RATE ENHANCEMENTS AND QUASI-PERIODIC DYNAMICS DURING FORCED CONCENTRATION CYCLING OF CO AND O_2 OVER SUPPORTED Pt–SnO$_2$

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Abstract—Forced reactant cycling of carbon monoxide–nitrogen and oxygen–nitrogen streams over Pt–SnO$_2$ in a differential reactor results in enhancements of the reaction rate of up to 9 times that of the optimal steady state. Dynamic features common to periodically forced reaction systems were experimentally observed. In addition, quasi-periodic behaviour under forced concentration cycling was also observed. Transient response experiments combined with see-through FTIR analysis confirm an underlying Langmuir–Hinshelwood-type mechanism. Spectral analysis of the quasi-periodic patterns identified at least three time constants of different orders of magnitude. The nature of the patterns also indicated a reaction mechanism which included one or more "reservoirs" of reactants and/or reaction intermediates.

INTRODUCTION

It is now accepted that periodic operation of catalytic reactors can under certain circumstances lead to enormous enhancements in reaction rate and selectivity over traditional steady-state operation. Variables cycled have included reactor temperature, pressure, flowrate, and reactant feed concentrations.

In its simplest form periodic operation is the transient step up and step down experiment now so commonly employed to aid in the deduction of reaction mechanisms. These dynamic kinetic studies are not new (Wagner and Hauffe, 1939) and have been referred to as perturbation or relaxation techniques. The use of dynamic studies in heterogeneous catalysis has been reviewed (Hulbert and Kim, 1966; Kobayashi and Kobayashi, 1974; Bennett, 1976). The method has been extensively employed to arrive at the mechanism of CO oxidation over supported cobalt oxide, Co$_3$O$_4$–Al$_2$O$_3$ (Kobayashi and Kobayashi, 1976; Perti *et al.*, 1985; Perti, 1980).

An introduction to the deliberate periodic operation of chemical reactors is given by Bailey (1973, 1977). At that time experimental proof of the benefit of periodic operation was limited. Since then many papers have appeared, both theoretical and experimental, concerning improvements in performance and/or selectivity. Recent experimental studies have observed rate enhancements for CO oxidation during reactant concentration cycling over different catalysts [V$_2$O$_5$ (Abdul-Kareem *et al.*, 1980); Pt–Al$_2$O$_3$ (Oh *et al.*, 1978); Pt–Al$_2$O$_3$ (Cutlip, 1979); Pt–Rh–Al$_2$O$_3$ (Schlatter *et al.*, 1983); Pt–Rh–Al$_2$O$_3$ (Taylor and Sinkevitch, 1983); Pt–Al$_2$O$_3$ (Barshad and Gulari, 1985a); Pt–Al$_2$O$_3$ (Cho and West, 1986); Pd–Al$_2$O$_3$ (Zhou *et al.*, 1986); and Pt–Al$_2$O$_3$ (William *et al.*, 1985)]. These works demonstrate that rate en-

hancements of at least an order of magnitude over steady state can be obtained. In all cases intermediate periodic operation resulted in the optimal rate. Improvements were dependent upon the amplitude and frequency of the forcing. The large rate enhancements reported were generally limited to feed streams with low average O$_2$/CO ratios, rather than being observed over the entire inlet CO–O$_2$ concentration parameter space.

A variety of complex behavior patterns are common during the oxidation of carbon monoxide over noble metals. For example, autonomous self-sustaining oscillations and other instabilities have been observed experimentally for CO oxidation over supported and unsupported platinum under a variety of reaction conditions. This dynamic behavior, along with the multitude of proposed models has been the subject of comprehensive reviews (Engel and Ertl, 1979; Sheintuch and Schmitz, 1977; Razon and Schmitz, 1986). The periodic and aperiodic (deterministically chaotic) oscillations experimentally observed for autonomous CO oxidation have been analyzed employing methods such as Fourier power spectral analysis, Poincaré sections, and by determination of the Kolomogorov entropy of the attractor [e.g. Razon *et al.* (1986)]. The natural frequencies of such systems can also, under certain conditions, be determined with the aid of multi-time-scale analysis (Aluko, 1983).

Several low to moderate temperature (75–200°C) catalysts which oxidize CO are available. These include Pt, Pd and SnO$_2$ as well as SnO$_2$–CuO gel. Extensive work on CO oxidation over tin oxide catalysts has been reported (Fuller and Warwick, 1973, 1974). This block of literature deals with SnO$_2$–CuO gel catalysts as well. Bimetallic catalysts have also been investigated. A palladium–tin oxide combination was determined to be active at low temperatures (Bond *et al.*, 1975) as was Pt–Sn (Baronnettii *et al.*, 1985). Investigation of the impreg-

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nation step in the formation of Pt–Sn catalysts determined that a complex formed during that step led to the higher activities. This complex formation was observed only for Pt/Sn mole ratios larger than unity.

The purpose of this study was to characterize the behavior of a bimetallic Pt–SnO$_2$ catalyst for low-temperature CO oxidation. Specifically we wanted: (1) to prepare and characterize the steady-state behavior of the catalyst, (2) to determine the underlying type of reaction mechanism which governs the system, (3) to characterize the behavior of our catalyst under periodic operation, and (4) to determine the minimum number of time constants which would be necessary to model the system.

