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TRANSIENT STUDIES OF CARBON MONOXIDE OXIDATION OVER PLATINUM CATALYST

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The applicability of transient techniques to the study of the catalytic oxidation of carbon monoxide is discussed. It is shown that at 100-150°C adsorption and desorption equilibria between the gas phase and catalyst cannot be assumed, and an elementary step formulation may be used to predict both multiple steady states and transient behaviour.

A detailed understanding of the oxidation of carbon monoxide over platinum catalyst at atmospheric pressure is still not available in spite of extensive theoretical and experimental effort. In particular, the existence of multiple steady states and a rich variety of oscillatory behaviour has not yet been accounted for quantitatively. In this note the value of transient techniques is illustrated briefly and it is shown that the derived reaction parameters may be used to predict observed behaviour in both steady state and non-steady state experiments using an elementary step formulation.

The literature contains many references to account for isothermal multiple states as well as oscillatory behaviour. The models that have been proposed include (a) surface heterogeneity leading to rate constants which are a function of surface coverage [1,2], (b) precursor states [3], (c) the formation of relatively inert buffer species such as metal oxides [4], and non-isothermal models [5] in which the instabilities are attributed to temperature effects.

The reaction studied was the oxidation of carbon monoxide at atmospheric pressure over pellets of alumina supported platinum catalyst.

$CO + \frac{1}{2}O_2 \rightarrow CO_2$.

The catalyst used was 0.5% platinum by weight, deposited on porous pellets of $\frac{1}{8}$ inch diameter. The gas mixtures employed were O-6%CO, O-6%O₂ in argon. A complete description of the experimental arrangement and catalyst properties is given by Cutlip and Kenney [6]. The system consists of a stainless steel

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reactor with a recycle line. Step changes in feed concentration can be produced by a valve assembly. The gas flowrates are precisely measured with a bubble flow meter. The reactor outlet is connected to a magnetic deflection mass spectrometer. An electronic peak select unit allows up to four mass numbers to be continuously monitored. The output from the peak select is connected to a PDP 11/45 computer for automatic and fast data logging. The data thus stored in the computer can be analysed later.

Experimental runs consisted of first pretreating the catalyst with either oxygen or carbon monoxide for about half an hour, and then switching to a mixture of carbon monoxide and oxygen.

Experiments were carried out between 160–185°C during the course of this work, while experiments carried out previously by Hawkins [7] and Goodman [8] were used to evaluate the rate constants between 100 and 150°C.

A simple elementary step model is considered here and appears to be sufficient. The mechanism consists of three main steps; they are:

(i) adsorption and desorption of CO on the platinum;

(ii) dissociative adsorption and desorption of O_2 :

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(iii) surface reaction between adsorbed CO and O together with;

(iv) adsorption and desorption of CO₂ on the alumina support.

The Eley-Rideal step, in which reaction between adsorbed O and gaseous CO occurs, is neglected. The product CO_2 is assumed to be desorbed immediately on formation. All the rate constants are assumed to be independent of surface coverages. Then the equations can be written as:

$$Z_{v} = Z_{0} - C_{4} - C_{5},$$

$$R_{1} = k_{1}C_{1}Z_{v} - k_{-1}C_{4}, \quad R_{2} = k_{2}C_{2}Z_{v}^{2} - k_{-2}C_{5}^{2},$$

$$R_{3} = k_{3}C_{4}C_{5}, \quad R_{4} = k_{4}C_{3} - k_{-4}C_{6},$$

$$\sigma = R_{3} - R_{1} - R_{2} - R_{4},$$

$$\tau \dot{C}_{1} = F_{C_{1}} - C_{1} - R_{1} - \sigma C_{1}, \quad \tau \dot{C}_{2} = F_{C_{2}} - C_{2} - R_{2} - \sigma C_{2},$$

$$\tau \dot{C}_{3} = F_{C_{3}} - C_{3} + R_{3} - R_{4} - \sigma C_{3}, \quad \tau \dot{C}_{4} = R_{1} - R_{3}.$$

$$\tau \dot{C}_{5} = 2R_{2} - R_{3}, \quad \tau \dot{C}_{6} = R_{4}.$$
(1)

The dimensionless rate constants and the various parameters are defined in the appendix; σ is a volume change factor reflecting the stoichiometry of the reaction.

