JOURNAL OF CATALYSIS 55, 76–87 (1978)

Spurious Limit Cycles and Related Phenomena during CO Oxidation on Supported Platinum

PHILIP VARGHESE, JAMES J. CARBERRY, AND EDUARDO E. WOLF

Department of Chemical Engineering, University of Notre Dame,
Notre Dame, Indiana 46556

Received May 4, 1978

A study of CO oxidation on Pt/α-Al_2O_3 catalyst was carried out in the temperature range 370 to 420°K, in oxygen. Attention was devoted specifically to isothermal limit-cycle phenomena in this reaction. Spurious limit-cycle phenomena resulting from trace impurities in the oxygen stream were observed. Some characteristics of these, and the conditions under which they occur were elucidated. Further, changes in catalytic behavior proceeding from modifying treatments in oxidizing and reducing environments were noted and related to similar phenomena reported by other authors.

INTRODUCTION

Carbon monoxide oxidation on platinum catalysts represents one of perhaps two heterogeneous catalytic reactions in which sustained oscillatory or limit-cycle phenomena have been reported under isothermal conditions. An extensive and thorough review of the subject by Sheintuch and Schmitz (*1*) has successfully delineated the extent of presently available experimental and theoretical insight into these phenomena.

The above review was instrumental in pointing out the short falls in the existing body of work and also the need for more discriminating studies, both theoretical and experimental. Some theoretical conditions for the existence of limit-cycle phenomena with some of the more commonly employed elementary reaction step sequences were further explored by the same authors (*2*). Employing such features as, an activation energy dependence on surface coverage and, oxidation/reduction of the metal, they derived theoretical expressions that admitted to sustained limit cycles. However, they had no success in matching theoretical and experimental results. From their work, however, it is obvious that a first and very formidable question, namely that concerning the nature of surface species and metal oxidation states, remains open.

Cutlip and Kenney reported in their experimental study (*3*) on supported platinum in a gradientless reactor that, (a) dramatic oscillations are observable during the simultaneous oxidation of carbon monoxide and 1-butene and, (b) no oscillations (apart from a few irreproducible instances) were observed for carbon monoxide oxidation in itself. A second and by no means trivial question is suggested by the above result: To what extent can unanticipated interaction with low concentration impurities produce spurious limit-cycle phenomena?

Repeating well-known results, we point out that the existing body of steady state

0021-9517/78/0551-0076$02.00/0
Copyright © 1978 by Academic Press, Inc.
All rights of reproduction in any form reserved.

TABLE 1

Catalyst Properties

	α-Alumina properties
Pellet size (in.)	3/16
BET area (m^2/g)	5.3
Range of pore radii (Å)	4000–300
Total pore vol (cm^3/g)	0.27
Pellet density (g/cm^3)	1.9
	Catalyst properties
Metal loading (wt% Pt)	0.035
H_2 titration value (μl/g)	27.34
Active metal area (m^2 Pt/g)	0.0272
H/Pt ratio	0.415
Av crystallite size (Å)	21.3

rate data has been adequately described in terms of the following sequence of elementary reaction steps

$$CO + S \rightleftarrows CO\text{–}S, \quad (1)$$

$$O_2 + 2S \rightleftarrows 2O\text{–}S, \quad (2)$$

$$CO\text{–}S + O\text{–}S \rightarrow CO_2 + 2S, \quad (3)$$

$$CO + O\text{–}S \rightarrow CO_2 + S, \quad (4)$$

where the first two steps are taken to be at equilibrium and the relative importance of the last two, Langmuir–Hinshelwood and Eley–Rideal steps respectively, are not agreed upon. It may also be noted that the above reaction mechanism is not suitable for modeling the observed limit cycle phenomena (*1*, *2*).

The results presented in this paper were obtained as part of an ongoing study of CO oxidation, in which we encountered limit cycles of both, the clearly spurious, and other kinds. We have attempted to elucidate the conditions favoring the appearance of such spurious limit cycles, as also their response to certain variables in the reaction environment. In addition, other results will in part corroborate recent findings (*4*, *5*) which indicate that, especially with regard to metal oxidation–reduction states, supported platinum may represent a far more complex entity than previously supposed.

EXPERIMENTAL METHODS

Catalyst. The platinum catalyst employed in our studies was prepared and characterized in our laboratory.

It consisted of 0.035 wt% platinum on α-alumina. The low metal loading maintained approximately the same ratio to total support area as metal loadings commonly employed on higher area supports, and held out the prospect of reduced activity per gram leading to minimized heat and mass diffusional interference.

The catalyst was prepared by impregnating $\frac{3}{16}$ in. pellets of α-alumina (type T-708, Girdler Chemical) with hexachloroplatinic acid. The catalyst was then dried for 8 hr at 398 K followed by treatment at temperatures of 498 and 598 K for 1 hr each, in flowing argon. Hydrogen (20.4% in argon) was then introduced and a reduction of 773 K for 8 hr followed. Following procedures established as reliable in an earlier paper (*6*) the reduced catalyst was degassed in flowing argon for 16 hr at this temperature. The system was then cooled down to room temperature and the Benson–Boudart hydrogen titration technique was employed to arrive at dispersion data on the supported platinum.

