m7$	CO_2 desorption from support

1. Introduction

The oxidation of CO over platinum catalysts has attracted considerable interest since the first report of rate oscillations during the oxidation of CO in air over a single Pt/Al_2O_3 pellet. Oscillations have since been observed during CO oxidation in single-pass and recirculating reactors with the catalyst in the form of metal wires (Galway *et al.* 1985) foils, coils and beds of supported catalyst particles. In the case of recirculating reactors, the oscillations persist in the region where changes in the recycle ratio have no effect, indicating that external heat and mass transfer effects are not their cause. Reports of observed cases of oscillations in CO oxidation are extensively reviewed by Mukesh *et al.* (1983) and Razon & Schmitz (1986). Rate oscillations in CO oxidation have been reported too, at ultra-high vacuum (UHV) conditions by Imbihl *et al.* (1986). Periodic surface structural transformations are associated with sustained temporal oscillations in the rate of CO oxidation on Pt (100) at UHV and have been analysed in terms of the dynamics of surface reconstruction by Andrade *et al.* (1989). This transformation is shown by scanning low-energy electron diffraction (LEED) to involve a wave-like propagation of alternating bands of two surface structural modifications across the entire crystal surface area. The connection between such findings and oscillatory processes at atmospheric pressure on polycrystalline catalyst samples is still a matter for conjecture. Isothermal reaction rate oscillations have been described in the oxidation of propene over a Pt wire by Scheintuch & Luss (1981) in the temperature range 175–228 °C. Multiple steady states were also reported, and have been analysed using singularity theory with particular attention being paid to the interaction between multiple steady states, symmetry breaking and the interpretation of kinetic measurements (Scheintuch & Luss 1983; Scheintuch *et al.* 1989).

Rate oscillations have also been observed during the simultaneous oxidation of CO and one or more alkenes, when the alkene is 1-butene, ethene, 2-butene and a mixture of propene and ethene (Capsaskis 1985). The search for models which can describe the isothermal oscillatory phenomena in CO oxidation has led to the investigation of a multitude of theoretical models. The proposed causes for such oscillations can be broadly divided into: (*a*) surface temperature fluctuations (Lagos *et al.* 1979; Jensen & Ray 1982); (*b*) surface coverage dependent activation energies (Pikios & Luss 1977); (*c*) slow reversible adsorption of 'inert' species competing with reactants for surface sites (Eigenberger 1978); (*d*) slow alternate oxidation and reduction of the catalyst surface (Sales *et al.* 1982); (*e*) formation of reactant islands on the catalyst surface (Mukesh *et al.* 1984); (*f*) nonlinearities in high-order reaction systems (Morton & Goodman 1981).

In this paper, we report an experimental investigation of the oscillatory behaviour of CO/propene oxidation on a supported Pt catalyst. We also demonstrate that an elementary step model for CO oxidation, augmented by steps for the reversible adsorption and oxidation of an alkene, is then shown to lead to oscillatory states. Using rate constants values derived from separate experiments on the adsorption and reaction of CO and of propene, a much simpler model, does indeed apply in the expected region of the parameter space and supports the assumptions of the more general model.

2. Experimental

The experimental apparatus consists of a gas mixture preparation facility, an isothermal flow reactor and a detector unit. It has been described elsewhere in a related study on butene by Mukesh *et al.* (1983). Its principal features are that the feed mixtures are prepared in advance of each experiment. One of two feed streams leads to the reactor. A solenoid-operated valve allows rapid instantaneous changes in the feed stream leading to the reactor, causing a step change in reactor feed concentration and/or flow rate. The reactor consists of a metal bellows pump for gas recirculation and a catalyst bed inside an oven. This combination has been shown to approximate to a gradientless stirred tank reactor. Residence time characteristics are important in defining the reactor–reaction characteristics of the system. The catalyst bed consists of seven parallel channels bored in a cylindrical metal block of a total volume of 48.5 cm^3. The total catalyst charge (usually 10.04 g) is distributed equally between these channels and the catalyst is held in place by wire gauzes. The pressure in the reactor is 81–87 cm Hg†. The temperature is measured by two thermocouples inserted into the catalyst bed.