EXPERIMENTAL

Catalysts and reagents

Two catalysts were employed in this study. The first was a bimetallic platinum–tin oxide. In order to ensure the active complex formation for such a catalyst large quantities of tin in comparison to platinum were used. This catalyst was employed throughout the study. The second catalyst was a 0.5 wt % Pt on an alumina support. This monolith has been used in a previous work (Barshad and Gulari, 1985a) and was also employed during part of the periodic studies.

The preparation of the Pt–SnO$_2$ catalyst involved four steps. Chloroplatinic acid (Aldrich) was dissolved in hydrochloric acid, and the solution used to coat tin oxide powder (Aesar) to the desired loading. The coated powder was then calcined at 400°C in air. The resulting powder was suspended in acetone and coated onto a 20 mm diameter Engelhardt cordierite monolith. Before use, the catalyst was reduced in H$_2$

for 3 h. Preparation of the 0.5 wt % Pt–Al$_2$O$_3$ monolith is reported elsewhere (Barshad, 1985).

The gases used were 99.99% pure N$_2$ (Air Products), 99.6% pure O$_2$ (Matheson) and 99% pure CO (Air Products). Iron carbonyl in the supply CO gas was determined not to be a problem at the low temperatures of this study.

Apparatus

The reactor system used in this study is shown schematically in Fig. 1. Inline NDIR detectors were used to monitor conditions at the reactor outlet, and a Digilab FTS-20C FT-IR was employed to monitor conditions in the reactor. Transparent windows of KCl were used in the reactor for this purpose. The reactor was that employed in a previous study (Barshad and Gulari, 1985b) fitted to the 2.22 cm long, 1.91 cm diameter monolith. The area shaded in Fig. 1 was equipped with heating coils, insulation, and was temperature controlled within ± 1 K. Thermocouples as well as an infrared (IR) thermometer (Omega OS-600) monitored the temperature. Once it was determined that the thermocouples read substantially the same as the IR thermometer, the latter was disconnected. During the periodic operation experiments the transparent windows were replaced with stainless steel disks and the reactor loop was further insulated.

Three solenoid valves located on each of the inlet streams were used to impose step or square wave concentration functions. The needle valves following these solenoids were used to set a steady-state flow in such a way that, when one of the reactants was switched off, the total flow rate and concentration of the other reactant remained unchanged. The inlet flow
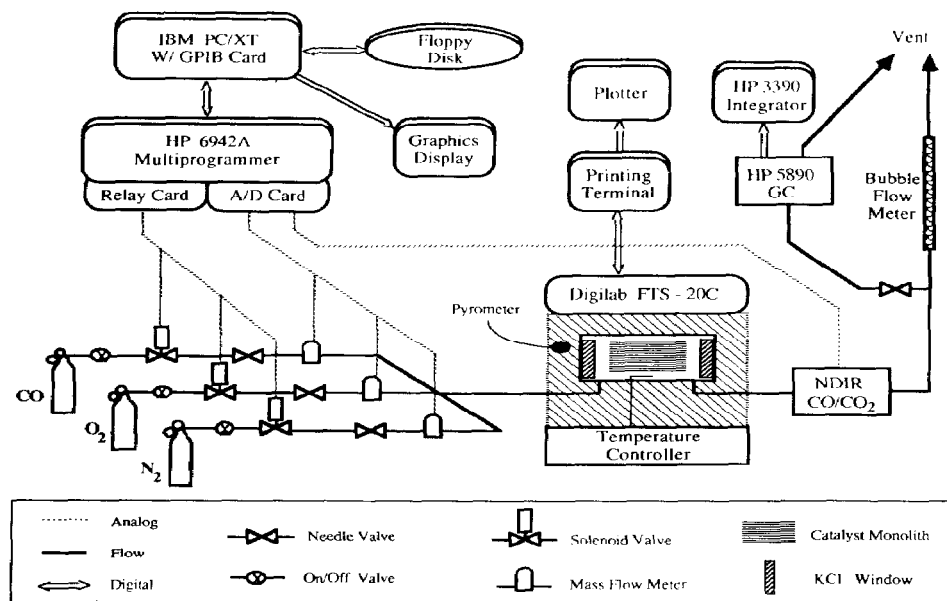

Fig. 1. Schematic diagram of the reactor and data acquisition system.

rates were measured individually with Kurz mass flow meters (model 500-3), calibrated against a bubble flow tube. The response time to 95% of the final reading was 25 ms. Tubing length was kept to a minimum to prevent distortion of the concentration pulses. The reactor was operated at a pressure of 140 kPa. Measurable pressure variations were not noticed during periodic operation, assuring constant residence time and accurate IR measurements. System response for rectangular CO and CO_2 pulses through the reactor (packed with a blank monolith) indicated that the square wave form was not significantly distorted.

Data acquisition was accomplished with an HP-6942A multiprogrammer and an IBM PC/XT equipped with a GPIB card, as can be seen in Fig. 1. This enabled continuous monitoring of the CO and CO_2 concentrations and the proper alignment between the inlet square wave and outlet concentrations. Data were stored on floppy disks, and could be integrated and/or displayed in graphical form in real time. Due to the lower conversions obtained during steady-state operation, data analysis for these experiments was accomplished with a HP5890 GC and a HP3390 integrator.