Table 1 provides a listing of information so obtained as well as manufacturer supplied data on the α-alumina itself.

Apparatus. Steady state rate data and limit-cycle phenomena were studied using the apparatus depicted in Fig. 1.

It consisted of a metering and mixing section for gases, a gas purifying or water saturating section, a spinning basket type gradientless CSTCR and an analysis section.

Gases were metered by fine metering valves through calibrated flow meters to a mixing junction. Up to three gas streams could be metered and mixed in this fashion.

Provision existed for employing bubble flow meters when the flow rate in question was too small to be accurately measured by a rotameter. Concentrations thus obtained could be checked by means of the gas chromatograph. In the purifying section the gas stream could be passed through traps to remove water vapor and CO_2, or alternately, water vapor could be deliberately introduced into the gas by means of bubbling devices maintained at room temperature. We estimated the water content of the stream thus treated to be about 2% on a wet basis. The reaction mixture was then fed to a CSTCR 350 cm^3 in volume, containing 9.84 g of the catalyst. The reactor was maintained at the appropriate temperature by means of a Tecam Model TC4A three mode temperature controller.

Effluent gases from the reactor were analyzed by a Beckman Model 315A continuous infrared analyzer for carbon dioxide and by a Carle Model AGC 111 gas chromatograph. A bubble flow meter at the end of the system provided accurate measurement of the total volumetric flow rate. The reactor was operated at essentially atmospheric pressure.

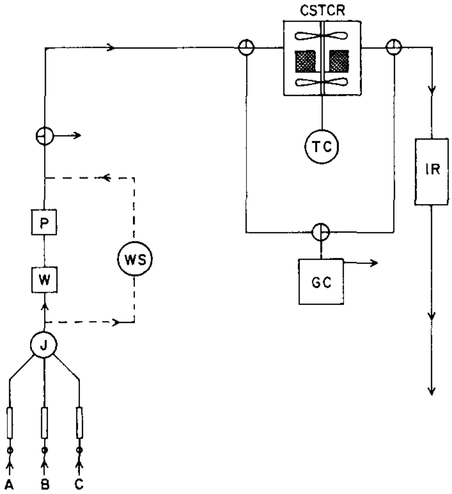

FIG. 1. Experimental apparatus; (A) CO supply, (B) O_2 supply, (J) mixing junction, (W) H_2O trap, (P) CO_2 trap, (WS) water saturator, (CSTCR) continuous stirred tank catalytic reactor, (TC) temperature controller, (IR) infrared CO_2 analyzer, (GC) gas chromatograph.

TABLE 2

Analyses of Oxygen Used

"Pure" oxygen	ppm
Linde Zero grade, electrolytically obtained	
Nitrogen	<180
Total hydrocarbons as	
Methane	<0.5
Argon	<5
"Impure" oxygen	
Linde Extra Dry grade, obtained from air separation	
Nitrogen	<3000
Total hydrocarbons as	
Methane	<30
Argon	<1000
H_2O	<10
$CO–CO_2$	<300

The experimental unit used in catalyst preparation and characterization has been described elsewhere (*6*).

RESULTS

The reported results were obtained on a reaction mixture of CO in oxygen. Since no diluent was employed in this mixture, it consisted mainly of oxygen and the problem of minimizing trace impurities reduced to one of obtaining a pure source of oxygen. The "pure" oxygen was manufactured electrolytically (Linde Zero grade) and a manufacturer supplied analysis is shown in Table 2.

Experimental procedure consisted of observing reaction rate vs concentration behavior under isothermal conditions. While the generation of steady state rate vs concentration data was not the primary goal, such data were used as a means of following changes in catalytic activity, both gradual as in slow deactivation and sudden as found with certain catalyst treatments. It was ascertained early on that pretreatment of the catalyst in oxygen, for 2 hr at 473 K prior to reaction, assured satisfactory

TABLE 3

Different Stages in Catalyst Behavior

Stage No.	Initiating catalyst treatment	Reaction environment	Observed phenomena
1	Fresh catalyst.	Pure O_2, temp, 370–410 K	Steady state multiplicity; no oscillations; activity as in Fig. 2.
2	Catalyst exposed to reactants at $\simeq$473 K: reaction light-off observed.	Pure O_2, temp, 370–410 K	Rates as in stage 1; oscillations observed (Fig. 3) near rate maxima; oscillations not damped by "wet" feed.
3	Catalyst treated for 4 hr at 573 K in pure O_2.	(a) Pure O_2, temp, 370–410 K	Fivefold reduction in activity; oscillatory phenomena in pure O_2 eliminated.
		(b) Impure O_2, temp, 370–410 K	Large sustained oscillations observed (Fig. 4); steady states not obtainable with dry feed; oscillations suppressed and inhibited steady states obtained by "wet" feed (Fig. 5).
4	Catalyst treated for 2 hr at 573 K in pure O_2; then 8 hr at 773 K in H_2	(a) Pure O_2, temp, 370–523 K	No measurable H_2 chemisorption; no activity; moderate recovery of activity after long (24 hr 523 K) treatment in O_2 (Fig. 7); induction period of 75–90 min at start of each run; no oscillatory states in pure O_2.
		(b) Impure O_2, temp, 390–430 K	Large sustained oscillations (Fig. 8); properties as in stage 3 (b).

