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Oscillatory States in the Oxidation of Carbon-Monoxide on Platinum

The trend observed on variation of the operating conditions during CO oxidation on platinum in a CSTR is as follows: stable states → simple oscillations → multipeak oscillations → stable states. Analysis of the experimental results indicates that a third or higher order system of differential equations is necessary to describe most of the observations.

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SCOPE

Self-sustained oscillatory states have been observed in several solid catalyzed oxidation reactions and have inspired several studies into the kinetics of these processes. The status of research into catalytic oscillations was reviewed by Sheintuch and Schmitz (1977) and by Slinko and Slinko (1978). The occurrence of isothermal oscillations seem to indicate that this behavior is caused by intrinsic kinetic rate processes. The interest in oscillatory catalytic reactions is due to the expectation that these studies will enhance our fundamental understanding of heterogeneous catalysis and that the knowledge of the mechanisms underlying this behavior will enable the assessment of the potential practical application of the phenomenon.

This paper presents a comprehensive account of oscillatory states in the oxidation of carbon monoxide on a Pt foil in a mixed reactor, in order to provide new insights into kinetic modeling of oscillatory catalytic reaction and to present new dynamic features of such states. The basic features of the cycle and the effect of flow rate have already been presented by Sheintuch and Schmitz (1977) and Plichta and Schmitz (1979); some intriguing and complicated phenomena such as multiplicity of limit cycles were presented by Sheintuch and Schmitz (1978). The analysis of the observations is qualitative only, in terms of basic principles and notions aimed at answering such questions as how many and what type of dynamic variables are required to explain the observations.

CONCLUSIONS AND SIGNIFICANCE

Three characteristic regimes exist in the oxidation of carbon-monoxide on platinum foil in a CSTR, as an operating variable (space velocity, feed concentration) is varied. At low CO concentrations and at large concentration the system is stable. At intermediate concentrations oscillatory states are observed. Two subregimes exist in the oscillatory regime: one where the oscillatory states are simple (one-peak-per-cycle), and a second where multipeak oscillations are observed. Several observations of multiplicity of oscillatory states and of nonstationary-aperiodic (termed chaotic) states are cited. Analysis of the uniformity of the features of the cycle revealed that deviations in the period, amplitude, and time average are small.

Analysis of the observations and experimental limit cycles presented in the plane of reaction rate vs. CO concentration indicates that: (a) the simplest system of differential equations necessary to describe the observations of simple oscillations is a second-order one accounting for two dynamic variables: a gas phase concentration and surface concentration; (b) a third or higher order system is necessary to describe the observations of multipeak oscillations, chaotic behavior, and the increase of the amplitude with that of space velocity.

EXPERIMENTAL SYSTEM

To avoid heat and mass transport resistances and the uncertain effects of dispersed crystallites, size and structure, the experiments were conducted with a Pt foil in a perfectly mixed (CSTR) gradientless reactor. An impeller rotating at 2,400 rpm provided a recirculating flow, forced upward in the annular area between the foil and the reactor wall, and downward through the inside of the cyclindrically shaped foil. The reactor walls, made of stainless steel (type 304) were coated with high-temperature aluminum point to avoid catalysis by the walls.

Two different foils, of 0.002 in thickness (obtained from Engelhard Ind.) and of 0.0025 in thickness (A. D. Mackay), were used in the course of this research. Both were of area 191 cm^2 and 99.995% purity. The feed consisted of 0-4% CO (CP grade), 10-20% oxygen (dry grade) and nitrogen (extradry grade). The pressure in the 460 cm^3 reactor was atmospheric and CO_2 concentration in the effluent stream was measured continuously using a CO_2 (infrared) analyzer.

A detailed description of the experimental system along with the pretreatment procedures which were applied are given by Plichta and Schmitz (1979). They have shown that while the gas phase temperature was time-invariant during the oscillations, the surface temperature oscillated with an amplitude of several degrees (<4°C).

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TABLE 1. STABILITY OF FEATURES OF A CYCLE (RUN NO. 4)

Cycle no.	Period Min	Lower	Peaks (% conv.) 1st upper	2nd upper	Terms in Fourier Appr. avg. conv.	2nd cos	4th cos
5	25.15	40.8	82.6	74.3	51.1	−15.4	5.73
10	26.50	40.2	78.0	75.6	50.0	−15.9	6.26
15	26.55	40.3	82.2	74.4	50.6	−14.7	4.23
After Perturbing	13.80	39.6	74.9	—	50.0	−13.9*	4.12*

*Main terms were 1st cosine and 2nd cosine.