Experimental scope and techniques

The majority of experiments were conducted with nitrogen as the diluant. The total flow rate employed was kept constant at 200 cm^3/min at 27°C (except where otherwise noted). At these conditions the reactor residence time is slightly under 2 s. Transient and steady-state reactions were carried out at several temperatures ranging from 82 to 142°C. The response of the system to steps up and down in CO and O_2 was investigated using the GC-IR capability of our IR spectrometer.

All steady-state experiments employed a pretreatment technique designed to eliminate the effects of hysteresis and surface memory phenomena from our results. The protocol was reduction by 10% CO–N_2 for 20 min after CO_2 was no longer detected in the outlet, followed by oxidation in 10% O_2–N_2 30 min after CO_2 was no longer detected in the outlet. This pretreatment normally took an hour to complete before each run. The system was then allowed to equilibrate under reaction conditions for 1 h before recording the outlet conditions. Based upon preliminary runs, we found that this time was sufficient for the system to reach a steady state.

Transient experiments typically consisted of a pretreatment period during which one of the reacting gases in a diluant stream was sent into the reactor at a constant flow rate, a purge period during which the gas phase in the reactor was filled with the diluant gas, and a reaction period during which the other reactant was sent into the reactor mixed in the diluant stream. Reactor outlet concentrations were monitored during the entire process. The purge period was essential to prevent competitive adsorption from clouding the

results. It was established that the purge time did not result in the desorption of surface species.

Periodic operation was forced upon the system by switching between 10% CO in N_2 for t_{CO} s and 10% O_2 in N_2 for t_{O_2} s. The fraction of the cycle period in which CO is flowing is defined as the CO duty fraction. Periods from 10 to 250 s and CO duty fractions from 0.01 to 0.9 were investigated over temperatures ranging from 82 to 142°C. The time average rate of reaction was calculated over several cycles (typically 50) after a cyclic steady state was achieved. A larger number of cycles were integrated to determine the time average rate when quasi-periodic behavior was observed and only after the initial large oscillations had died out. Additional methods employed within the region where quasi-periodic behavior was observed are presented along with the results of those experiments.

RESULTS AND DISCUSSION

Steady-state characterization

Steady-state experiments covered a wide range of CO and O_2 (from 0.25 to 8% CO and 2–9.75% O_2) concentrations at each temperature (82, 100, 117, 133 and 142°C). Data so obtained were used to fit a reaction rate expression of a Langmuir–Hinshelwood form:

$$r = \frac{k_r K_{CO} K_{O_2}^{0.5} C_{CO} C_{O_2}^{0.5}}{(1 + K_{CO} C_{CO} + K_{O_2}^{0.5} C_{O_2}^{0.5})^2} \tag{1}$$

to allow for comparison to published activation energies. The k_r values at various temperatures were plotted in an Arrhenius plot to estimate the activation energy for the surface reaction. The value of the activation energy so obtained was found to be 23.6 kcal/mol, the same as on Pt–Al$_2$O$_3$, leading us to believe that the steady-state reaction is almost support-independent.

The maximum steady-state oxidation rate was located within the range of inlet CO concentrations employed for each temperature investigated. These maxima occurred at higher CO concentrations than those observed for CO oxidation over Pt–Al$_2$O$_3$.

Transient response experiments

The main goal of the transient response experiments was to determine the relative importance of the Eley–Rideal and Langmuir–Hinshelwood mechanisms. Figure 2 presents the transient concentration of CO and CO_2 in the reactor as observed by FTIR during steps up and down in CO with simultaneous steps down and up in O_2. Note that the production of CO_2 is essentially within one peak in both cases, possibly indicating that there is only one species each of CO and O_2 on the surface which take part in the reaction. These transients were at 142°C. Carbon dioxide is produced almost immediately after CO enters the reactor (for the CO step up case), while for the O_2 step up there is a distinct time lag as indicated by the arrows in Fig. 2. This induction time is similar
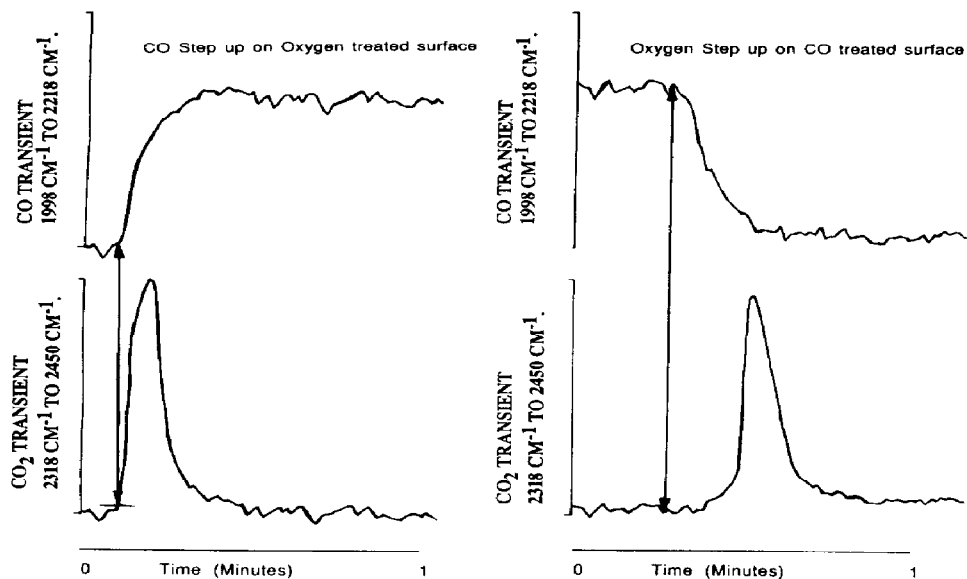
Fig. 2. Transient response to a step up/down in CO, down/up in O_2 at 142 °C. Vertical arrows indicate the presence or absence of an induction time