reproducibility of steady state rates—checks being made within periods of up to 5 days. Such pretreatment was thereafter employed as standard procedure prior to each kinetic run. At some points during the experiments, the catalyst was subjected to somewhat more severe treatment. These treatments often initiated different catalyst behavior, notably with respect to activity and limit cycles, in succeeding runs. A summary of the distinct stages and the attendant behavior thus observed, which are described in detail below, is given in Table 3.

Early runs carried out in the temperature range 370 to 410 K produced the familiar "abnormal" kinetic behavior shown in Fig. 2, which roughly illustrates the level of activity within the said range of temperature. Incompleteness of the rate curve was due to a combination of high rates and a generally shallow slope of the reactor operating line (see for example broken line on Fig. 2), which in conjunction with the well-known (7) steady state multiplicity caused sampling perturbations near the rate maxima to be large enough to drop the reactor to the low conversion steady state. The residence times being chosen largely with a view to aiding detection of limit cycles and the steady state rates being employed merely as indicators of catalyst activity, the above was not considered a significant problem. In searching for oscillations, however, the infrared analyzer was employed as the sole instrument of outlet gas analysis, thus allowing an unperturbed and close approach to the rate maxima.

Notably enough, in this first series of runs (stage 1) we were unable to observe oscillatory behavior over a range of temperatures (370–410 K) and residence times (15–90 sec).

A series of three runs at higher temperatures ($\simeq$473 K) were then carried out. An analysis of the steady state data so obtained showed quite clearly, both from calculations and experimentally, that the reaction rate was high enough for heat diffusional limitations and the consequent nonisothermality to have led to catalyst light-off. Studies were therefore resumed in the lower temperature range used earlier.

At this point (stage 2), although steady state rates corresponded well with the original runs shown in Fig. 2, in this instance an approach to the rate maxima invariably resulted in the appearance of sustained oscillations. These oscillations were similar to those reported by McCarthy *et al.* (*8*) in that they occurred in a narrow region near the rate maxima, displayed increasing amplitudes with increasing CO concentrations within that region, and were simple in nature bearing no clear similarity to the usually observed relaxation type oscillation. They were not only consistently reproducible but also unaffected by saturating the feed gas stream with water vapor, using the device earlier described.

Exact reproductions of two such oscillations in CO_2 concentration are shown in Fig. 3, one obtained under dry and the other under "wet" feed stream conditions.

An extended high temperature (4 hr at 573 K) treatment in oxygen effected two changes in the catalyst (stage 3), (a) it reduced the steady state activity by a factor of 4 to 5 (based on an average of ratios at different CO concentrations) over the same temperature range of 370 to 410 K and, (b) it eliminated the oscillatory phenomena described above. We were never again able to observe oscillations in the CO–pure oxygen system.

We then provided for the use of a different grade of oxygen manufactured by the air separation process (Linde Extra Dry), a manufacturer supplied analysis of which is also given in Table 2 and which will be hereafter referred to as "impure" oxygen.

Radically different behavior was observed when the impure oxygen was used in the reaction. Large and sustained limit-cycle phenomena were observed. These could be most commonly characterized as having multipeak cycles of the relaxation type. Representative sections of two such cycles are shown in Fig. 4. The time

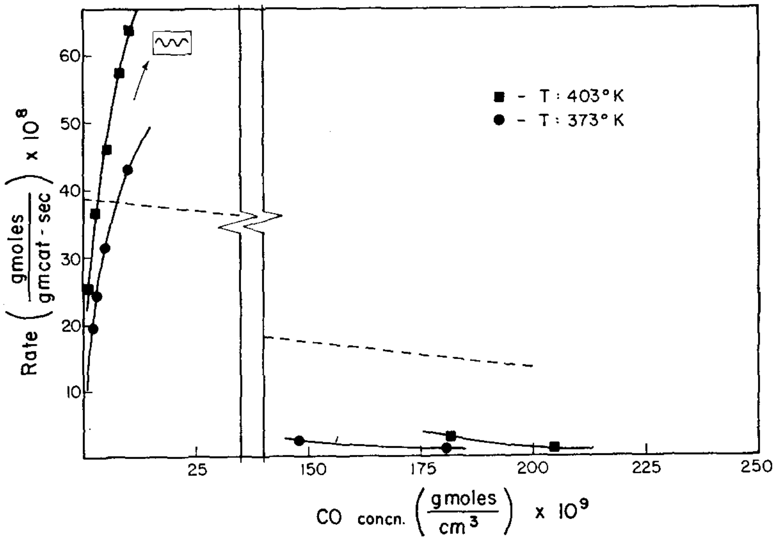

FIG. 2. Initial rates vs concentration data in pure oxygen.