Two different batches of catalyst have been used. Both of these are commercially available 0.5% w/w Pt on γ-Al_2O_3 and are in the form of $\frac{1}{8}$ in‡ diameter cylinders. *In situ* titrations with oxygen and CO, however, show catalyst II to possess a four-fold greater concentration of active sites than catalyst I. Details of this estimation and other catalyst properties are also listed by one of us (Capsaskis 1985). The detector section consists of a VG Micromass-6 mass spectrometer and a PDP 11/45 mini-computer. Rapid sequential monitoring of up to four species is possible with this type of mass spectrometer and the raw data is logged by the computer for subsequent conversion to mole fraction values and graphical presentation. The

† 1 cm Hg ≈ 1333 Pa. ‡ 1 in = 2.54×10^{-2} m.

Figure 1

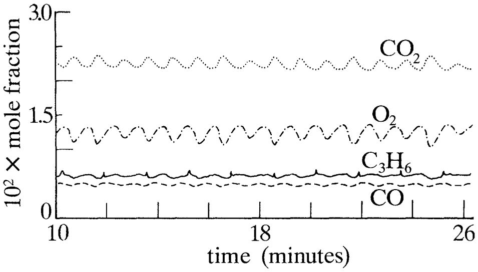

Figure 2

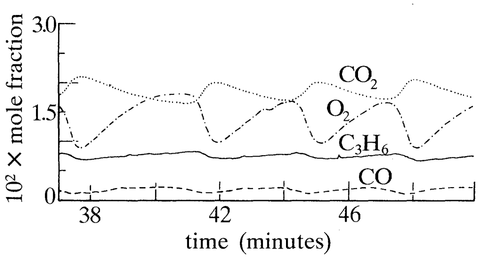

Figure 3

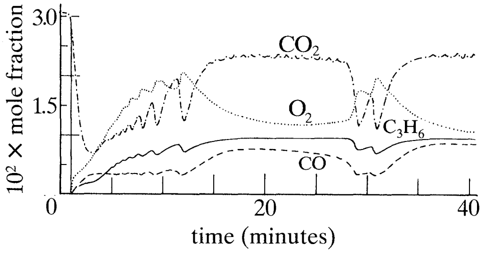

Figure 1. Observed oscillations following a switch in gas feed composition from 3% O_2 to 1% C_3H_6, 2% CO and 3% O_2. Reactor volume = 45 cm^3; total gas pressure = 1.07 bar (1 bar = 10^5 Pa); catalyst charge = 10.05 gm; temperature = 150 °C; gas flow rate = 75.5 cm^3 min^{-1}.

Figure 2. Observed oscillations following a switch in gas feed composition from 3% O_2 to 1% C_3H_6, 2% CO and 3% O_2. Temperature = 135 °C; gas flow rate = 37.5 cm^3 min^{-1}. Other variables as in figure 1.

Figure 3. Observed oscillations following a switch in gas feed composition from 3% O_2 to 1% C_3H_6, 2% CO and 3% O_2. Temperature = 135 °C; gas flow rate = 50 cm^3 min^{-1}. Other variables as in figure 1.

standard form of experiment designed to investigate the presence of oscillatory states in the oxidation of CO/propene mixtures, consists of catalyst pretreatment with a mixture of either 2% CO or 3% oxygen in argon for about one hour at experimental conditions, followed by a step change to the reaction mixture, typically 1% propene, 2% CO and 3% oxygen. The 'stoichiometric' amounts of oxygen used should be noted. Extensive investigations of our own indicate very different dynamic behaviour in the oxidation of carbon monoxide compared with the experimental results obtained when using a large excess of oxygen. Excess oxygen has been used by many other groups. A detailed account of the results is not given here but three experimental figures are shown illustrating, as was found in CO/butene/O_2 mixtures, that reactor residence time is an important experimental variable which can lead to sine wave oscillations (figure 1), distorted sine waves (figure 2) and multi-peak oscillations (figure 3). Periodic spikes of long period (20 mins) can also be observed for various combinations of parameters.

3. The full theoretical model

The model used here is an extension of the elementary step model (ESM) proposed by Goodman *et al.* (1982) to explain the dynamic behaviour of CO oxidation over supported Pt in a CSTR. This has its origins in a Langmuir–Hinshelwood model, with two reactant species competing for surface sites but without the assumptions (i) that all reversible steps are at equilibrium and (ii) that the surface reaction step is the rate determining one. The present model is thus based on the following assumptions.

1. All gas phase species compete for the same catalyst sites.
2. CO adsorbs linearly onto one catalyst site.
3. Oxygen adsorbs dissociatively.
4. Reaction occurs only between adsorbed species.
5. All hydrocarbons are completely converted to CO_2 and H_2O.
6. The surface oxidation of propene proceeds through a reactive intermediate and is overall first-order in adsorbed oxygen.