to those observed by others [e.g. Goodman *et al.* (1982), Dwyer and Bennett (1982), Bonzel and Ku (1972) and Zhou and Gulari (1986)] on different catalysts and supports. In general, the change in support does not seem to influence this feature.

At 142°C, the induction time for a step up in CO is zero, while for the O_2 step up, it is around 14 s. Thus, to achieve rate enhancement by periodic operation, one has to operate at longer times than these for each reactant. Similar transients were also recorded at other temperatures. The induction time as well as the peak time for the CO_2 peaks increased at lower temperatures, indicating that they may be activated processes.

Barring the induction time, the form of the CO_2 peak is the same in both experiments, indicating that as far as the reaction is concerned, both the reacting species are similarly located on the surface of the catalyst. Had one species been participating in the reaction in a different manner from the other species, the two transients would have looked markedly different. These results effectively rule out the Eley–Rideal type of mechanism.

Periodic operation

Reactant concentration forcing between 10% CO and 10% O_2 was the mode of periodic operation studied. The time average maximum rate was determined in the CO duty fraction/cycle time plane by plotting isorate contours as in Fig. 3.

Several features concerning the contour plots of the reaction rate are of interest. For cycle periods slightly shorter than that at the maximum rate, the reaction rate is independent of the CO duty fraction, and very sensitive to the cycle period. For CO duty fractions slightly greater than that at the maximum rate, the reaction rate is independent of the cycle period, and very sensitive to the CO duty fraction. The maximum is bracketed on all sides by low rate regions for different reasons. For short times, the cycling frequency is so fast that the surface cannot respond to it and thus the system is in a relaxed steady state (Fig. 4). For long times, the cycling frequency is so slow that peaks in CO_2 production are separated by large valleys of low production, thus lowering the average production. Intermediate cycling results in the optimal production of CO_2. At high CO duty fractions, CO saturates the surface while at low duty fractions, O_2 dominates the surface.

The position of the optimal reaction rate on the cycle time, CO duty fraction plane is dependent upon temperature. This behavior is shown in Fig. 5. The change in the optimal period and CO duty fraction can also be shown in terms of the lengths of the respective CO feed and O_2 feed portions of a cycle (Fig. 6). One notes that the position of the optimum moves towards longer cycling times as temperature drops, which was to be expected from the fact that the induction time increased with decreasing temperature. Similarly, the optimal CO duty fraction dropped as one went to lower temperatures, indicating that at lower temperatures the tendency of the catalyst surface is to saturate with CO. Also note that the optimal duty fraction can be greater than 0.5. This was not observed for similar experiments on Pt–Al_2O_3 (Barshad and Gulari, 1985a). The importance of the O_2 induction time is also evident from Fig. 6. For periodic operation at temperatures below approximately 130°C, the optimal t_{O_2} must be greater than the
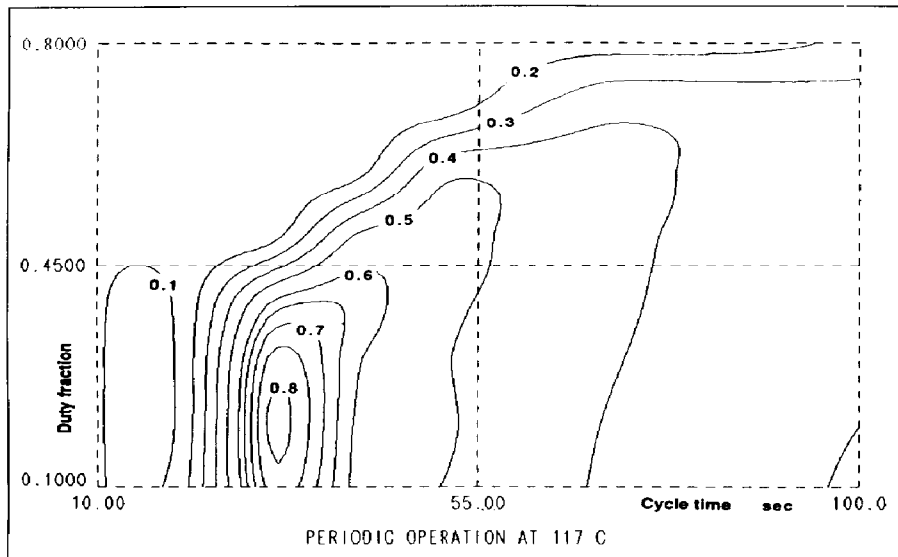
Fig. 3. Isorate contour plot for periodic operation in the CO duty fraction, cycle time plane for 117 °C. Isorate contour scales are proportional to the CO_2 concentration at the reactor outlet.
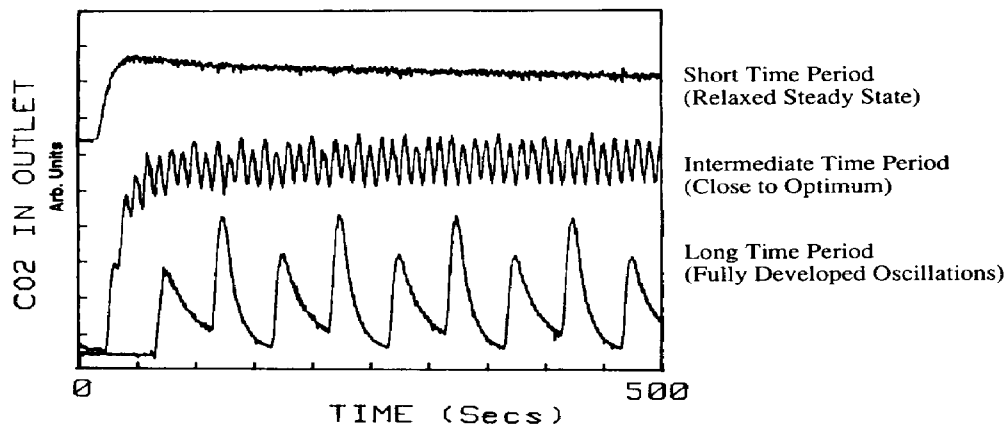