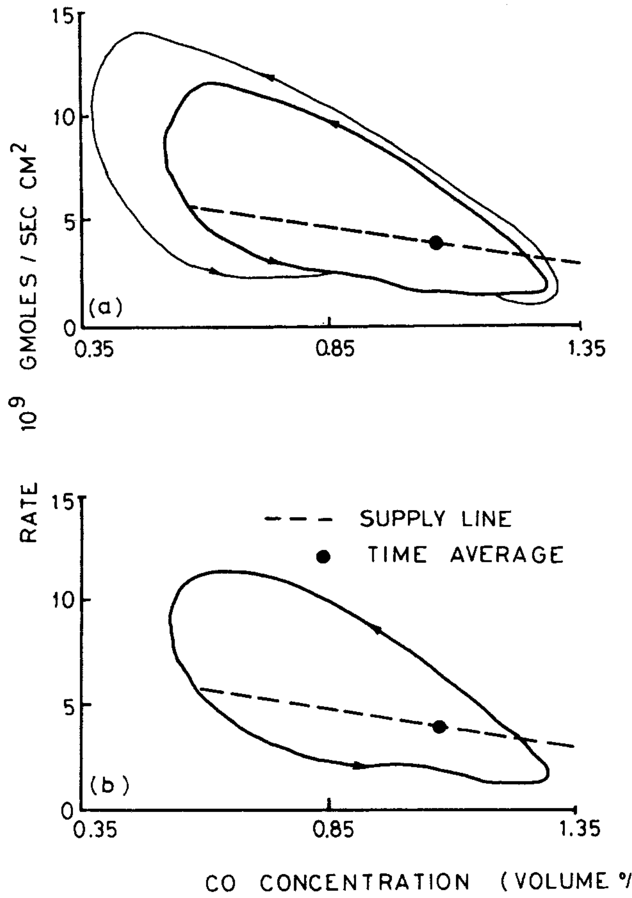

Figure 1. Multiplicity of periodic states: presentation in the rate vs. CO concentration plane (Run No. 4).

FEATURES OF THE LIMIT CYCLE

To study changes in the features of the oscillatory state over a long period of time and to ascertain that oscillatory behavior is sustained and is not part of a long transient, the experimental system was run under constant operating conditions (Run No. 4) for 18 cycles (10 hours), when it exhibited double-peak cycle oscillations—presented in Figure 4(a) in Sheintuch and Schmitz, 1978. A comparison of the features of the 5th, 10th, and 15th cycles (Table 1) revealed that differences in the periods and in the time average conversions were smaller than 2%, and did not exhibit any systematic trend, and that the 2nd cosine and 4th cosine were the largest terms in the Fourier Series used to describe the cycles.

In the process of data acquisition and analysis of oscillatory states, the CO_2 analyzer output was converted into an array of analyzer deflection vs. time. For each point the conversion was calculated, the array was smoothed, and time instantaneous derivative and reaction rate were computed. The limit cycle was then presented in the reaction rate vs. CO concentration plane.

The limit cycle of the 15th cycle presented in this form (Figure 1a) is self-intersecting, indicating that at least three dynamic variables are needed to describe the system. For large CO concentrations where propagation is slow, the trajectories of the two "loops" follow roughly the same path. For low CO concentrations, where the system propagates at high velocity, the trajectories are noncoinciding curves. The ratios between the periods of the first and second "loops" are 0.98, 0.98, and 1.22 for the three cycles respectively.

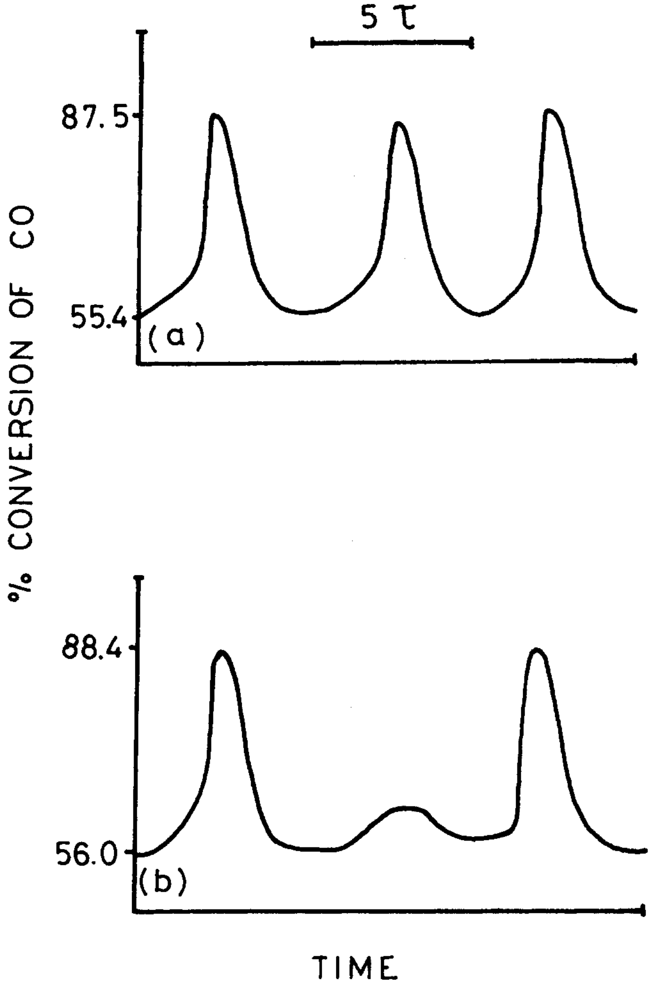

Figure 2. Multiplicity of periodic states (Runs No. 8-9, space velocity: 0.012 s^{-1}). (a) Simple oscillations (b) Multipeak Oscillations