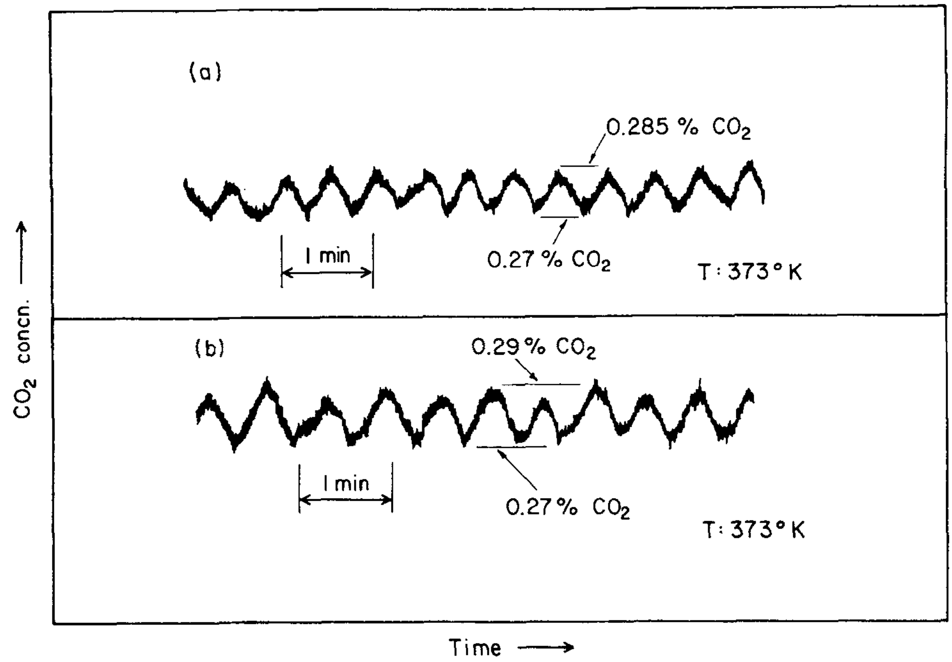

FIG. 3. Oscillations in pure oxygen, (a) dry stream, CO feed concn = 0.31%, total flow rate = 368 cm^3/min; (b) "wet" stream, CO feed concn = 0.31%, total flow rate = 368 cm^3/min.

averaged CO_2 production was clearly lower than that available at the steady state in pure oxygen for identical feed and temperature. Further, no *steady* states seemed to exist over most of the ascending portion of the rate vs concentration curves. That the CO_2 was produced by conversion of CO and not from impurities in the oxygen was evident from the fact that the impure oxygen by itself produced no measurable CO_2 at temperatures as high as 480 K. The impure oxygen did not produce any permanent effect on the catalyst since replacing it with pure oxygen led to the recovery of earlier behavior both in qualitative and quantitative terms.

One notable feature of the limit cycles obtained in impure oxygen was that unlike the earlier observed oscillations, these could be suppressed and a steady state obtained, by saturating the feed gas with water vapor. Steady state rate curves thus obtained showed significant inhibition when compared with rates in pure oxygen. Such a comparison is made in Fig. 5. We verified that such inhibition is not attributable to the water by itself, by establishing that a "wet" run in pure oxygen produced little if any inhibition of rates.

The behavior of these limit cycles in impure oxygen was also investigated with reference to increasing temperatures. Figure 6 shows the variation of one such oscillatory state with increasing temperature, all other variables being constant. Note that with increasing temperature the amplitude as well as the "period" of the cycles decreased while the maxima of the cycles remained relatively constant.

Next, an attempt was made to determine if any of the changes which the catalyst had undergone in the reaction environment were reversible. The catalyst was treated in pure oxygen at 573 K for 2 hr and subsequently reduced in hydrogen (20.4% in argon) for 8 hr at 773 K and then degassed in flowing argon at the same temperature for 16 hr. The reducing and degassing steps were identical to those employed at the time of catalyst preparation.

