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Fourier Transform Infrared Spectroscopy Studies of Surface Reaction Dynamics

II. Surface Coverage and Inhomogeneous Temperature Patterns of Self-Sustained Oscillations during CO Oxidation on Pt/SiO_2

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Transient methods of Temperature-Programmed Reaction (TPR) and Concentration-Programmed Reaction (CPR) have been used to uncover regions of self-sustained oscillations of CO oxidation on a 5 wt% Pt/SiO_2 catalyst. The surface dynamics of the oscillations were studied using Fourier Transform Infrared (FTIR) spectroscopy and sensitive surface-temperature measurements. Surface-temperature excursions up to 150°C are recorded while adsorbed CO oscillates by as much as 60% of total coverage. The oscillations are shown to occur only within the high-to-low steady-state transition region which shifts from the stoichiometric point toward the lean CO region as the temperature is lowered. Multiple surface-temperature measurements reveal that extreme spatial nonuniformity and propagating waves of high reaction fronts are common in the region of CO inhibition and during oscillations. It is shown that the localized hot spots occur in regions which sustain higher reaction rates while CO inhibition prevails in other regions of the catalyst. Oscillations in CO_2 production appear to be the result of fluctuating zones of high and low reaction rates, and therefore represent averages over spatially inhomogeneous surface states, rather than over spatially uniform states as has been customarily assumed.

INTRODUCTION

Numerous experimental studies have demonstrated the occurrence of self-sustained oscillations during the oxidation of carbon monoxide over supported and unsupported platinum catalysts (*1–17*). Similar behavior has been observed in a variety of other heterogeneously catalyzed oxidation reactions (H_2, NH_3, and light hydrocarbons) and extensive review papers are available (*18–21*). Although a limited number of studies have observed oscillatory states arising from system impurities (*4–6*), the majority of researchers in the field now believe that intrinsic reaction kinetic processes underlie the observed dynamic behavior.

Considerable efforts have been devoted to the mathematical modeling of oscillatory catalytic reactions and various schemes have been proposed. It has now been demonstrated that the interplay of mass transport and Langmuir–Hinshelwood kinetics does not yield oscillatory behavior (*18, 22*). Models of surface processes involving formation of subsurface oxides (*23, 24*), coverage-dependent activation energies (*25*), existence of two forms of adsorbed species (*1, 21*), interplay of mass transport between protrusions on the roughened surface of a catalytic wire (*26*), interplay of mass and heat transport with the microscopic structure of supported catalyst particles (*27*), and the possibility of catalyst surface phase transformations (*28, 29*) have been proposed. These theoretical studies have had varying success for predicting oscillations of one form or another, but none has attained a generally accepted status as a result of failure to predict the experimental results when realistic parameters are used,

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or an inability to exhibit the long periods of the oscillations usually observed in catalytic reactions.

The expanding literature on the subject of oscillations is due in part to the novelty and diversity of the phenomena. Another factor contributing to the multitude of experimental studies and proposed models, is the fact that the majority of the observations reported so far are in terms of bulk variables (concentration and temperature) instead of surface variables. Measurements in terms of bulk variables do not permit unique determination of the underlying surface processes involved, and researchers have to assume the nature of such processes to simulate the bulk behavior. Unfortunately, different surface reaction models can yield similar overall (bulk) behavior.

The scarcity of direct measurement of surface variables during self-sustained oscillations has prompted us to investigate this phenomena using the powerful transient capability of Fourier Transform Infrared Spectroscopy (FTIR). FTIR is particularly suited for transient studies on supported catalysts since it provides full high-resolution spectra faster than dispersive instruments, and high ir throughput. Computerized FTIR data acquisition and supporting software are used in this study, along with sensitive surface-temperature measurement and bulk gas measurements to simultaneously document the behavior of surface and bulk variables during self-sustained oscillations.

While many authors have reported the existence of isothermal oscillations (*4–14*), several experimental and theoretical studies of supported catalysts have provided evidence that the temperature of the metal particles is much hotter than the support (*30–38*). However, as in earlier investigations in our laboratory (*5, 13*), quasi-isothermal behavior is often observed when thermocouples with large time constants are used, and apparent isothermal behavior is reported. In Part I of this study (*32*), we reported direct measurement of catalyst temperatures differing by more than 100°C from the reactor temperature. These measurements, obtained through the use of a delicate foil thermocouple having millisecond-response time, suggest the occurrence of a complex energy transport process in the quenching region of the CO oxidation reaction. Further results presented in this work indicate a role of this mechanism in the observed oscillations which suggests an intrinsic nonuniformity and strict nonisothermality, at least for the oscillations on supported catalysts.