The oscillatory state described in Figure 1 was approached from low CO concentration. (After the operating conditions had been established, CO was introduced into the system.) After the 18th cycle, the system

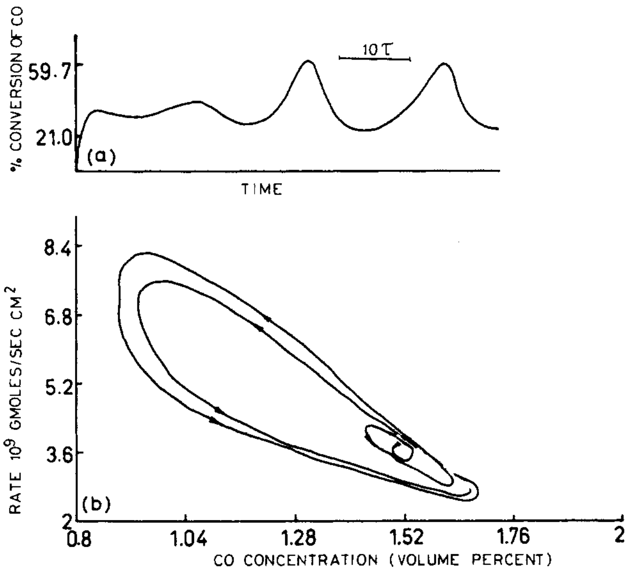

Figure 3. Development of the oscillatory state. (a) Time Trace Starting with the Introduction of CO (b) Corresponding Trajectory (Run No. 5, s.v. = 0.0103 s^{-1})

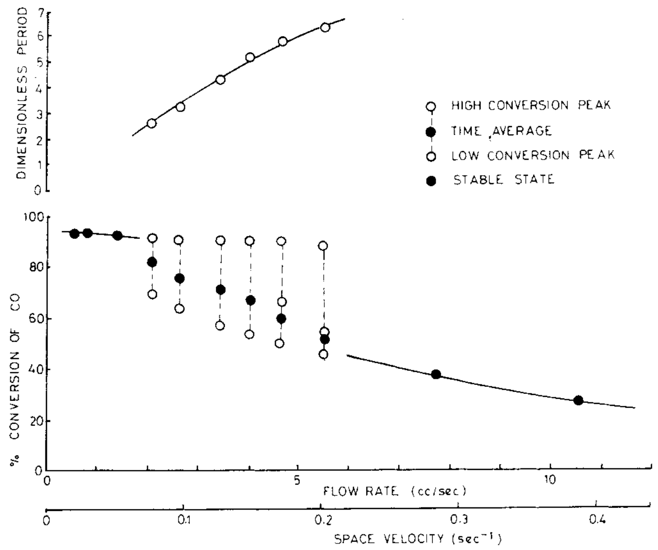

Figure 4. Effect of space velocity of the state of the system (Run No. 1, 217°C).

was perturbed by increasing the flow rate, thus increasing the CO concentration in the reactor. Upon returning to the original conditions, the system exhibited simple one-peak-per-cycle oscillations (Figure 1b, Table 1). Comparison of the features of the two oscillatory states which exist under the same operating conditions shows that: the simple cycle has the same time average conversion and about half the period of that of the double peak cycle; and the main terms in the Fourier Series, describing the simple cycle, correspond to those of the double-peak cycle. Comparison of the limit cycles, when presented in the phase plane, shows resemblance between the simple cycle and the inner loop of the double-peak cycle.

Another example of multiplicity of limit cycles is presented in Figure 2 (Run No. 8-9). Cycle (a) was observed when approached from low CO concentration, and is characterized by a period of 6.55 min, and an average conversion of 63.7%. A day later, the flow rate was swept from high to low, and cycle (b) was obtained under the same operating conditions, showing three peaks per cycle, with a period of 21.28 min and 62.3% average conversion. Comparison of the reaction rates at the stable high flow rate regime showed that no deactivation occurred between the two runs.

Multiplicity of limit cycles was also observed by Zuniga and Luss (1978) in the study of H_2 oxidation over a Pt wire. In their observations, like this report, the system exhibited two cycles of multiple periods; however, in their study the two states belong to different branches of the steady state curve, showing significant differences in the average rate.

Figure 3 presents the trajectory leading to an oscillatory state, starting from the moment CO was introduced into the system which was set at the operating conditions (Run No. 5, 0.0103 s^{-1}). When presented in the rate-concentration plane, the trajectory develops in the form of an unstable focus, leading to simple oscillations with a period of 33.6 min and 32.2% average conversion.