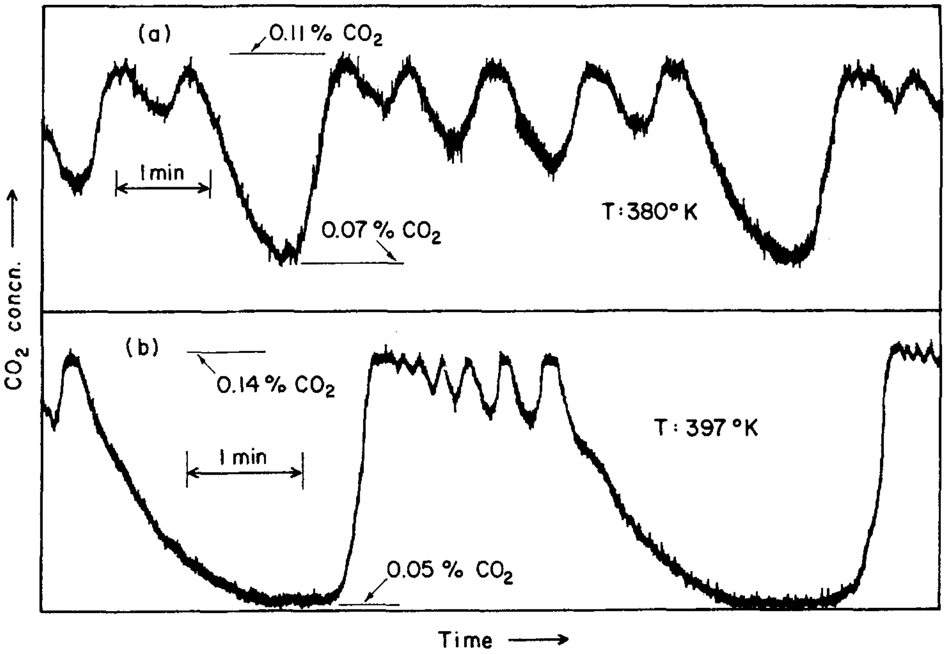

FIG. 4. Oscillations in impure oxygen (dry stream), (a) CO feed concn = 0.117%, total flow rate = 368 cm³/min; (b) CO feed concn = 0.37%, total flow rate = 368 cm³/min.

An attempt to characterize the active area of the catalyst thus obtained (stage 4), by chemisorption and hydrogen titration surprisingly revealed no measurable chemisorption or titration at room temperature. Further, the catalyst also showed no activity in reaction at temperatures as high as 523 K. The catalyst was then left at 523 K in flowing pure oxygen for 24 hr. At the end of that period, kinetic runs were resumed using the usual pretreatment. Some activity had been recovered as

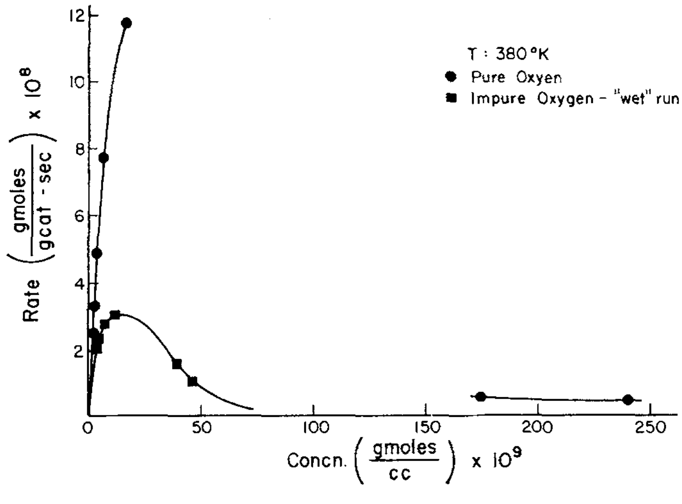

FIG. 5. Comparison of rate vs concn curves obtained in pure (dry stream) and impure ("wet" stream) oxygen.