EXPERIMENTAL

Apparatus and Procedure

A detailed description of the experimental apparatus has been given elsewhere (*32*), consequently only a brief description is presented below along with some important modifications to the infrared-cell reactor.

The two main components of our experimental system are the FTIR spectrometer and a specially designed infrared-cell reactor. The FTIR spectrometer (Digilab FTS-15C) is equipped with a high throughput source and a liquid-nitrogen-cooled Hg–Cd–telluride detector to provide high sensitivity for transmission studies of supported catalyst samples. A Nova 3 minicomputer equipped with a 5-Mbyte hard disk enables continuous real-time data acquisition and storage of thousands of complete ir spectra during experiments lasting up to 5 h. Subsequent analysis enables the baseline-corrected peak height to be followed as a function of time for any ir-active adsorbed species and some strongly absorbing gas-phase species. The results in this work are presented in what we call a "spectragram," which represents the absorbance maximum for a particular species at a selected frequency plotted as a function of time, rather than as individual spectra.

Special features of our design are: (i) programmable flow and temperature controllers which permit concentration and temperature-programmed transient operation, (*ii*) the use of sensitive foil thermocouples which can be placed in direct contact with the catalyst surface to yield what is referred to hereafter as the "surface temperature."

Two modes of transient experimentation are used in our studies. During temperature-programmed reaction (TPR), the temperature is increased quasilinearly and then decreased likewise while keeping the reactant concentrations constant. During concentration-programmed reaction (CPR) the flow rate of carbon monoxide (CO-CPR) or oxygen (O_2-CPR) into the gas mixture was increased linearly for a 1- to 2-h period and then decreased likewise while maintaining the reactor at constant temperature. The use of TPR and CPR along with surface-temperature measurements and continuous ir collection (5000–18,000 spectra per run) permits unique dynamic observations which are independent of the noise or perturbations introduced when variables are abruptly changed (step changes). Self-sustained oscillations were obtained by first reaching regions of instability during TPR or CPR experiments. After having entered an unstable region, the programming mode was halted and all inputs were subsequently maintained at steady-state conditions.

Infrared-Cell Reactor

Results reported in Figs. 1–4 were obtained using the small volume (6 cm^3) ir reactor described in detail elsewhere (*32*). It was constructed from two Varian Conflat flanges fitted with sapphire windows and a single-surface thermocouple. The gas stream was directed to flow countercurrently in series past each side of the catalyst wafer through one inlet and one outlet port.

The results shown in Figs. 5 and 6 were obtained in a modified design of the previous version. The modified reactor has 2.5-cm CaF_2 windows held tight against Grafoil (high-purity graphite produced by Union Carbide) gaskets to form a mount to the flanges which is leak-free and capable of withstanding high temperatures. An additional improvement in the current design in that one inlet and one outlet is provided per flange so that the flow configuration along the catalyst wafer can be cocurrent or counter current. The results presented in Figs. 5 and 6 were obtained with the gases flowing parallel on each side of the wafer in a countercurrent flow. The catalyst holder, which also serves as the reactor gasket, was redesigned to promote mixing between