The Langmuir–Hinshelwood assumption that heats of adsorption are independent of surface coverage is highly suspect but allowing for such effects makes the analysis unwieldy and is not justified.

The reaction mechanism can be expressed as:

$$\begin{gathered}
\mathrm{CO}+\mathrm{s}\leftrightarrow\mathrm{CO}-\mathrm{s},\\
\mathrm{O_2}+2\mathrm{s}\leftrightarrow 2\mathrm{O}-\mathrm{s},\\
\mathrm{COs}+\mathrm{Os}\rightarrow\mathrm{CO_2}+2\mathrm{s},\\
\mathrm{C_3H_6}+\mathrm{N_s\,s}\leftrightarrow\mathrm{C_3H_6}-\mathrm{N_s\,s},\\
\mathrm{C_3H_6}-\mathrm{N_s\,s}+9\mathrm{O}-\mathrm{s}\rightarrow 3\mathrm{CO_2}+3\mathrm{H_2O}+(\mathrm{N_s}+9)\mathrm{s},\\
\mathrm{C_3H_6}+\mathrm{s'}\leftrightarrow\mathrm{C_3H_6}-\mathrm{s'},\\
\mathrm{CO_2}+\mathrm{s'}\leftrightarrow\mathrm{CO_2}-\mathrm{s'}.
\end{gathered}$$

Points of note here are (*a*) that the catalyst support (Al_2O_3) does absorb propene and CO_2 (sites s′) and these are included in the kinetic analysis, the absorption and desorption parameters being determined experimentally using catalyst-free support and (*b*) the reaction representing the oxidation of propene is lumped as a single step which it is recognized is a collapsed version of a complex sequence of reaction steps. The rate equations for the reactor–reaction system thus involve the variation of gas phase species, x_i, catalyst surface species z_i and adsorbent surface species z'_i. Rates of adsorption from gas to solid are denoted by r_{pi} and desorption by r_{mi}. The surface oxidation reactions, for adsorbed CO and propene r_3 and r_5, are represented as following second-order kinetics between this reactor with adsorbed oxygen atoms.

The full model thus takes the form:

$$\mathrm{d}x_1/\mathrm{d}t = (x_{1\mathrm{F}}-x_1)/\tau - r_{p1} + r_{m1} + x_1\,\Sigma, \tag{1}$$

$$\mathrm{d}x_2/\mathrm{d}t = (x_{2\mathrm{F}}-x_2)/\tau - r_{p2} + r_{m2} + x_2\,\Sigma, \tag{2}$$

$$\mathrm{d}x_3/\mathrm{d}t = (x_{3\mathrm{F}}-x_3)/\tau - r_{p4} + r_{m4} - r_{p6} + r_{m6} + x_3\,\Sigma, \tag{3}$$

$$\mathrm{d}x_4/\mathrm{d}t = -x_4/\tau + r_3 + 3r_5 - r_{p7} + r_{m7} + x_4\,\Sigma, \tag{4}$$

$$\mathrm{d}z_1/\mathrm{d}t = r_{p1} - r_{m1} - r_3, \tag{5}$$

$$\mathrm{d}z_2/\mathrm{d}t = 2r_{p2} - 2r_{m2} - r_3 - 9r_5, \tag{6}$$

$$\mathrm{d}z_3/\mathrm{d}t = r_{p4} - r_{m4} - r_5, \tag{7}$$

$$\mathrm{d}z'_3/\mathrm{d}t = r_{p6} - r_{m6}, \tag{8}$$

$$\mathrm{d}z'_4/\mathrm{d}t = r_{p7} - r_{m7}, \tag{9}$$

where

$$r_{p1} = k_{p1}\,x_1\,c_{\mathrm{TOT}}\,z_{\mathrm{v}}, \tag{10}$$

$$r_{m1} = k_{m1}\,z_1, \tag{11}$$

$$r_{p2} = k_{p2}\,x_2\,c_{\mathrm{TOT}}\,z_{\mathrm{v}}^2, \tag{12}$$

$$r_{m2} = k_{m2}\,z_2^2, \tag{13}$$

$$r_3 = k_3\,z_1\,z_2, \tag{14}$$

$$r_{p4} = k_{p4}\,x_3\,c_{\mathrm{TOT}}\,z_{\mathrm{v}}^{N_{\mathrm{s}}}, \tag{15}$$