Fig. 4. CO_2 profiles for periodic operation resulting from 5-s period, 0.5 CO duty fraction at 117 °C, 100-s period, 0.5 CO duty fraction at 117 °C, and 20-s period, 0.5 CO duty fraction at 117 °C.

induction time. For higher temperatures the optimal t_{O_2} is close to the induction time.

Periodic operation results in rate enhancements compared to traditional steady-state operation. The maximum time average reaction rates for both periodic and steady-state operation are plotted against temperature in Fig. 7. For the range of temperatures studied, periodic operation can result in a greater rate. At higher temperatures steady-state operation will undergo ignition (180°C), reducing, or possibly eliminating the gap between cyclic and steady-state operation. Maximum steady-state rates were obtained when much less CO was present in the feed stream, as compared to the time average feed CO in the periodic case.

Quasi-periodic behavior during periodic operation

A region of quasi-periodic behavior was located during cyclic operation of the reactor. This region is indicated in Fig. 8, a plot of the reaction rate contour as a function of time and duty fraction for cyclic operation at 117°C. At any other combination of operating parameters on this contour map there exists only one attractor and thus the CO_2 concentration transient approaches a unique cyclic steady state (as in Fig. 4). The CO_2 concentration in the reactor outlet within the quasi-periodic region is seemingly irregular. Integrating the area under the CO_2 curve each cycle yields the conversion for that cycle. The variation in conversion from cycle to cycle is within experimental error outside the quasi-periodic region, but becomes
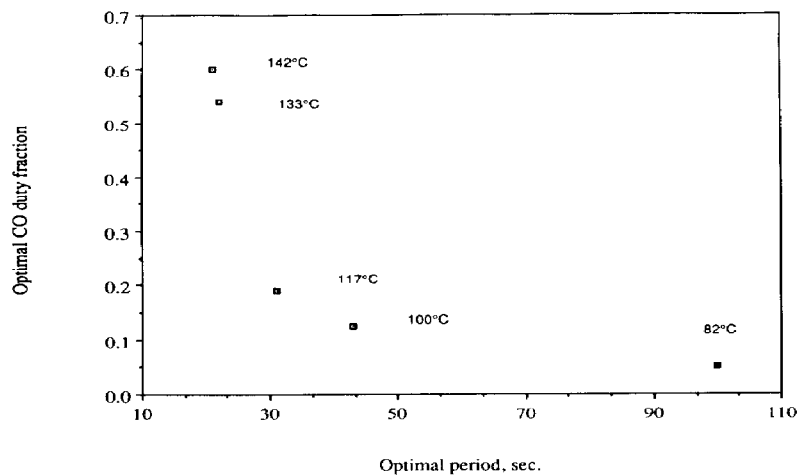
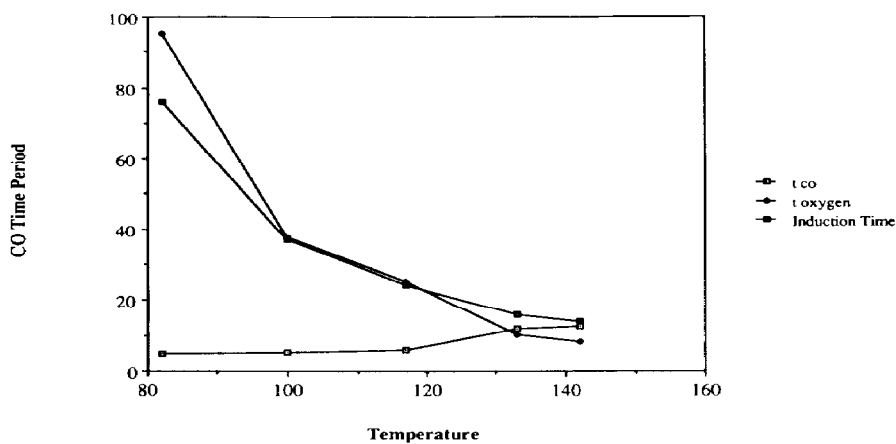Fig. 5. Location of maxima for four sets of mapping experiments, each at a different temperature.