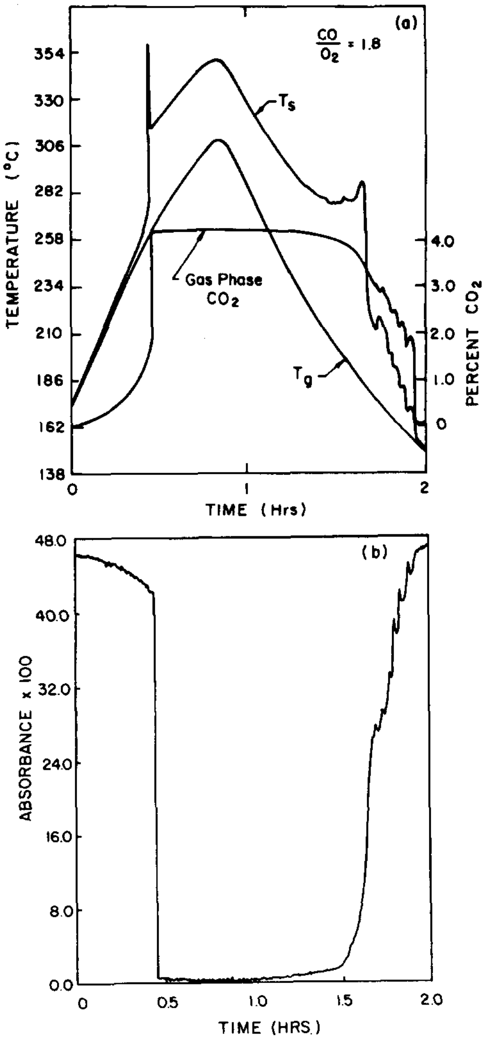

FIG. 1. TPR experiment with gas mixture of 9.0 cm^3/min CO, 5.0 cm^3/min O_2, and 160 cm^3/min N_2. (a) Programmed reactor temperature curve and response of CO_2 production and surface temperature. (b) Spectragram for linear-bonded CO.

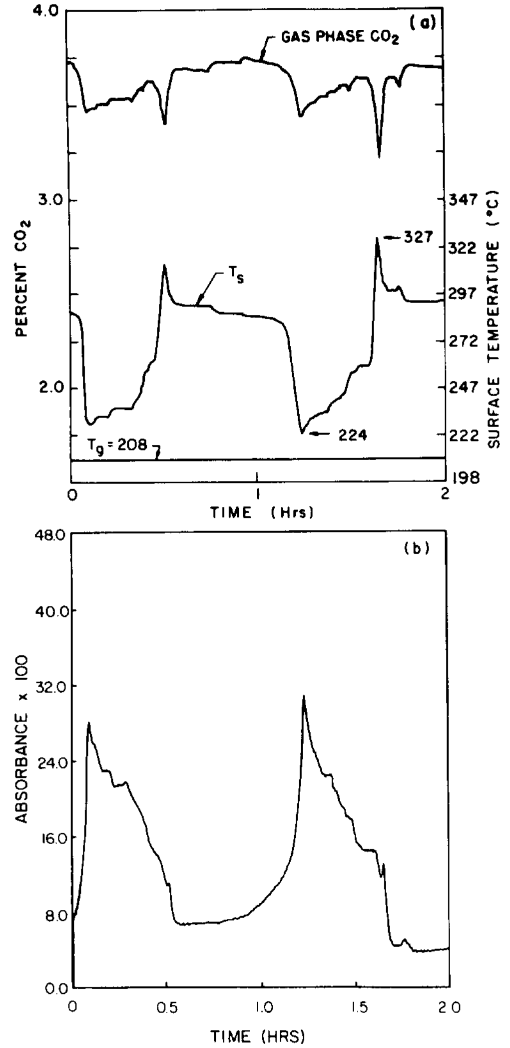

FIG. 2. Self-sustained oscillations recorded after stopping the programming at 208°C following the maximum in Fig. 1. (a) Oscillations of gas-phase CO_2 and surface temperature. (b) Spectragram of adsorbed CO oscillations.

the two sides of the reactor. The reactor flanges and catalyst holder were machined so that the mounted catalyst wafer is positioned symmetrically within the reactor volume.

Another significant improvement with respect to the previous design is the addition of feedthroughs which enable the insertion of four sensitive foil thermocouples in contact with the catalyst, a gas-phase thermocouple, and a sixth one to measure and control the reactor-wall temperature. The delicate foil thermocouples (Omega, type K) used for surface-temperature measurement have a millisecond-response time enabling direct measurement of local catalyst temperature excursions. This measurement, which we call the "surface temperature," primarily represents the temperature of the catalyst support, although some influence from localized crystallite overheating above the support temperature cannot be ruled out. This unique feature was described in detail previously (*32*) and has