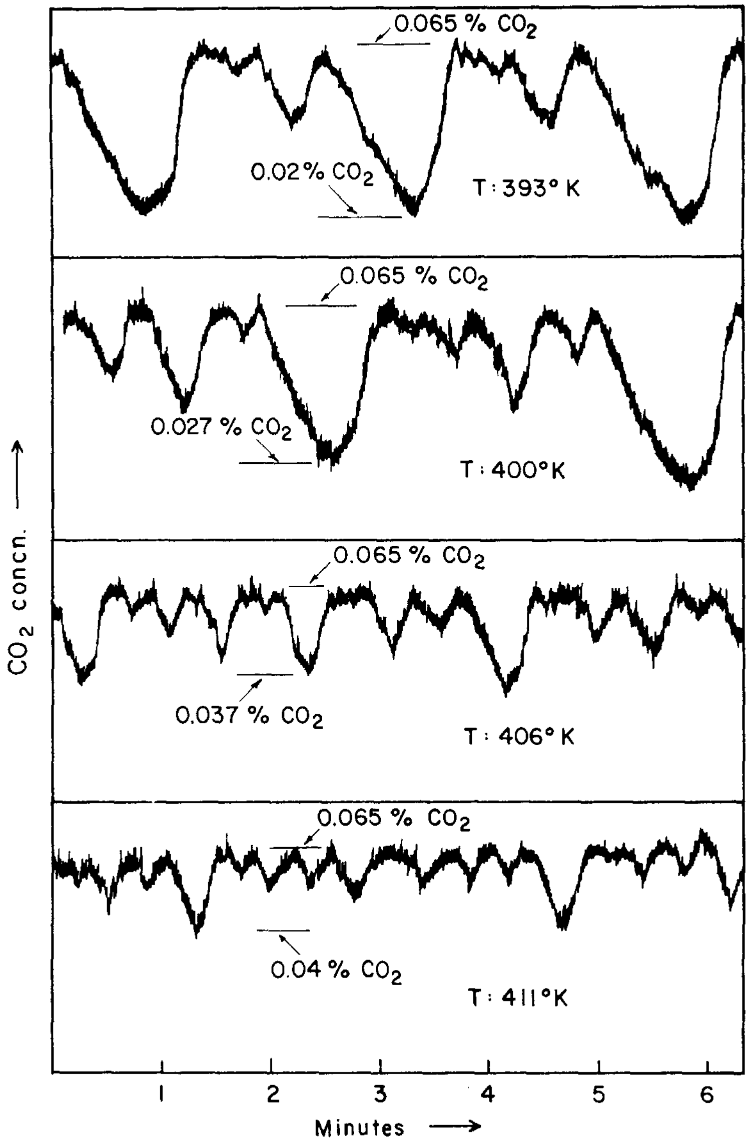

FIG. 6. Temperature variation of single oscillatory state in impure oxygen, CO feed concn = 0.11%, total flow rate = 368 cm^3/min.

evidenced by the steady state rates in pure oxygen shown in Fig. 7 (notice however the significantly higher range of temperatures employed in these runs), but at least one significant difference in catalyst behavior was observed. On introduction of the reaction mixture to the catalyst after cooling down from the pretreatment step (2 hr, 473 K in pure oxygen, as before) the catalyst invariably took between 75 and 90 min to achieve the first reaction steady state. The intervening period was marked by a slow monotonic increase in CO_2 production. Subsequent steady states were obtained with no difficulty and within minutes of changing inlet concentration. None of the earlier series of runs had displayed this characteristic, which is to say that catalyst response to CO in the feed was immediate in all those cases.

Again, no limit cycles were observed in pure oxygen and limit cycles, with all the previously noted characteristics, proliferated in the impure oxygen. Figure 8 shows some limit cycles seen at this stage of experiments—of which part (a) is a segment of a state which could only be described as "chaotic," i.e., having no periodicity whatsoever.

We attempted, unsuccessfully, to induce oscillations in pure oxygen by adding small amounts of C_2H_4 to the feed stream. Whether, because the chosen hydrocarbon was unsuitable for the purpose, or because it was not present in sufficiently low concentration, or both, all we observed was substantial conversion of the C_2H_4 itself.

Finally, we attempted to characterize the catalyst and obtained a hydrogen titration value of 1.2436 μl/g of catalyst representing a severe reduction of titratable platinum area in comparison with the fresh catalyst.

DISCUSSION

The effects of using the impure oxygen were: (a) the creation of sustained limit-cycle phenomena and (b) an inhibition of catalytic activity as reflected both in the time averaged and the maximum observed rates of CO_2 production. In the "wet" state the limit cycles were suppressed, while the inhibition effect was made more evident by a comparison of the rates thus obtained with the pure oxygen rates. The inhibition effect was for this and earlier described reasons not substantially connected with the wet or dry state of the gases. It is reasonable to suppose therefore that the impure oxygen contains some inhibitor/inhibitors which in the dry state produce oscillations in addition to inhibiting the reaction. It may be noted that Hegedus *et al.* (*9*) observed the suppression of multiplicities by water, during CO oxidation in an integral reactor. From our data, it would appear that water by some yet unknown mechanism prevents the renewal of active surface occupied by the inhibitor(s), thus leading to a non-oscillatory inhibited steady state.

Table 2 displays the manufacturer supplied analyses of the two gases. If, as seems reasonable, one excludes the inerts such as nitrogen and argon from consideration, it would appear that the significant difference lies in the total hydrocarbons content of

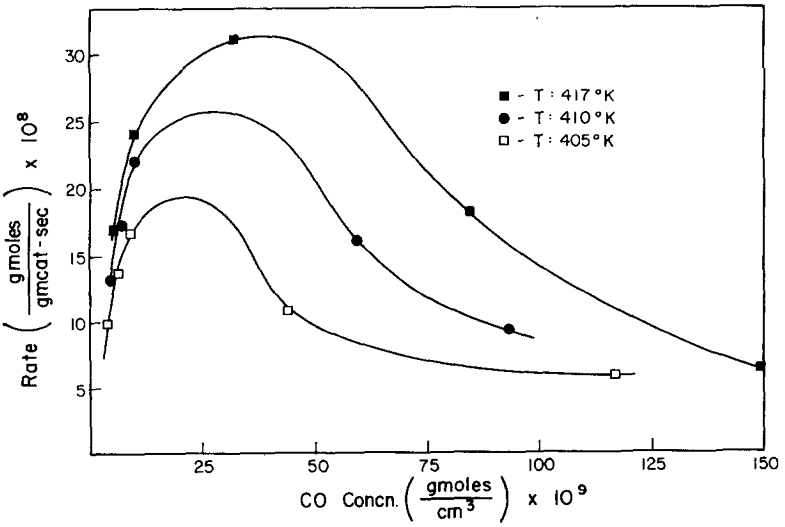

FIG. 7. Rate vs concn data representing activity recovered after second reduction in H_2.