Fig. 6. Optimal combination of t_{CO} and t_{O_2} at various temperatures.
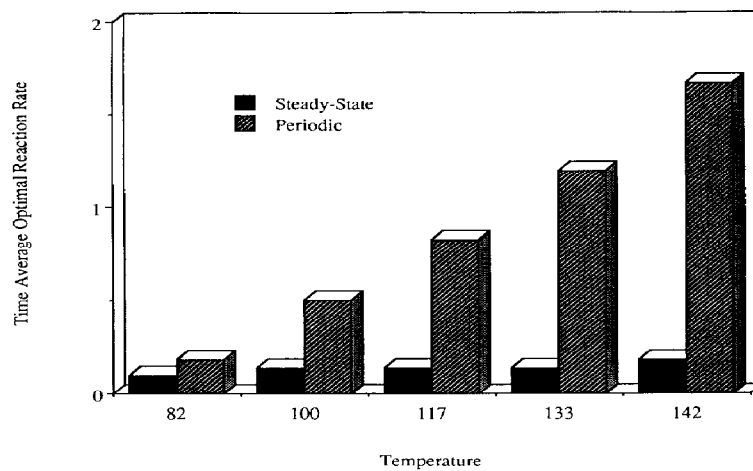
Fig. 7. Optimal conversion for periodic concentration forcing and traditional steady state operation at various temperatures.
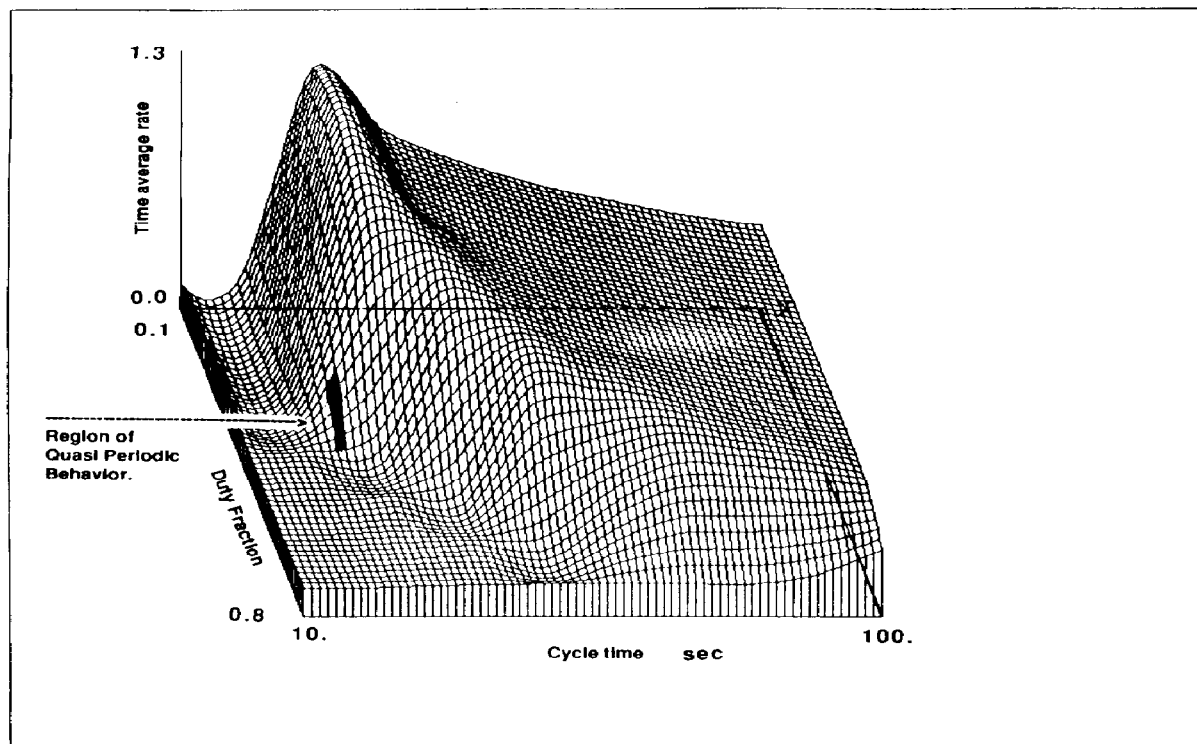
Fig. 8. Region of quasi-periodic dynamics for periodic operation at 117 °C.

seemingly unstable as one enters the region. A series of plots bearing out this fact is reproduced (Fig. 9). Qualitatively similar results were obtained even when the progression was repeated without pretreatment between runs. One particular experiment (0.3 CO duty fraction, 20-s cycle) was repeated several times. For both CO and O_2 pretreatments the qualitative features of the oscillations were reproduced for over 1000 cycles. These later experiments were analyzed in order to determine the nature of the observed behavior.