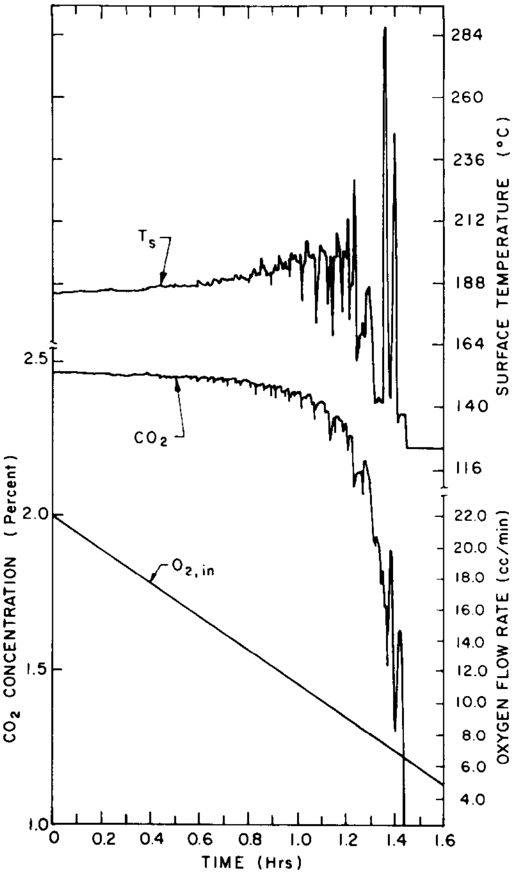

FIG. 3. O_2-CPR experiment at 126°C in which oxygen flow rate was slowly decreased from 22.0 to 5.0 cm^3/min with CO and N_2 constant at 9.5 and 200 cm^3/min, respectively. (a) Surface-temperature excursions during the transition. (b) The programmed change in oxygen flow rate and CO_2 production instabilities prior to complete quenching.

been an extremely valuable source of information concerning surface events.

The orientation of the four surface thermocouples relative to the flowing gases is demonstrated in Figs. 5c and d. The filled circles represent a contact point on the viewer's side of the catalyst, while the open circles represent contact on the backside of the wafer. The thermocouples sample four points at the corners of a 1-cm^2 region at the center of the wafer. This arrangement provides information on temperature gradients in the axial direction as well as in both directions perpendicular to flow. The surface thermocouple in the previous design was positioned near the reactor inlet at the location corresponding to $T_{s,1}$ in Fig. 5c.

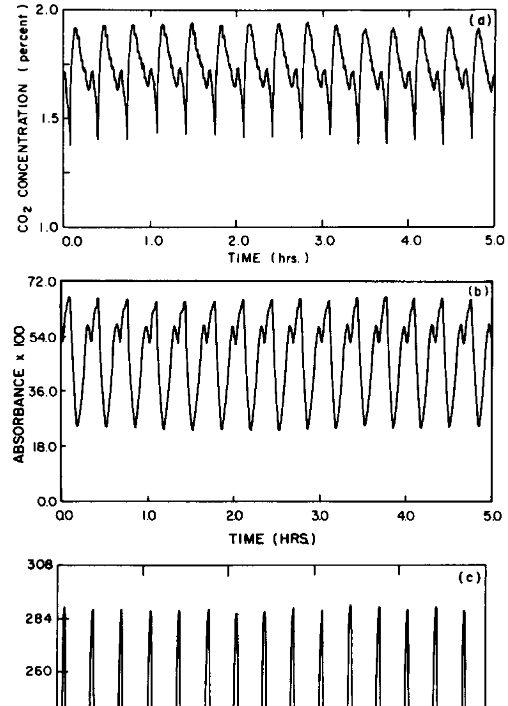

FIG. 4. Self-sustained oscillations obtained at same conditions as Fig. 3 by stopping the oxygen programming at 8 cm^3/min. (a) CO_2 production. (b) Spectragram of adsorbed CO. (c) Surface temperature.

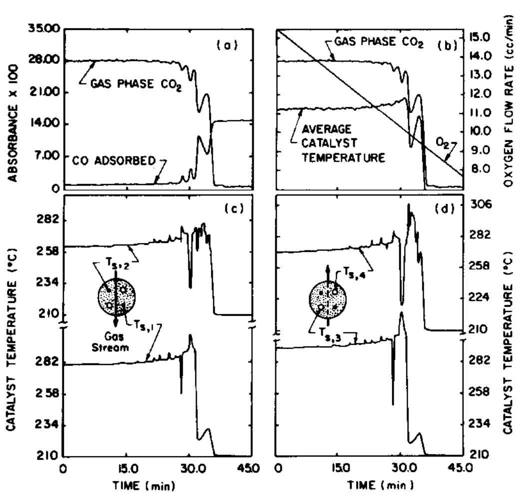

FIG. 5. O_2-CPR experiment with four surface thermocouples and diluted catalyst wafer. Constant conditions are $T = 210°C$, $N_2 = 200$ cm^3/min, and $CO_2 = 12$ cm^3/min while oxygen decreases from 15.5 to 7.5 cm^3/min. (a) Spectragrams for CO_2 and adsorbed CO. (b) Spectragrams for CO_2 and average catalyst temperature along with the programmed change in oxygen flow rate. (c) Two thermocouple responses and schematic of their positions relative to flow; ○ = thermocouple on backside from viewer. (d) Two thermocouple responses and schematic of their positions; ● = thermocouple on front side.