$$r_{m4} = k_{m4}\,z_3, \tag{16}$$

$$r_5 = k_5\,z_3\,z_2, \tag{17}$$

$$r_{p6} = k_{p6}\,x_3\,c_{\mathrm{TOT}}\,z'_{\mathrm{v}}, \tag{18}$$

$$r_{m6} = k_{m6}\,z'_3, \tag{19}$$

$$r_{p7} = k_{p7}\,x_4\,c_{\mathrm{TOT}}\,z'_{\mathrm{v}}, \tag{20}$$

$$r_{m7} = k_{m7}\,z'_4 \tag{21}$$

and

$$x_1 = c_i/c_{\mathrm{TOT}} \tag{22}$$

$$z_i = ms_i/Vc_{\mathrm{TOT}}, \tag{23}$$

$$z_0 = ms_0/Vc_{\mathrm{TOT}}, \tag{24}$$

$$z'_i = ms'_i/Vc_{\mathrm{TOT}}, \tag{25}$$

$$z'_{\mathrm{sup}} = ms_{\mathrm{sup}}/Vc_{\mathrm{TOT}}\ , \tag{26}$$

$$z_{\mathrm{v}} = z_0 - z_1 - z_2 - N_{\mathrm{s}}\,z_3, \tag{27}$$

$$z'_{\mathrm{v}} = z_{\mathrm{sup}} - z'_3 - z'_4, \tag{28}$$

$$\Sigma = r_{p1} - r_{m1} + r_{p2} - r_{m2} + r_{p4} - r_{m4} + r_{p6} - r_{m6} + r_{p7} - r_{m7}. \tag{29}$$

A feature of the model is that interactions between gas phase and surface concentrations are explicitly included. This is necessary when following the reaction through time-varying gas phase concentrations for dispersed metal catalysts since, in contrast to foil and wire studies, a mechanism is required to account for the synchronized behaviour of the separate metal particles on the catalyst. The surface capacity, z_0, is defined above as the ratio of the total number of catalysts sites to the number of gas phase molecules in the reactor and provides a qualitative measure of the loading as well as the dispersion in various reactor systems. The term denoted by Σ corrects for the change in volumetric flowrate in the reactor due to the reaction stoichiometry and can be ignored in all further discussion of this model.

It should be noted that, whereas the gas-phase concentrations are made non-dimensional by normalizing with respect to the overall concentration, the surface concentrations are expressed not in terms of surface coverage fractions, θ, but of surface coverage fractions multiplied by the surface capacity, i.e.

$$z_i = ms_i/Vc_{\mathrm{TOT}} = (ms_0/Vc_{\mathrm{TOT}})\,\theta_i = z_0\,\theta_i. \tag{25}$$

The advantage of this dimensionless formulation rather than the usual one is that, in terms of θ the rate term k_{m1} would include an implicit term in the number of catalyst sites per unit of catalyst mass, which is a function of catalyst activity, preparation and dispersion. Using the formulation described above, the concentration of sites is treated explicitly and, therefore, the kinetic constants can be considered to be independent of the catalyst properties and to be applicable across various Pt/Al_2O_3 catalysts, regardless of preparation, activity or dispersion. The number of surface sites onto which one propene molecule adsorbs, N_s, for which no universally agreed value could be found in the literature, was derived by *in situ* titrations of the catalyst using oxygen and propene (Capsaskis 1985). Assuming that only integral values of N_s are possible, the value derived from these titrations is 1.

Oscillating reactions usually require an autocatalytic step in the reaction network. Autocatalysis manifests itself here through the observation that CO_2 does not adsorb on platinum. Thus the reaction of CO or propene with a surface largely covered with oxygen, accelerates as long as oxygen coverage remains high and further sites become available as oxygen is removed by reaction. The rich variety of oscillations found has analogues in the theoretical study by Gray & Scott (1990) of two parallel homogeneous reactions, one of which is autocatalytic.