When the oscillatory state was approached from a large CO concentration (same operating conditions as above, with space velocity of 0.0109 s^{-1}), the cycle established was a double-peak cycle with a period of 68.72 min and 31.0% average conversion. The trajectory approached the limit cycle from the outside. In both approaches to the oscillatory state, the state was established relatively fast.

THE EFFECT OF OPERATING CONDITIONS

After regeneration of the catalyst, its activity declined slowly; in the course of each experimental run, however, the activity varied very little. The qualitative trends which were observed were similar at each activity level.

The effect of flow rate on the state of the system is presented in Figure 4. As the flow rate is increased, a smooth transition (soft bifurcation) from a stable state to an oscillatory state occurs. Time average conversion decreases, while the amplitude and the period (made dimensionless with respect to residence time) increase with flow rate. Changing the flow rate from 4 to 4.6 cc/s leads to bifurcation from a simple cycle to a multipeak cycle. Upon further increase in flow rate, beyond 6 cc/s, the oscillations suddenly disappear (hard bifurcation) and the system becomes stable.

The same effect of the operating variable on the state of the system was observed when oxygen pressure is decreased, or when CO feed concentration is increased; the transition (bifurcation) points observed in the various runs, which are numbered according to their chronological order, are summarized in Table 2. Multiplicity of oscillatory states was observed in the range B2-B3, and in cases of multiplicity, the state was considered a multipeak cycle. Two distinct types of multipeak cycles were observed: 1. those with almost equidistant peaks (for example, Figure 2); and 2. those whose cycles resemble a superposition of oscillations (for example, Figures 5 and 6). For the former type, the periods in Figures 4 and 5 are taken to be the total period divided by the number of peaks.

Our observations indicate that the stable states lie outside the region of CO concentrations where oscillatory states existed.

TABLE 2. SUMMARY OF EXPERIMENTAL RESULTS

Run No.	Temp. °C	Feed Conc Vol. % CO	O_2	Space Velocity 1/s	Bifurcation Points B_1	B_2	B_3	Osc. Regime [1] Vol. %	Largest[2] Instantaneous Rate 1/s	Rate[2] at 2% CO 1/s
1	217	1.95	19.0	pv	0.0061	0.016	0.024	0.16-1.05	13.2	6.12
5	179	2.085	19.2	pv	<0.0033[3]	0.105	0.011	0.25-1.65	4.9	1.25
6	150.5	2.075	19.8	pv		<0.0027[4]		0.24-1.53	3.3	0.45
8-9	258	2.04	19.6	pv	0.0048	0.011	0.016	0.20-1.09	10.5	6.52
13	266	1.99	19.4	pv	0.013	0.06	n.d.	0.15-1.75	122.9	n.d.
15	271	1.99	19.3	pv	0.011	0.032[5]	n.d.	n.d.	49.2	n.d.
2	217	2.1	pv	0.0090	—	—	10.1[6]	0.15-1.15	—	n.d.
10	257	pv	19.2	0.0128	0.76	—	2.15	0.25-0.98	9.8	6.50
4	218	2.15	12.94	0.012	—	—	—	—	—	—

Notation

B_1 = soft bifurcation to simple osc. state; B_2 = bifurcation to multipeak osc. state; B_3 = hard bifurcation to stable state (average values of the parameter varied at the states on both sides of the bifurcation point).

pv = parameter varied during the experimental run.

n.d. = no data available.

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[1] Range of CO concentration where oscillatory states were observed.

[2] Expressed as turnover number 1/s; $1.2 \cdot 10^{15}$ sites/cm².

[3] Lower space velocities could not be attained.

[4] Only one state, of multipeak nature was observed.

[5] Bifurcation to chaotic state.

[6] Hard bifurcation from simple osc. to stable state was observed as O_2 conc. decreased.

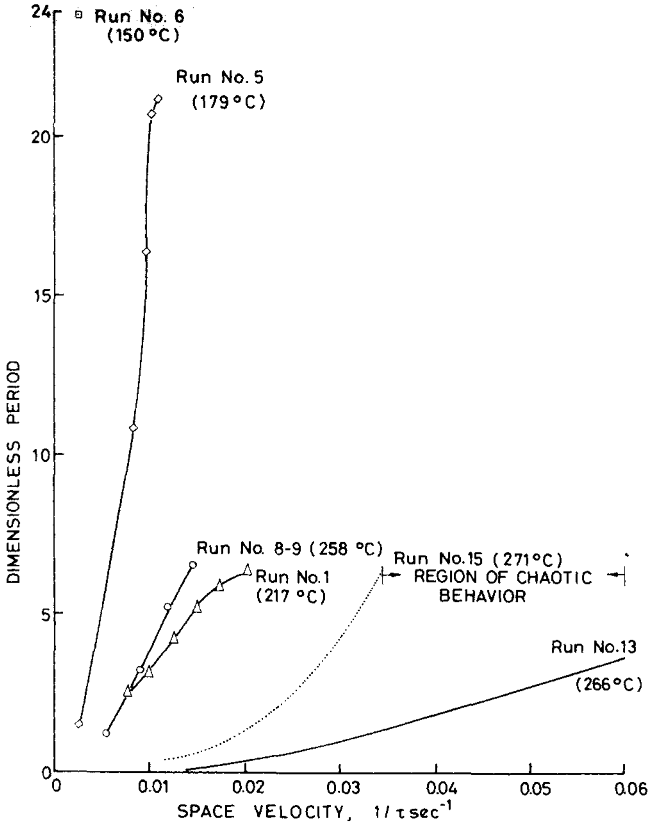

Figure 5. Regions of oscillatory states at different activity levels.