Catalyst Properties

The current CO oxidation studies were performed over a 5 wt% Pt/SiO_2 catalyst. The catalyst sample was prepared by incipient wetness impregnation of silica gel (Harshaw) with a solution of chloroplatinic acid of the desired composition. After drying, the catalyst was first oxidized at 300°C in a flow reactor for 6 h and then reduced for 12 h in 20% H_2/He at 200°C. Carbon monoxide chemisorption measurements indicate that the Pt dispersion is 16.9% corresponding to an average crystallite size of 68 Å. A catalyst disk, 2.0 cm in diameter

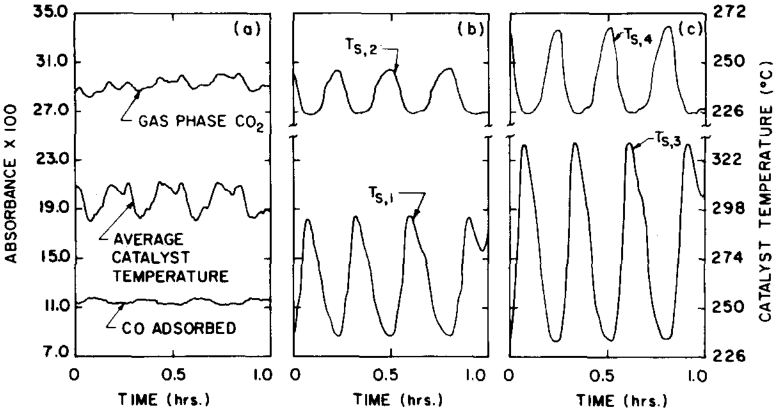

FIG. 6. Self-sustained oscillating waves with four thermocouples and a diluted wafer at constant T = 200°C, N_2 = 200 cm^3/min, CO = 27 cm^3/min, O_2 = 14 cm^3/min. (a) Spectragrams of CO_2, adsorbed CO, and average catalyst temperature. (b) and (c) Oscillatory readings of surface thermocouples numbered according to Fig. 5.

and 0.1 mm thick, was pressed from 0.03 g. of the powder under a pressure of 10,000 lb/in^2. The wafer was again reduced *in situ* in the ir reactor for 2 h at 200°C prior to each run.

RESULTS

In Part I of this work (*32*) we reported results from TPR and CO-CPR studies of CO oxidation on the same Pt/SiO_2-supported catalyst. Among the various novel results reported, it was noted that these programming techniques provided a systematic method of locating oscillatory behavior. As shown below, these oscillations occur only in a narrow window of operating conditions, thus it is not surprising that they are often not detected, thereby leading investigators to question the occurrence of this phenomena or to attribute it to extraneous factors.

Figure 1a displays results of a TPR experiment in terms of surface and gas-phase temperature, and CO_2 production (obtained from the ir analyzer), whereas Fig. 1b shows the FTIR absorbance data for the linear bonded, adsorbed CO as a function of time. The gas flow rates were held constant at 160, 9.0, and 5.0 cm^3/min, respectively for N_2, CO, and O_2. The FTIR data was obtained by coadding a preset number of scans (usually 10), storing the data as a set (about 1000 sets per run), and using a special software which displays the baseline-corrected absorbance peak height at specified frequencies (2360 ± 20 cm^{-1} for CO_2 and 2070 ± 20 cm^{-1} for CO) as a function of time, in what we refer to as a "spectragram."

The overall feature of Fig. 1 have been described in detail for similar TPR results reported previously (*32*). Relevant to this paper is the temperature reversal (overheating followed by rapid cooling) observed in the decreasing temperature branch of the TPR. Such a maximum in surface temperature appears to be a characteristic of the surfaces processes which precede the quenching of the reaction and thus may play an important role in the oscillation phenomena.

It should be noted that during TPR and CPR experiments, the slow programming rates used in our studies do not introduce artificial lags in the systems dynamic response so that the results within stable regions can map the steady-state behavior over a range of temperature or concentration. In unstable regions, the results will be representative of the nature of the unstable or oscillatory behavior that would be observed if all variables were held constant in that region.