Integration of the CO_2 concentration history over the time period of the forcing yields a function inherently discrete in nature and thus can be analyzed by auto-correlation, or Fourier spectral analysis without resort to a stroboscopic map. These spectral–analytical functions can aid in determining whether the process is truly periodic, chaotic or quasi-periodic in nature. Without such tests characteristic responses of the system as a result of the forcing may be mistakenly interpreted as noise or external fluctuations in a control.

For a time series

$$T = x_1, x_2, x_3, x_4, \ldots x_{2n} \qquad (2)$$

the autocorrelation function is defined as

$$A(n) = \frac{\sum_{i=1}^{n} x_i x_{i+n}}{\sum_{i=1}^{n} x_i} \qquad (3)$$

The differentiated form of the data:

x_i = time average conversion for cycle i — time average conversion for cycle $i+1$ (4) was autocorrelated. For the CO pretreatment experiment part of the results are presented in Fig. 10. At least three time scales are evident: a short time scale equal to the cycle time, an intermediate scale of approximately 12 cycle times, and a long time scale around 175 cycle times. The maximum $A(n)$ value within each group of 12 cycles represents another intermediate level of oscillation; however, the period is not as well defined as the other three periods. Autocorrelation of the O_2-pretreated surface led to the same number of time scales. Similar experiments (resulting in quasi-periodic behavior) and analysis over the $Pt–Al_2O_3$ catalyst revealed only two time scales, that of the forcing and one intermediate of approximately 12 cycle times. The $Pt\ Al_2O_3$ experiment was not of sufficient duration to conclusively state if a long time scale existed.

Based upon the above results it seems that there exist slow and intermediate processes unique to the $Pt–SnO_2$ catalyst. These could possibly be attributed to a slow bulk and surface Sn oxidation mechanisms as Sn has been shown to exist in either the Sn^{4+} on the Sn^0 states under catalytic conditions (Lieske and Volter, 1984). Other phenomena such as metal lattice or surface rearrangement (of the Sn and/or Pt) could possibly explain the long time scale. A multitude of mechanisms exist to explain the intermediate time scale common to both $Pt\ Al_2O_3$ and $Pt–SnO_2$, i.e. Pt
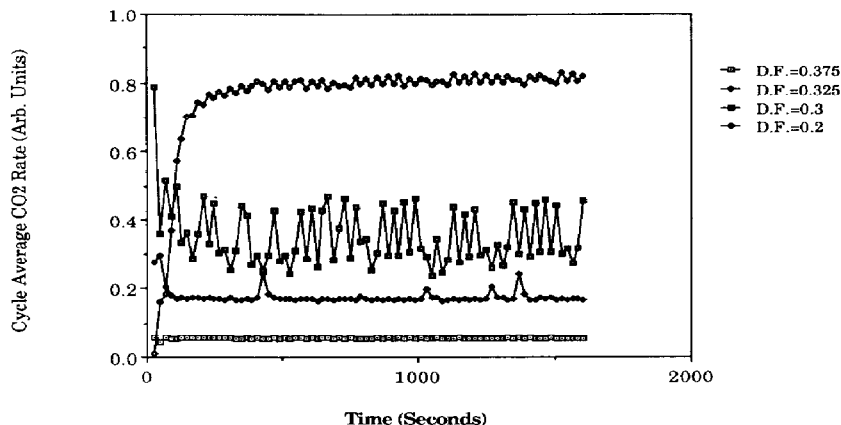
Fig. 9. Time average conversion per cycle for a CO duty fraction series through the quasi-periodic region at 117 °C and a 20-s period (CO pretreatment): (a) 0.375 CO duty fraction, (b) 0.325 CO duty fraction, (c) 0.3 CO duty fraction, (d) 0.2 CO duty fraction.
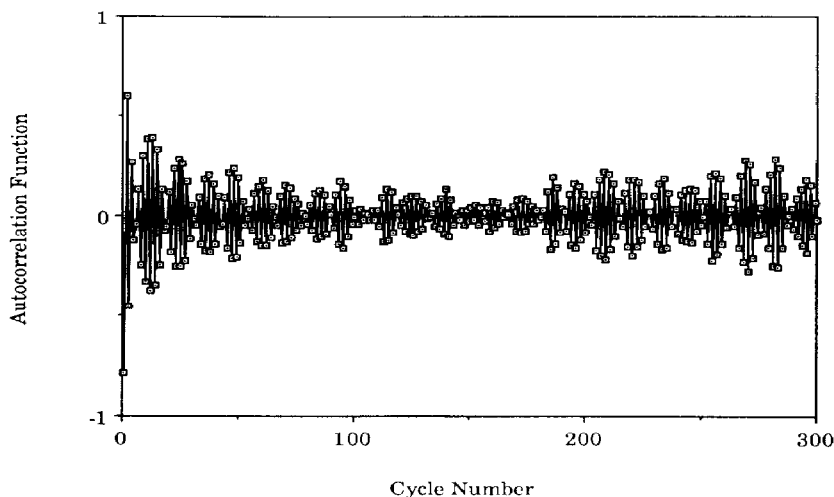

Fig. 10. Autocorrelation of the differentiated conversion data for a run lasting over 1000 cycles (20-s period, 0.3 CO duty fraction, at 117 °C).