The model consists of eight parameters. The parameters $k_1, k_{-1}, k_2, k_{-2}, k_3$ and Z_0 can be evaluated from CO and O_2 transients and k_4 and k_{-4} can be derived solely from the CO₂ transient. The capacity factor is also included in the parameter estimation, to allow for inaccuracies involved in the determination of surface sites concentration.

The system of differential equations is stiff and hence conveniently in-

<i>k</i> ₁	k_1	k 2	k2	k 3	k_4/k_{-4}
3.4×10 ⁴	10.3	1.92×10 ⁵	0.0	4.3×10 ⁶	130

Table 1 Rate constants at $q_F = 25 \text{ cm}^3/\text{min}$ and temperature = 100°C

tegrated using a modified Gear's method. This is a six parameter minimisation problem and the residuals to be minimised are the difference between experimental CO and O_2 concentration and the corresponding simulated values over a period of time.

The parameters were estimated at various temperatures ranging from 100–185°C. The corresponding activation energies and frequency factors are evaluated by assuming an Arrhenius type relation

$$k_{i} = k_{0} e^{-E_{i}/R_{T}}.$$
 (2)

The parameter values estimated at 100°C are given in table 1. Fig. 1 compares the experimental transient and the corresponding simulation. It is found that the model is able to predict the transient fairly well, at all temperatures. From fig. 1 it can be seen that the model is not only able to predict the steady state values of the gas phase concentrations but also the time at which the observed rapid fall in O_2 gas phase concentration takes place, and



Fig. 1. Comparison of experiment and simulation at 100°C. Step from 2% CO to $1\%CO-3\%O_2$ mixture (simulation and experiment). Flow rate 24.90 cm³/min NTP; pressure 20.0 Torr; temperature 100°C. Experimental points: (\diamondsuit) CO, (\bigtriangleup) O₂, (\bigcirc) CO₂.



Fig. 2. Effect of k_{-1} on O₂ gas phase transient at 100°C; flow rate 24.90 cm³/min NTP; pressure 20.0 Torr; temperature 100°C: (\blacklozenge) $k_{-1}=0.0$, (\blacktriangle) $k_{-1}=4$, (\blacklozenge) $k_{-1}=7$, (\blacksquare) $k_{-1}=13$, (I) $k_{-1}=20$.

the time at which the surface switches essentially from CO to O_2 coverage. Though the reactor residence time is about 2 min, the reaction transient time is about 9 min.

In fig. 2 the effect of k_{-1} on the oxygen gas phase transient at 100°C is shown. For very low values of k_{-1} the system is at a low conversion state, where CO almost covers the surface. For dimensionless k_{-1} greater than 6, oxygen is able to dislodge the CO and hence the system moves to a high conversion state. The time at which the switching of the surface takes place depends on the CO desorption constant, and it decreases as k_{-1} is increased.

From the parameters estimated it is found that the surface reaction is fast, and adsorption and desorption steps of both gases play an important part in determining the observed rate behaviour. The desorption rate constant of oxygen is negligible at low temperatures. It is significant that for a large range of k_{-1} and Z_0 values the final steady state oxygen gas phase concentration is unaltered, but that variation in parameter values lead to quite different transients. This illustrates the potential of transient measurements in discriminating between alternative kinetic models, a number of which might correlate equally well steady state rate variations at different concentrations and temperature.

In particular, fig. 3 depicts the predicted reactor gas concentrations when the input composition is cycled, together with the predictions of three different Langmuir-Hinshelwood models, all of which correlated steady state rate data reasonably well. Without exception, these fail to describe the dynamic behaviour in which the input gas composition is alternately swiched between different levels. The rate parameters obtained from transient measurements applied to an elementary step model provide an adequate fit.



DIMENSIONLESS TIME

Fig. 3. Observed and predicted transients with five switches: (\times) , (\bigcirc) experimental points; (\blacksquare) elementary step model; (1), (2), (3) HW model. T 100°C; flow rate 40 cm³/min.

Dimensionless time	Feed ^{a)}
0-2	U
2-3.5	U ₁
3.5-5	
5-6.5	
6.5-10	U _u

^{a)} $U_u = 6\%CO - 3\%O_2$; $U_1 = 1\%CO - 3\%O_2$.