The oscillatory regime seems to be bound: over a large range of temperatures and activity levels, oscillatory states were not observed for CO concentrations below 0.15% and above 1.8%. The last two columns in Table 2 present information on the activity of the system. The largest instantaneous rate was always observed in the oscillatory regime. If we view the system as composed of two antagonistic processes of different characteristic velocities, the largest rate observed can be taken as the time characteristic of the fast step in the mechanism. The rate at 2% CO was calculated by extrapolation and is tabulated as an indicator of the activity of the system in the different runs.

The effect of space velocities on the state of the system for various temperatures and activity levels is summarized in Figure 5. Figure 5 clarifies that the period is a very sensitive probe for the activity of the catalyst, and that a decrease in temperature or activity of the system would have the same effect as a decrease in residence time. As the temperature is decreased, or as the activity declines, the oscillatory regime is shifted to lower space velocities. A comparison of Run No. 1 (conducted at 217°C) and Runs No. 8-9 (253°C) reveals that the decline in activity is compensated by the increase in temperature, leading to similar characteristics of the oscillations (e.g., period, bifurcation points).

At 150°C only one oscillatory state was observed (at a low space velocity), with a period of 146 min. The time trace of that state and the limit cycle are presented in Figure 6. The complex nature of the cycle resembles the superposition of two oscillators with different time scales. The highest activity was observed at a temperature of 266°C (Run No. 13) with a new catalyst foil. Soft bifurcation to oscillatory state occurred at a space velocity of 0.013 s^{-1}, yielding almost periodic oscillations with periods of 8 s, and an amplitude of less than 1% conversion (Figure 7a). The oscillatory states did not disappear even at the highest attainable space velocity (0.14 s^{-1}), where large oscillations of a complex nature and large amplitudes were observed. The effect of space velocity on the shape of the cycle is shown in Figure 7. As the flow rate is increased, the cycle changes from an almost periodic one to a relaxation oscillation, and at large flow rates a superimposed cycle of a small amplitude is developed. No claim can be made about the periodicity of the large amplitude cycle (Fig. 7c); although the basic features of the cycle are retained, the details of the superimposed cycle are not.

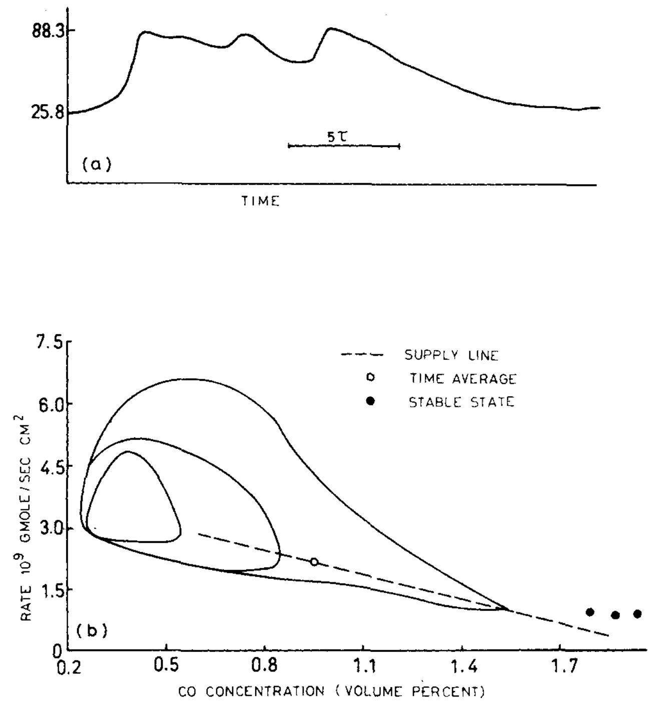

Figure 6. Oscillatory and stable states at low temperature (Run No. 6, 150.5°C). (a) Time Trace of a Long Cycle (s.v. = 0.0027 s^{-1}) (b) Corresponding Limit Cycle and Stable States

The experiments were repeated in Runs 14 and 15, under the same conditions as Run 13, to study the effect of the deactivation process which was fast at the region of high activity. The lower activity in Run 15 led to a lower time-average conversion and a larger period (Figure 5). For small space velocities, the state was periodic. However, at space velocity of 0.032 1/s a bifurcation to a time-dependent aperiodic state occurred (Figure 7d). Three chaotic states were recorded. To test the reproducibility of the characteristic behavior, the system was shifted back to the oscillatory regime, leading to an oscillatory state and then back to the chaotic regime, where chaotic states reappeared.