4. Steady-state and dynamic solutions

The ordinary differential equations (ODEs) above, cannot be integrated analytically to describe the evolution of the reaction system with time. Furthermore, because of the range of orders of magnitude of the rate constants, the set of equations is stiff. The recommended method for numerical integration of still systems of ODEs is Gear's variable-step–variable-order method and this was used. The integration routine stores information on the history of the dependent variables in the form of first and higher-order derivatives, rather than as values at previous time stops, so allowing the algorithm to be implemented with a time step appropriate to the stiffness of the problem at that integration step. As regards the steady static solution of the equation a computational problem arises due to the possibility of three vectors of gas and surface concentrations being solutions of the system for a given set of rate parameters, feed concentrations, surface capacity and reactor residence time. Most of the standard routines available in subroutine libraries cannot guarantee the identification of all possible roots of a set of equations. For this reason, a special program was written with the aim of locating all steady states of the model. The method involved solving subsets of these equations at specific small intervals of various variables (CO gas mole fraction, propene and oxygen surface dimensionless concentrations) and finding these values which led to all equations being valid. A search of these variables from their lower limit (0) to their maximum leads to the location of all possible roots. This program was used in conjunction with stability analysis routines which derived the characteristic coefficients at each solution point.

5. Simplified model

Even when a consistent set of parameters can be obtained to describe the dynamics of the system, the dimensionality of the problem is large and in order to bring the model into a form whose phase space can be visualised, it is necessary to reduce it to third-order. If this is to be achieved, six of the ODEs set out above must be replaced by algebraic equations. Conclusions drawn from the qualitative behaviour of the experimental system and of the full model suggest for which variables the time-dependent variation might be neglected in a first-order approximation.

The most obvious candidates for replacement by algebraic equations are the mass balances on the species adsorbed on the catalyst support, i.e. equations (8) and (9). Thus, the following restrictions apply:

$$\mathrm{d}z_3'/\mathrm{d}t = 0, \quad \mathrm{d}z_4'/\mathrm{d}t = 0.$$

Inspection of the experimental occurrence of spontaneous oscillations indicates that, the gas phase concentrations of CO′ and propene in the reactor do not oscillate appreciably. Thus a further two differential equations may be replaced by algebraic ones by setting

$$\mathrm{d}x_1/\mathrm{d}t = 0, \quad \mathrm{d}x_3/\mathrm{d}t = 0,$$

leaving five ODEs. Since propene adsorption on the support is no longer a time-varying process and has been eliminated, the mass balance on gas phase CO_2 (equation (4)) is no longer relevant, since it affects no other equation. Of the remaining four ODEs, one more must be set to zero. If x_2 is set to zero, then the model becomes unrealistic, since inspection of the experimental results shows that the exit concentration of oxygen clearly varies periodically with time. So, the choice is narrowed down to setting either $\dot{z}_1 = 0$(CO) or $\dot{z}_3 = 0$(propene). In the case where $N_s = 1$ the model is unaltered by mutual exchange between z_1 and z_3, except for the stoichiometric coefficients. Thus, the surface concentration of CO is chosen as the time-independent variable. The model reduces to:

$$\mathrm{d}x_2/\mathrm{d}t = (x_{2\mathrm{F}} - x_2)/\tau - r_2, \tag{26}$$

$$\mathrm{d}z_2/\mathrm{d}t = 2r_2 - r_3 - 9_{r5}, \tag{27}$$

$$\mathrm{d}z_3/\mathrm{d}t = r_4 - r_5, \tag{28}$$

$$r_1 - r_3 = 0, \tag{29}$$

$$\tau r_1 = x_{1\mathrm{F}} - x_1, \tag{30}$$

$$\tau r_4 = x_{3\mathrm{F}} - x_3, \tag{31}$$

where the r_i are defined in equations (10) through to (21) above.

6. Simulation results

The search for mathematical models which will predict sustained spontaneous temporal oscillations has concentrated on searches for sets of ordinary differential equations which, for certain parameter values, lead to stable periodic solutions, known as 'limit cycles'. For second-order systems, the Poincare–Bendixson theorem provides the easiest means of finding limit cycles, but this powerful theorem unfortunately does not apply to third or higher order systems. Furthermore, the tools of stability analysis, linearization round a steady state and examination of the eigenvalues arising, provide no means of identifying limit cycles unless the system has a unique unstable steady state, in which case a stable limit cycle must exist

Table 1. *Calculated values of* CO *oxidation kinetic parameters at* 135 °C

k_{p1}	6.642×10^{6} cm^3 mol^{-1} s^{-1}	k_{m1}	0.380 s^{-1}
k_{p2}	1.680×10^{7} cm^3 mol^{-1} s^{-1}	k_{m2}	0.000 s^{-1}
k_3	2.938×10^{8} s^{-1}		
k_{p6}	1.900×10^{5} cm^3 mol^{-1} s^{-1}	k_{m6}	8.840 s^{-1}
k_{p7}	1.373×10^{5} cm^3 mol^{-1} s^{-1}	k_{m7}	1.000
z_0	0.1209	z_{sup}	1.706×10^{5}

around it. Linearized stability analysis applied to equations (26)–(31) shows such a steady state can occur and gives parameter ranges for which the limit cycle exists. Here experimental results, numerical computations of the ninth-order model and results from the reduced third-order model are compared.