{e.g. island theories, overlayer rearrangement and surface nonlinearities [see Aluko (1983) and Razon and Schmitz (1986)]}.

The quasi-periodic behavior was also observed at other temperatures, always in the same neighborhood of the maximum reaction rate observed. At lower temperatures the intermediate time scales increased in length. The duration of these experiments was not long enough to determine any change in the long time scale.

Further information concerning the reaction mechanism can be gained by examining the return plot (Fig. 11) for the experimental data partially shown in Fig. 9. The data tend to lie in three regions: a linear portion to the right, and two groups on the left side of the return map. One notes from such a plot that a cycle that has an average conversion which is high (greater than 0.18)

is always followed by one which is low (0.15–0.175), while a low-conversion cycle may be followed by a either a high-conversion cycle or another low-conversion cycle. The ratio of conversion from one cycle to the next is predictable when the first cycle is of high conversion. This ratio can be determined from the slope of the line formed for high-conversion cycles. No such relationship exists when the first cycle is of low conversion.

This behavior indicates that there must be a mechanism which allows for one or more reversible reservoirs of reactants, for example an inactive surface species, able to convert back and forth to an active form or more likely reversible oxygen storage on the tin oxide surface layer. Island theories might also exhibit the necessary supply mechanism, as the interior of a particular species cluster acts as a reservoir
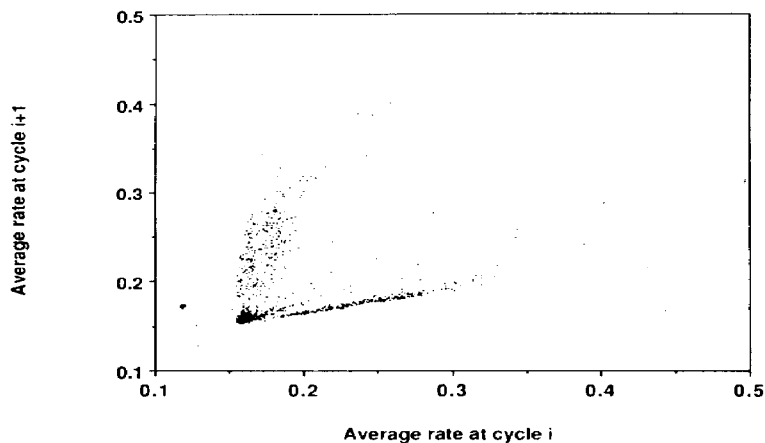
Fig. 11. Time average conversion per cycle return map for a run which exhibits quasi-periodic dynamics during concentration cycling (20-s period, 0.3 CO duty fraction, at 117 °C). Plotted are 300 cycles starting with the 600th cycle into the experimental run.

for the reaction taking place at the island circumference (Silverberg *et al.*, 1985). After a high-conversion cycle, when species clusters are small, the islands are buffered from each other due to the large fraction of empty catalytic sites. It is important to note that the quasi-periodic behavior occurred under isothermal conditions, and temperature variations were not observed during the reaction.

CONCLUSIONS AND SIGNIFICANCE

We have shown that the oxidation of CO over a Pt–SnO$_2$ catalyst proceeds by way of a modified Langmuir–Hinshelwood mechanism. Periodic operation by reactant concentration forcing may result in rate enhancements over conventional steady-state operation. A single maximum in reaction rate exists in the CO duty fraction, cycle time plane. This fact and the dependence of the optimum upon temperature is understood by considering the characteristic induction times for the process and the quenching of the reaction by complete coverage of the surface by a single component.

In addition at least three characteristic time scales have been identified for the process. These were identified by auto-correlation of the complex dynamic behavior observed. Besides the forcing frequency there exists at least one time scale involving the tin oxide and one, possibly more, characteristic time scales for the Pt. That the mechanism must contain a buffer, or supply feature is deduced from the return plot of the quasi-periodic behavior observed. Quasi-periodic behavior and bifurcations from periodic to quasi-periodic behavior have been experimentally observed. While these features are common in periodically forced systems, they had previously been observed for heterogeneous catalyzed reactions only during theoretical simulations [e.g. Kevrekidis *et al.* (1986a–c)] and the reaction between NH$_3$ and NO (McKarnin *et al.*, 1986).

In conclusion, therefore, transient and periodic operation of a complex reaction can provide critical information in determining the underlying mechanism. Spectral–analytical techniques, which can be applied to data from such experiments, identify the characteristic time scales involved in the process and thus aid in the evaluation of rival models.

NOTATION

A	autocorrelation function
C	gas phase concentration, kg mol/m^3
K	adsorption equilibrium constant, m^3/kg mol
k_r	surface reaction rate constant, kg mol/(kg surface catalyst)(s)
n	half the number of points in the time series **T**
r	reaction rate, kg mol/(kg surface catalyst)(s)
T	time series
t	duration of the particular phase of cycle, s
x	difference between time average conversion for a given cycle and the next cycle

Subscripts

i	refers to the ith cycle
CO	refers to carbon monoxide
O$_2$	refers to oxygen
CO$_2$	refers to carbon dioxide

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