Self-oscillatory behavior can be observed for the conditions of Fig. 1, only within the region beginning with the onset of surface-temperature reversal at 210°C and ending with quenching of the reaction at 155°C. This region is split at 185°C where the surface temperature rises to the maximum of 287°C followed by a sudden cooling to 220°C. The CO surface coverage (Fig. 1b) rises very slowly in the first part of the temperature reversal and then following the maximum, it increases rapidly to about 50% coverage while the surface temperature is in its region of rapid cooling. Up to this point the CO_2 production shows the strong inhibition effect of increasing CO coverage. Beyond the region of rapid cooling, the CO coverage, surface temperature, and CO_2 production all show evidence of oscillatory behavior for the remainder of the temperature programming until the quenched, low steady state is reached.

Different forms of self-sustained oscillatory behavior can be observed when the temperature programming is halted in the first part of the temperature reversal region (210–185°C) prior to the reversal maximum, or in the region following the rapid cooling of the surface temperature (185–155°C). The oscillations in the high-temperature region are characterized by long periods (1 h) and large changes in CO coverage and surface temperature, yet comparatively small changes in CO_2 production. Figures 2a and b show the oscillatory state obtained by stopping the programming when the reactor temperature was 210°C. The peak-to-peak amplitude changes of such oscillations are 0.5% for the CO_2 outlet concentration, about 100°C for surface temperature (Fig. 2a), and about 56% for CO coverage (Fig. 2b). In the first cycle, the surface temperature first increases, along with a slight increase in CO_2 production and a decrease in CO coverage in what appears to be a sequence of stepwise processes. Then the surface temperature spikes through a maximum along with a decreasing CO_2 production and a barely detectable reversal in surface CO followed by a rapid decrease in CO coverage. Next, surface temperature decreases slowly at first followed by rapid cooling. CO coverage steadily increases and then reaches its maximum while CO_2 production changes very little at first and then decreases to reach a minimum, which is the start of a new cycle.

If the reactor temperature was stopped between 185 and 155°C, oscillations with similar features but shorter periods and smaller amplitudes could be observed. In this case, however, surface temperature and CO_2 production were in phase but varied inversely with CO coverage.

Oxygen CPR results, displayed in Fig. 3, represent the decreasing half of a typical O_2-CPR experiment described previously (*32*). These results were obtained at a gas-phase temperature of 126°C and at N_2 and CO flow rates of 200 and 9.5 cm^3/min, respectively. In this case the high steady state was first attained by increasing the oxygen until ignition occurred at which point the oxygen was programmed to decrease from 22.0 to 5.0 cm^3/min over a 2-h period. The data shows the development of a wide range of instabilities which become more severe as the CO inhibition increases and finally quenches the reaction at a CO/O_2 ratio of 1.4.

At first the CO_2 production in Fig. 3 remains fairly constant, surface temperature begins to gradually increase and adsorbed CO is not detectable (not shown). Further decreases in oxygen partial pressure lead to steadily larger spikes and chaotic temperature excursions from which the average surface temperature can be seen at first to increase, followed by a sharp decrease, in an analogous manner to results presented previously for this type of experiment (*32*). At the onset of the surface-temperature fluctuations, adsorbed CO became detectable and exhibited similar chaotic behavior throughout the quenching region. The first observable fluctuations were in the low coverage range (<10%) and correspond to the region where the surface-temperature spikes were on the average increasing. In this region the CO_2 production shows some inhibition but does not reflect the chaos measured in the surface variables. In the region of the maximum and subsequent decrease in average surface temperature, the surface coverage fluctuations were much larger and centered around the range of 20 to 60% of the coverage maximum. These adsorbed CO excursions produce a more severe inhibition effect on the reaction, as can be seen by the greater amplitude of the CO_2 production excursions nearing the point of quenching. Indeed, the final fluctuations prior to quenching are the most extreme for all variables, most notably the surface temperature, which spikes twice to values nearly 150°C above the reactor temperature. During this surprising behavior, the CO_2 production decreased to a pronounced minimum under the influence of increasing CO coverage near 90% of the coverage maximum.

This experiment uncovered a wide range of CO/O_2 ratios (1.0–1.4) in which the reaction was unstable. As expected, a wide variety of self-sustained oscillatory behavior could be observed by repeating the experiment and stopping the programming at various oxygen concentrations. The majority of these states were conspicuously nonperiodic or chaotic in nature, while a few would converge to a stable limit cycle after an induction period of several hours. The most striking of these, shown in Fig. 4, occurred in the region of the significant temperature excursions at an oxygen flow rate of 8.0 cm^3/min with the same reactor temperature, and CO and N_2 flows as for Fig. 3.