Given the number of adjustable parameters (rate constants) in the model for the oxidation of CO/alkene mixtures over supported Pt catalysts, an *ab initio* numerical search for limit cycle solutions is a substantial problem. In this study, the method chosen to reduce the number of adjustable parameters was to determine from separate experiments the relevant kinetic parameters using the same supported Pt catalyst as that over which oscillations in CO/propene oxidation were observed.

1. The values of the kinetic parameters for the oxidation of CO (constants k_{p1}, k_{m1}, k_{p2}, k_{m2}, k_3) and k_{p7} and k_{m7}, reversible adsorption constants for CO_2 on an alumina, as well as z_0.

2. The values of the kinetic parameters for the reversible adsorption of propene on the Al_2O_3 support (constants k_{p6}, k_{m6} and z_{sup}).

This leaves only the kinetic parameters for the propene oxidation over Pt (constants k_{p4}, k_{m4}, k_5) as adjustable parameters in the search for limit cycle solutions to the model equations.

The method of estimation of the kinetic parameters mentioned above is described in detail elsewhere (Capsaskis 1985; Goodman *et al.* 1982). Briefly, following pretreatment of the catalyst with one reactant at a certain temperature and residence time, a step change in feed composition is made and the mole fraction of the various species in the reactor output measured as a function of time. The same step change can be modified using the ODE model and estimates of the rate constants, and the mole fraction of the various species in the reactor output predicted. The divergence between measured and predicted response can be used as an objective function, whose minimisation provides the best estimates of the rate constants, the values of the kinetic parameters can be optimized to minimize the divergence between the experimental and the calculated response of the reactor. Table 1 gives the above kinetic parameters at 135 °C which were determined by calculating activation energies from such calculated values at 90 °C, 120 °C and 150 °C.

By using the values in table 1 as constants, one can employ values for k_{p4}, k_{m4} and k_5 derived from applying the same transient technique to the oxidation of propene in the absence of CO as starter values for searches through the corresponding parameter space for limit cycle behaviour of the model. For a residence time of 23.3 s (equivalent to a flowrate of 100 cm^3 min^{-1} NTP through the reactor), and a reactant mixture consisting of 1% C_3H_6, 2% CO and 3% O_2, the following parameters ranges lead to limit cycle solutions for the full model: k_{p4} (1.00×10^{7}–2.00×10^{7} cm^3 mol^{-1} s^{-1}); k_{m4} (0.330 s^{-1}); k_5 (3.33×10^{3} s^{-1}).

The limit cycle for $k_{p4} = 1.95\times10^{7}$ cm^3 mol^{-1} s^{-1} is reproduced in figure 4*a*.

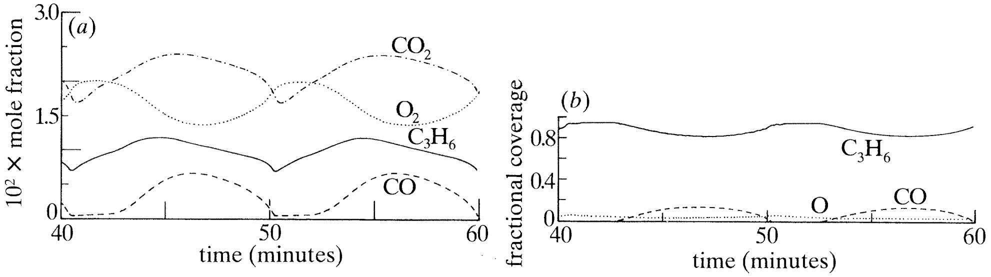

Figure 4. (*a*) Simulated gas phase concentrations as functions of time. (*b*) Simulated surface concentrations as functions of time. Kinetic parameters as in table 1 and $k_{p4} = 1.95 \times 10^7$ cm^3 mol^{-1} s^{-1}, $k_{m4} = 0.335$ s^{-1}, $k_5 = 3.30 \times 10^3$ s^{-1}.