The inhibition of the steady state reaction rate for oxidation by carbon monoxide is well known qualitatively. The detailed form of the envelope can be obtained by integrating the non-linear differential equations numerically. Fig. 4 shows the predicted envelope for the system at 100°C. This is different

Table 2 Rates for the Hougen-Watson models considered in fig. 3

Model 1	Model 2	Model 3
$\overline{k_{\rm F}k_{\rm CO}k_{\rm O_2}^{1/2}P_{\rm CO}P_{\rm O_2}^{1/2}} (1 + k_{\rm CO}P_{\rm CO} + k_{\rm O_2}^{1/2}P_{\rm O_2}^{1/2})^2$	$\frac{k_{\rm F}k_{\rm CO}k_{\rm O_2}P_{\rm CO}P_{\rm O_2}}{(1+k_{\rm CO}P_{\rm CO}+k_{\rm O_2}P_{\rm O_2})^2}$	$\frac{k_{\rm F}k_{\rm CO}^2 k_{\rm O_2} P_{\rm CO}^2 P_{\rm O_2}}{(1 + k_{\rm CO} P_{\rm CO} + k_{\rm O_2} P_{\rm O_2})^3}$



Fig. 4. Steady state reaction rate curve and operating line at 100°C and $q_F = 50 \text{ cm}^3/\text{min}$: (1) rate curve, $F_{C_2} = 3\%$; (2) operating line, (a) $F_{C_1} = 1\%$, (b) $F_{C_1} = 2\%$.

in its detailed form from that suggested by others. Turner et al. [9] employed an elementary step model but their analysis does not include the effects due to changes in the gas phase concentrations with time in a continuous reactor. In fig. 4 there is a concave region lying at lower pressures than the pressure of carbon monoxide giving the maximum rate. In Turner's model the corresponding region lies at higher pressures. In spite of the apparent difference, our model degenerates into Turner's with appropriate rate constants and constant gas phase concentrations. Both models indicate the possible existence of multiple states for constant CO concentration in the neighbourhood of the maximum rate.

The stability analysis of the high conversion equilibrium state given by the intersection of the operating line with the convex part of the rate curve demonstrates that this is a stable intersection, and not unstable as a simple geometrical interpretation [10] might suggest. Steady state rate measurements confirm the predictions of this analysis in the low conversion region but there are difficulties in mapping the high conversion behaviour. This is not altogether surprising since this is perhaps where other effects, such as temperature gradients, could assume importance.

The rate parameters listed in table 1 differ appreciably from those obtained in high vacuum studies and their physical significance requires clarification. The sensitivity of the predicted transients to the exact values assumed for the rate constants is a strong indication that an elementary step model formulation provides an appropriate framework for discussing this reaction. In addition, the inclusion of associated parameters for butene adsorption, desorption and reaction is proving successful in explaining the rich variety of oscillatory effects we have observed [6]. These will be reported in later publications.

Appendix

Total gas phase concentration
Gas phase CO concentration
Gas phase O_2 concentration
Gas phase CO_2 concentration
Surface CO concentration
Surface O concentration
Surface CO ₂ concentration on alumina
Activation energy
Feed CO concentration
Feed O_2 concentration
Feed CO_2 concentration
Rate constants, dimensionless
Frequency factor
Dimensionless CO adsorption and desorption constant
Dimensionless O ₂ adsorption and desorption constant
Dimensionless surface reaction rate constant
Dimensionless CO ₂ adsorption and desorption constant on alumina
$=k_1(q_F/VC_T) [m^3 min^{-1} (kg-mole)^{-1}]$
$=k_{-1}(q_{\rm F}/V) [{\rm min}^{-1}]$
$= k_2 (q_F m) / (VC_T)^2 [m^3 \text{ kg min}^{-1} (\text{kg-mole})^{-2}]$
$= k_{-2}(q_{\rm F}m)/VC_{\rm T} [{\rm m}^3 {\rm kg}{\rm min}^{-1}({\rm kg-mole})^{-1}]$
$=k_3(q_Fm)/V^2C_T$ [kg min ⁻¹ (kg-mole) ⁻¹]
Mass of catalyst
Universal gas constant
Surface sites concentration, total sites per unit mass of catalyst
Reactor temperature [K]
Time [min]
Feed flow rate at NTP [cm ³ /min]
Volume of reactor [cm ³]
Capacity factor = mS_0/VC_T
Concentration of vacant sites
Residence time [min]
Steady state
Volume change factor

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