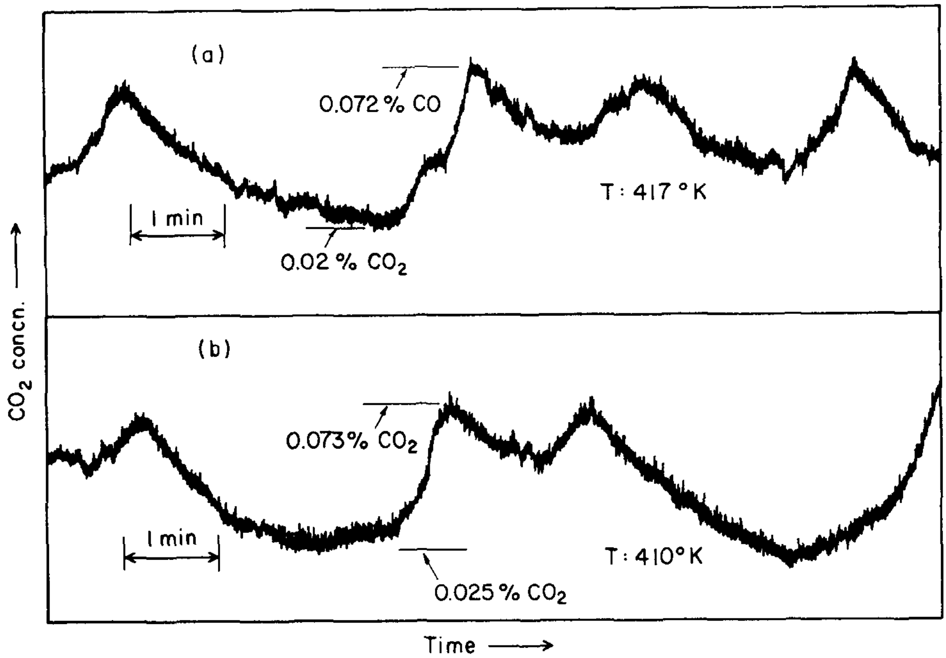

FIG. 8. Oscillations in impure oxygen (dry stream), (a) CO feed concn = 0.11%, total flow rate = 368 cm³/min; (b) CO feed concn = 0.12%, total flow rate = 368 cm³/min.

the gases. We employed mass spectrometric analysis in an effort to narrow down the inhibitor(s) to specific compounds. However, the impurities being present in parts per million, it proved too difficult to enumerate and quantify them under the extreme resolution levels that had to be used. We were, however, able to state definitely that no contaminant of molecular weight greater than 80 was present.

That the presence of hydrocarbons can cause limit cycles has already been shown by Cutlip and Kenney (*3*) using 1-butene, albeit in relatively large concentration. However, their results relate to a comparatively oxygen deficient reaction environment as also indicate that the 1-butene is a co-reactant with CO. We are unable to state whether our inhibitor(s) is also a co-reactant since even if so, any CO_2 formed would be in undetectably small amounts.

Among theoretical approaches that have attempted to model limit cycles in CO oxidation, that of Eigenberger (*10*) is relevant to our results. Employing an additional step

$$P + S \rightleftarrows P\text{–}S. \qquad (5)$$

with the first three kinetic steps represented in Eqs. (1) to (3), where P is an unidentified inhibitor, he successfully simulated oscillations of the relaxation type. The approach, while appearing somewhat contrived, originally, may in fact be a correct representation of systems such as ours.

There is reason to believe that the oscillations that were observed consistently over a section of the experimental program, in pure oxygen, were phenomena different from those obtained in impure oxygen. To the best of our knowledge, any special contamination of gas or catalyst during that period was unlikely. There were also marked differences between these oscillations and the other spurious variety, notably in the response to water vapor and the more limited region of appearance close to the rate maxima. The possibility that deviation from isothermality was responsible for the observed oscillations must be considered. The turnover rates being most indicative of the possibility of localized high temperatures, we computed these for a number of cases, basing them on the originally available active area. The spurious oscillations were observed at maximum turnover numbers (mol/sec-site) ranging from 0.01 to 0.47. These compare well with those prevailing in the work of other investigators [see Ref. (*3*) for a comparison] and non-isothermality may be ruled out here. However, the oscillations in pure oxygen were all observed at turnover numbers in the range 0.95 to 1.0. These are substantially higher than the turnover rates at which Cutlip and Kenney (*3*) were unable to observe oscillations in their system. The customary calculations of temperature difference between bulk gases and pellet, employing empirical correlations to obtain the film heat transfer coefficient, do not guarantee the absence of localized temperature excursions. For these reasons, it is difficult to state conclusively that temperature gradients were not present, in what we will call the "anomalous" oscillations in pure oxygen.

Some significance must attach to the events beginning and concluding the period in which these anomalous oscillations were observed. Ostermaier *et al.* (*4*) in their studies of NH_3 oxidation over supported platinum concluded that surface oxidation of the platinum took place to a large extent and resulted in deactivation of the catalyst. Speculation based on some of their qualitative results may be permitted even though NH_3 oxidation represents a reaction vastly different from CO oxidation. Perhaps significantly they found that catalyst light-off during reaction was capable of reactivating the catalyst. Although we observed no significant change in activity at that point, it should be noted that it was immediately after reaction under such light-off conditions, that the anomalous oscillations were observed. Also note that it was a high temperature (573 K) oxygen treatment that reduced catalyst activity and finally eliminated these oscillations.