Table 2. *Effect of a* 10% *increase in each kinetic parameter on the period and amplitude of limit cycles*

	τ min	$\delta\tau/\tau$ (%)	O_2 exit mole fraction amplitude (%)
base case	9.8	0	0.72
k_{p1}	10.8	10	0.85
k_{m1}	9.0	−8	0.60
k_{p2}	9.5	−3	0.22
k_3	9.8	0	0.72
k_{p4}	—	stable steady state	—
k_{m4}	—	stable steady state	—
k_5	9.7	−1	0.71
k_{p6}	9.9	1	0.69
k_{m6}	9.6	−2	0.74
k_{p7}	9.8	0	0.71
k_{m7}	9.8	0	0.72
z_0	—	stable steady state	—
z_{sup}	9.8	0	0.72

Inspection of the surface fractional coverages plotted in figure 4*b* indicates the predominance of adsorbed propene, which over one cycle occupies between 82% and 94% of the active sites on the catalyst.

In qualitative terms the dynamic behaviour of the system may be considered as arising from the well documented bistability of CO oxidation over a platinum catalyst. The presence of propene can in certain parameter regions induce hard relaxation oscillations between the low and high conversion states, and destabilizes the high conversion state giving soft smaller amplitude nearly sinusoidal oscillations. The presence of both types of oscillations explains the bursting of multipeak oscillations followed by a quiescent period.

The sensitivity of the limit cycle solution to the particular values of the kinetic parameters can be best estimated by displacing each by 10% from its value in table 1 and recording the effect of this perturbation on the period and amplitude of the limit cycle in table 2.

Inspection of this table shows that the behaviour of the system is most sensitive to the surface capacity term, z_0, as well as the rate constants for propene adsorption and desorption on the catalyst, followed in order of decreasing importance by the rate constants for CO and oxygen adsorption and CO desorption. Rate constants for

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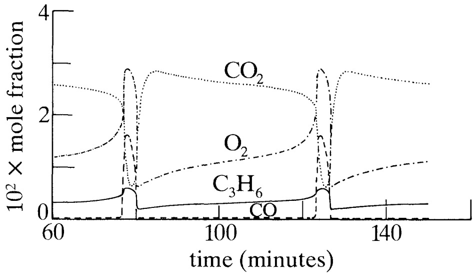

Figure 5. Simulated gas phase oscillations with a gas feed composition of 3% O_2, 0.5% C_3H_6 and 2% CO. Residence time = 12 s; rate constants in table 3.

Table 3. *Values of kinetic constants leading to limit cycles at* 150 °C

k_{p1}	1.835×10^7 cm^3 mol^{-1} s^{-1}	k_{m1}	1.228 s^{-1}
k_{p2}	2.205×10^7 cm^3 mol^{-1} s^{-1}	k_{m2}	5.640×10^{-3} s^{-1}
k_3	1.757×10^8 s^{-1}	—	—
k_{p4}	1.350×10^7 cm^3 mol^{-1} s^{-1}	k_{m4}	1.450×10^{-3} s^{-1}
k_5	3.300×103 s^{-1}	—	—
k_{p6}	1.803×10^5 cm^3 mol^{-1} s^{-1}	k_{m6}	8.134 s^{-1}
k_{p7}	1.732×10^5 cm^3 mol^{-1} s^{-1}	k_{m7}	1.000
z_0	0.141	z_{sup}	1.35×10^5

propene oxidation and adsorption on the support have a marginal effect and the remaining parameters have no observable effect. The model can also produce limit cycle solutions when propene is assumed to adsorb on two sites on the catalyst surface.

It is worth noting that, for the rate constants in table 3 which have been calculated from separate transient experiments at 150 °C, a feed mixture of 0.5% C_3H_6, 2% CO and 3% O_2 and a residence time of 12 s, lead to limit cycles with periods of 48 min (i.e. 230 residence times) (figure 5). This is an example of period lengthening where limit cycles of very long periods can arise from the interaction of fast reaction steps.

To test the validity of the approximation of the simplified third-order model proposed above to the full ninth-order model, the above values of the various kinetic parameters, which lead to oscillatory solutions of the full model, were substituted into the third-order model. The solution of the simplified model equations by the method outlined above gives a unique steady state for this set of kinetic parameters and residence time. Linearized stability analysis of this state indeed shows it to be an unstable steady state and, therefore, a stable limit cycle solution can be inferred to exist around it, in agreement with the predictions of the full ninth-order model. A further test of the validity of the approximation of the full ninth-order model by the third-order model is obtained by examining the sensitivity of the full and the simplified models with respect to the various parameters and in particular with respect to surface capacity and residence time. For the kinetic parameters given above and $z_0 = 0.121$, the limit cycle solution region exists within a narrow residence time range of 22–26 s and, within this range, the period of the limit cycles is rather insensitive to the residence time (figure 6).