The effect of oxygen concentration was studied at 217°C and 2.1% CO in feed (Run No. 2). At 19.2% O_2 the system exhibited

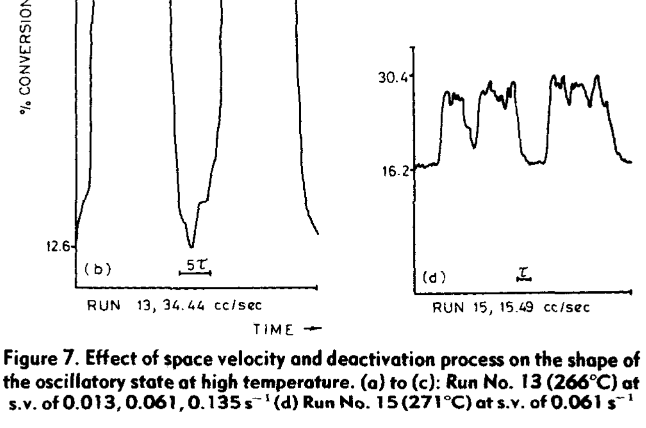

Figure 7. Effect of space velocity and deactivation process on the shape of the oscillatory state at high temperature. (a) to (c): Run No. 13 (266°C) at s.v. of 0.013, 0.061, 0.135 s^{-1} (d) Run No. 15 (271°C) at s.v. of 0.061 s^{-1}

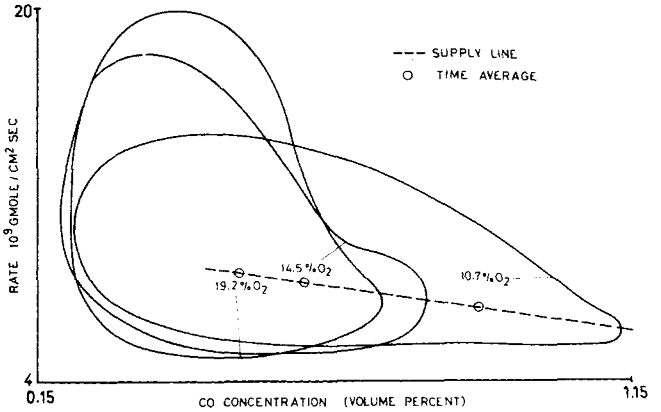

Figure 8. Effect of oxygen concentration on the shape of the limit cycle (Run No. 2).

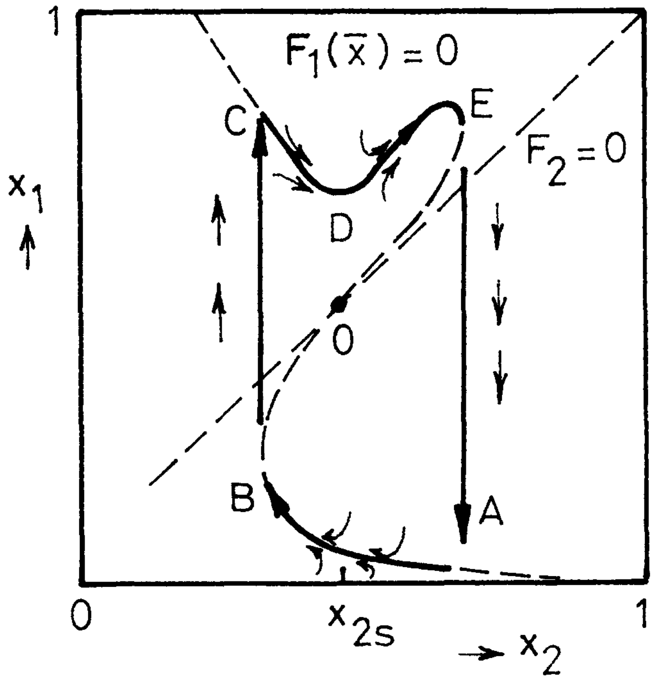

Figure 9. Multipeak oscillations in a second-order system with an autocatalytic gas-phase variable.