Whereas Ostermaier *et al.* (*4*) were able to reverse completely the oxidative deactivation of their catalyst by reduction in H_2 at 673 K for an unspecified period, our attempt to reverse changes in the catalyst by reducing in H_2 at conditions identical to those used in its preparation, yielded unexpectedly, a complete elimination of active area as measured by chemisorption and titration, as well as catalytic activity. This and the subsequent recovery of some activity upon treatment in oxygen may represent corroboration and extension to a reaction environment of the results reported recently by Dautzenberg and Wolters (*5*). They reported that lengthy treatments of supported Pt in H_2 at temperatures of 773 K and higher resulted in the highly dispersed Pt becoming "inaccessible" to H_2 chemisorption by way of a reaction that they hypothesized to be:

$$Pt + Al_2O_3 + xH_2 \rightarrow Pt\cdot Al_2O_{3-x} + xH_2O. \quad (6)$$

They, too, found that a partial recovery of chemisorptive platinum, after such "maltreatment" in hydrogen was effected by treatment in oxygen at high temperatures. Unlike them we found that such partial reactivation with oxygen was time dependent, taking in fact 24 hr for the very moderate recovery of activity shown in Fig. 7.

An interesting aspect of the final state of the catalyst was the slow increase in activity it displayed in establishing the first reaction steady state after each oxygen pretreatment. Although changes such as faceting have been observed in Pt crystallites when exposed to reaction conditions (*11*), the substantially lower temperatures employed here seem to preclude that possibility. Consequently the last observation must be considered indicative of some change with respect to metal oxidation states and/or oxygen species on the catalyst surface. We are unable to speculate as to why the catalyst did not show this behavior in runs prior to the second reduction. In any event this and the earlier changes in catalyst activity point to the importance of these oxygen related phenomena to CO oxidation on supported platinum. Boudart *et al.* (*12*) have advanced a credible qualitative explanation of isothermal oscillations in the H_2–O_2 reaction in excess oxygen, making appeal to just such phenomena.

We have shown that spurious limit-cycle phenomena in CO oxidation proliferate in the presence of oxygen containing trace impurities, tentatively identified as hydrocarbons, that are commonly encountered in many commercially supplied gases. In this case, we also found that these limit-cycle phenomena could be suppressed by water vapor in the reaction mixture. These observations point out that special attention should be paid to gas purities, in investigations of this kind, especially because of the disturbingly low levels of impurities that appear to be sufficient to provoke such spurious behavior. We also noted other oscillations whose freedom from nonisothermality we were not able to guarantee, and which we termed "anomalous."

Secondly, we have noted changes in catalyst activity and behavior with different oxygen and hydrogen treatments, that are generally in line with views currently being advanced on the nature of supported platinum. In the light of these, it appears that if limit-cycle phenomena which are undisputably isothermal and nonspurious are observed, explanations hinging on metal oxidation states and/or oxygen species on the surface, as being now attempted by other investigators (*2, 12*), stand the greatest probability of success.

ACKNOWLEDGMENT

The authors gratefully acknowledge support for this research by the National Science Foundation, Grant No. 7600699.

REFERENCES

1. Sheintuch, M., and Schmitz, R. A., *Catal. Rev. Sci. Eng.* **15**, 107 (1977).

2. Sheintuch, M., and Schmitz, R. A., 5th Int. Symp. on Chem. Reaction Eng., Houston, *ACS Symp. Ser.* **65**, 487 (1978).

3. Cutlip, M. B., and Kenney, C. N., 5th Int. Symp. on Chem. Reaction Eng., Houston, *ACS Symp. Ser.* **65**, 475 (1978).

4. Ostermaier, J. J., Katzer, J. R., and Manogue, W. H., *J. Catal.* **41**, 277 (1976).

5. Dautzenberg, F. M., and Wolters, H. B. M., *J. Catal.* **51**, 26 (1978).

6. Carballo, L. M., Serrano, C., Wolf, E. E., and Carberry, J. J., *J. Catal.* **52**, 507 (1978).

7. Carberry, J. J., "Chemical and Catalytic Reaction Engineering," McGraw–Hill, New York, 1976.

8. McCarthy, E., Zahradnik, J., Kuczynski, G. C., and Carberry, J. J., *J. Catal.* **39**, 29 (1975).

9. Hegedus, L. L., Oh, S. H., and Baron, K., *AIChE J.* **23**, 632 (1977).

10. Eigenberger, G., presented: 4th Int. Symp. Chem. Reaction Eng., Heidelberg, 1976.

11. Flytzani-Stephanopoulos, M., Wong, S., and Schmidt, L. D., *J. Catal.* **49**, 51 (1977).

12. Boudart, M., Hanson, F. V., and Beegle, B., presented: 69th Annu. AIChE Meet., Chicago, Ill., 1976.