The existence or not of limit cycle solutions as a function of surface capacity z_0 and residence time for the full model is also shown in figure 6. A similar investigation of the simplified model predicts a lower bound to the limit cycle region at a residence time of 19 s but no upper bound was located even when the residence time was set

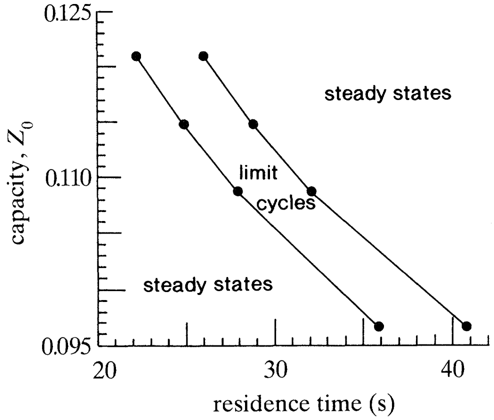

Figure 6. Calculated oscillatory region as a function of surface capacity z_0 and gas residence time for full model. Kinetic parameters as in table 1 and $k_{p4} = 1.95 \times 10^7$ cm^3 mol^{-1} s^{-1}, $k_{m4} = 0.33$ s^{-1}, $k_5 = 3.30 \times 10^3$ s^{-1}.

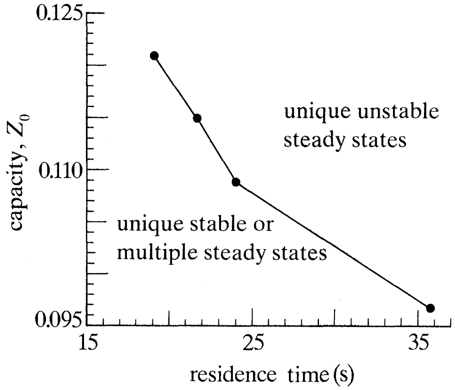

Figure 7. Calculated lower oscillation limit with surface capacity and gas residence time for simplified model. Parameters taken from table 3.

at 2000 s (figure 7). The region of oscillatory states moves to progressively higher residence times as the surface capacity is reduced (which is roughly proportional to either the dispersion or the activity of the catalyst). In summary the simplified model provides a useful prediction of the lower bounds of the oscillatory region but fails to predict the existence of an upper limit to the oscillatory region.

7. Conclusions

It is concluded that the simplified third-order model can approximate the behaviour of the full CO/propene oxidation system at low residence times (high flow rates through the reactor) but fails as the residence times becomes higher (the flow rate is reduced). For both the experimental system and the full model, with residence time as a coordinate on either side of the oscillatory region, conversion is very different. Consumption of oxygen, the limiting reactant is incomplete at residence times lower than the oscillatory boundary with neat total consumption of oxygen at residence times higher than the upper oscillatory boundary. It appears that the assumptions built-in to the simplified model are consistent with the low-residence-time/low-conversion régime but inconsistent with the high-residence-time/high-conversion régime. However, the investigation of the onset of limit cycle behaviour from the low-conversion steady-state régime is facilitated when an asymptotic model of lower dimensionality is permissible and the conceptual ease of working in a three-dimensional phase space provides a helpful insight into the appearance of oscillatory states.

Not discussed here is the experimental finding that the isothermal concentration oscillations extinguish on increasing the reactor temperature. This provides some evidence that the oscillations are not just due to thermal effects but are intrinsically related to reaction kinetics.

Also the temperature range for oscillations considered in this work is lower than that in some related studies reported in the literature. Thus, although the formation of a surface oxide is not required for the existence of oscillatory solutions of the model, such a step may become relevant at temperatures greater than 250 °C and the interaction of two oscillatory mechanisms may account for some of the complex oscillatory phenomena observed. The proposed elementary step model generates oscillatory solutions qualitatively similar to the observed concentration oscillations, using rate constants mostly derived from separate simpler experiments on the same system. Further, the model reflects the observed changes as the various parameters are changed.

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