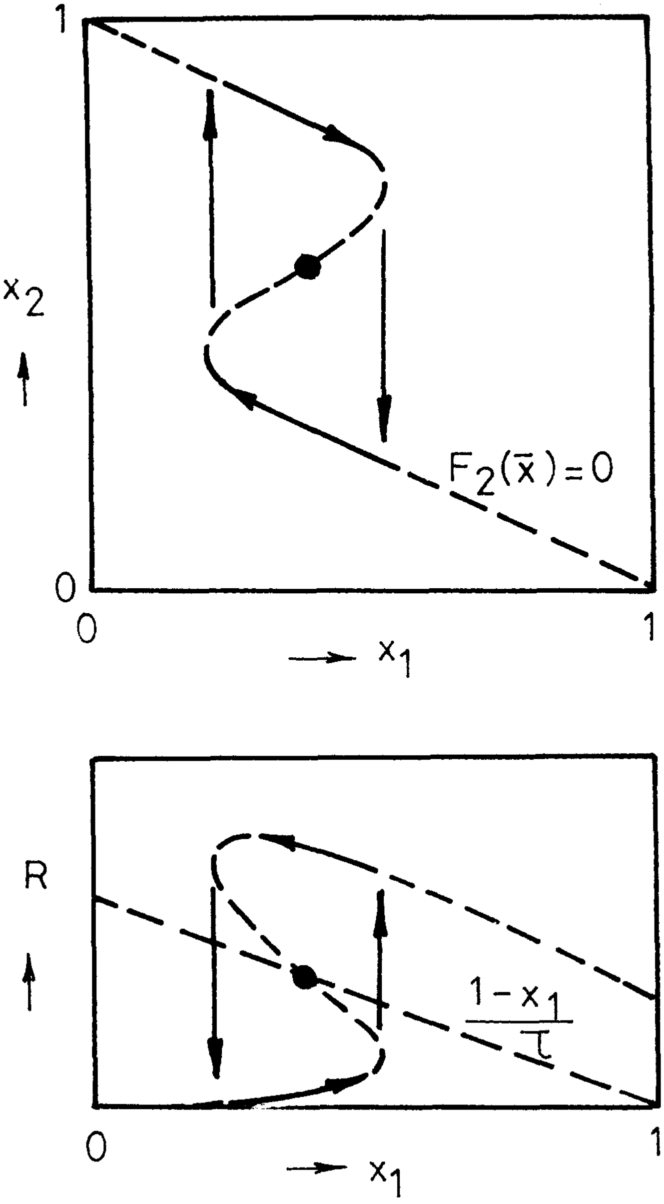

Figure 10. Relaxation oscillations in a second-order system with an autocatalytic surface variable.

simple oscillations of the relaxation type with a dimensionless period of 3.4. Decreasing oxygen concentration had the same effect as decreasing residence time, but changes in period and amplitude were small in the range above 14% O_2. As oxygen concentration further decreased from 10.7 to 9%, the state of the system changed from an oscillatory one, with average conversion of 60% to a stable one, with 24% conversion.

A similar dependence was observed by Zuniga and Luss (1978), when studying H_2 oxidation on Pt at 85°C. Decreasing O_2 pressure from 40 to 32% did not lead to significant change in the state of the system; while decreasing it further to 21% led to a stable system, with a decrease of order of magnitudes in the rate of reaction. The limit cycles observed at various oxygen concentrations (Figure 8) follow closely the same path at a low CO concentration (~0.2% CO), where propagation velocity is fast, and at low reaction rate. The cycles attain different paths at high concentrations and reaction rates.

The effect of increasing CO feed concentration (Run No. 10) was similar to that of increasing space velocity. However, the conversion at the stable regime on the left of B1 declined with decreasing CO feed concentration, indicating that at the low concentration regime the reaction order is higher than one.

RESULTS

In discussing the experimental results, several questions will be addressed. One basic question is: how many dynamic variables and what type of variables are required to describe the oscillatory behavior? The nature of the periodic states observed in most cases is simple in the sense that there exists one peak in each cycle. This behavior can be described by a second order system of differential equations, and most of the studies into kinetic modeling of catalytic oscillatory were limited to systems of that order (Sheintuch and Schmitz, 1977, 1978; Slinko and Slinko 1978), in the form:

$$\bar{\bar{L}} \frac{d\bar{x}}{dt} = \bar{F}(\bar{x}) \qquad (1)$$

with a constant-coefficient diagonal matrix L. Although, a third or higher order system is usually used to describe multipeak oscillations, one can construct a limit cycle of the form presented in Figure 9, which will yield double peak oscillations in the variable x_1 (e.g., CO concentration, the "measured" variable) and single-peak oscillations in the variable x_2 (e.g., a surface concentration, the "latent" variable). The limit cycle is constructed for a situation *where* the time scale or the capacity of x_2 is much larger than that of x_1, hence $L_{11} << L_{22}$. Under these conditions and if x_1 is an autocatalytic variable (e.g. with a Langmuir-Hinshelwood rate expression) and its null curve $F_1 = 0$ is multivalued in some range of x_2, the system will exhibit relaxation oscillations *where* it propagates along the stable branches of $F_1 = 0$ and then jump from one branch to the other. Double-peak oscillations in x_1 are realized when one of the stable branches of $F_1 = 0$ is nonmonotonic in the form presented in Figure 9. A similar figure can be constructed for a kinetic model *where* x_2 is the autocatalytic variable. Mapping the limit cycle into the rate (R) vs. concentration plane would yield a closed non-intersecting curve, if R is a monotonic function with respect to x_1 and x_2 in the domain where the oscillations exist. However, the requirement for positive feedback usually leads to a nonmonotonic rate function with respect to x_1 (e.g. a Langmuir-Hinshelwood rate expression) or with respect to x_2 (e.g. $R \propto x_2(1-x_2)^{\mu}$ used by Sheintuch and Schmitz, 1978).

If we assume that R is a non-monotonic function of x_2 having a maximum at x_{2s}, mapping of the limit cycle presented in Figure 9 into the (R, x_1) plane may yield a closed intersecting curve with two loops. Yet, such a mapping cannot account for the limit cycles of multipeak oscillations, characterized by two or more "concentric" loops (Figures 1 and 6) tangent to each other. These considerations indicate that a third or higher order system is required to predict the observations of multipeak oscillations.

A higher order system is also required to account for the observations of multiple oscillatory states and of chaotic behavior. The phenomenon of multiple oscillatory states with multiple period has also been observed in biological systems and are believed to result from interaction of oscillators (Pavlidis 1973). A third order model, composed of a kinetic oscillator coupled with an energy balance, was recently suggested by Schmitz et al. (1979) to account for chaotic behavior in non-isothermal catalytic systems.

The next question is the type of variables required to describe simple oscillations: these may be either gas phase or surface concentrations. A second order system utilizing two gas phase concentrations as its dynamic variables would predict oscillatory states, only if oxygen participates in some other reaction beside the main one and its conversion is significant (Sheintuch and Schmitz, 1977). Employing a second order system of two surface concentrations to describe the oscillations would require the assumption that the gas-phase concentration is in pseudo steady state. This assumption, however, is not supported by the experimental results.

The observation that the frequency of the oscillations is of order of magnitude of space velocity suggests that the gas-phase concentration is of crucial importance. This leads us to conclude that the most likely combination of variables is that of gas-phase and surface concentrations. Such a model would account for a "measured" variable (CO concentration) and a "latent" variable (e.g., adsorbed oxygen or metal oxide), where the mass capacity of the adsorbed phase is three orders of magnitude smaller than that of the gas phase in our experimental system. If the two rate determining steps take place in series, as in the case where these are adsorption and reaction or reaction by surface oxidation and reduction (Sheintuch and Schmitz, 1978), $L_{22} << L_{11}$; if x_2 is the autocatalytic variable, such a system would admit an oscillatory solution when $\partial F_2/\partial x_2 > 0$ in some domain of the phase plane (Figure 10). This system would be characterized by a multivalued rate curve and the steady state is the intersection of the rate curve and the supply line. States, which belong to the negative slope branch of the rate curve, are oscillatory states.

For $L_{22}/L_{11} << 1$, the system admits oscillatory solutions of the relaxation type and it will propagate along the stable branches of the rate curve, followed by fast propagation from one branch to the other. This will be evident in a fast rate variation, in a manner similar to some of our observations (Figure 8). The period of these oscillations would be in order of magnitude of the residence time in accordance with our observations. However, for the system presented in Figure 10, the amplitude of the relaxation oscillations would be independent of the space velocity—since $F_2(\bar{x}) = 0$ is independent of space velocity—contrary to our observations. Furthermore, the system presented in Figure 10 may admit stable solutions in the same regime of gas-phase concentrations where oscillatory solutions exist, contrary to the experimental observations.

A system, using gas phase and surface concentrations as its dynamic variable, may admit oscillatory solutions, when the gas phase concentration is the autocatalytic variable and when the two rate determining steps operate in parallel as in the situation of a fast reaction which accommodates itself to a slow surface modification (e.g., oxidation and reduction). If the time scales of the two steps are widely separated, the phase plane diagram will be of the form presented in Figure 9 and relaxation oscillations may be realized. The period of these oscillations, however, will be much larger than the residence time. These arguments indicate that a third order system of differential equations is necessary to account for the amplitude variation with space velocity.

Three regimes were observed as operating variables (e.g., space velocity, feed concentration, and temperature) were varied. At the region of low CO concentrations, the states were stable and the reaction order observed was larger than unity. Another stable regime existed for large CO concentrations, where the order of the reaction with respect to CO was small (negative or positive depending on the temperature). If oxygen adsorption is assumed to be a rate-determining step at large CO concentrations, the reaction rate at 217°C (Run No. 1) corresponds, in order of magnitude, to an oxygen-sticking coefficient of 10^{-7}. That value is within the range of oxygen-sticking coefficients reported in the literature. The rate observed at this range may be also explained by the assumption that surface reaction is the rate-determining step. Thus, no discrimination can be made between these two steps.

Oscillatory states were observed at intermediate CO concentrations. The variation of the limit cycle with oxygen concentration (Figure 8) may be interpreted in terms of two rate determining steps: one which shows little dependency on oxygen pressure (e.g., surface reaction, surface reduction) and is dominant at the lower section of the cycle; and one which is oxygen-dependent (e.g., oxygen adsorption, surface oxidation).

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