Besides the unique display of distinctly periodic surface coverage oscillations, the data in Fig. 4 is a striking demonstration of the capabilities of computerized FTIR spectroscopy. These results were extracted from 18,000 ir spectra which were recorded sequentially, without interruption over a 5-h period (1800 sets of 10 coadded scans). These oscillations are characterized by periodic changes in CO_2 production (0.5%), surface CO (over 50%), and surface-temperature oscillations on the order of 150°C. Each cycle has a 20-min period and is characterized by two subcycles which upon close inspection reveal that whenever CO coverage increases, CO_2 production decreases, and surface temperature increases. The relationship between CO_2 production and surface coverage is clearly dominated by the inhibition effect of accumulating CO coverage. Indeed, the large decreasing spike for CO_2 in the larger subcycle emphasizes the stronger inhibition effect when CO is in the range of 90% of the coverage maximum. It is precisely during this sharp decrease in CO_2 production that the surface temperature takes off on its excursion through a 150°C maximum.

The periodicity of these oscillations and the regularity of the patterns was indeed remarkable. Clearly the oscillatory pattern shown in Fig. 4 is quite different from those presented in Fig. 2, although the role of CO inhibition is clearly manifest in each case. As noted in our previous studies (*32*), blank runs were made with silica wafers to insure that the results, in particular the surface temperature, were not artifacts of experimental techniques. From the results of these runs we concluded that neither the stainless-steel reactor, the aluminum sample holder, nor the Chromel–alumel surface thermocouple were making any detectable contributions to catalytic activity. Runs carried out in the absence of the ir beam showed no difference in the oscillatory behavior indicating that it was not affected by the ir radiation. Furthermore, recent results obtained during the writing of this paper on a 2% Pd/SiO_2 catalyst also show the existence of a temperature reversal and oscillatory behavior. These experiments prove that our results are not affected by extraneous factors but rather uncover a characteristic behavior of relevance to CO oxidation on various supported noble metal catalysts.

The inordinate temperature excursions in Fig. 4 occurred precisely as the CO production was passing through a sharp minimum. This behavior is completely the reverse of what would be expected, and led us to explore the possibility of a localized behavior which was different from the bulk. In Part I of this work (*32*), we showed that the weak ir bands detected between 1800 and 2000 cm^{-1} were directly related to the surface temperature. Such bands always increased with increases in CO_2 production along the high steady state, in agreement with the surface thermocouple measurements, thus proving that the temperature was not localized to the site where the thermocouple was placed. However, analysis of these bands for the oscillations in Figs. 2 and 4 indicate a discrepancy with the thermocouple readings. The square wave pattern of the surface temperature in Fig. 2 was reflected in the ir bands, but not the high-temperature excursions. For the results in Fig. 4 however, the temperature-sensitive ir band mimicked perfectly the changes in CO_2 production, indicating that the average temperature of the catalyst was decreasing as the surface thermocouple recorded what must be viewed as a localized increase of about 150°C.

To verify whether or not such extreme nonuniformity could exist along such a small catalyst wafer, the modified version of the ir-cell reactor was constructed. The data in Figs. 5 and 6 were obtained using a countercurrent gas flow scheme and by recording readings from four surface thermocouples contacting the catalyst wafer in a square pattern as shown in Figs. 5c and d. Using the CaF_2 windows, an additional, highly temperature-sensitive band centered around 1310 cm^{-1} could be followed to yield a qualitative indication of the average catalyst temperature.

The results in Figs. 5 and 6 were carried out under site-limiting conditions, as opposed to the reactant-limiting situation present in our previous runs. This was undertaken to determine if the availability of excess sites was making the spatial nonuniformity possible, and to see if the form of the oscillations were different under site-limiting conditions. The conditions for site-limiting kinetics were obtained by pressing wafers with different dilutions of inert silica until the conversion during a benchmark CO-CPR run was noticeably diminished. Such conditions were found when a mixture of 90% silica and 10% of the original catalyst was used. The effective loading of these wafers was thus 0.5 wt% Pt/SiO_2.

Figure 5 shows the results of an O_2-CPR run performed in the same manner as in Fig. 3, but at 210°C, 200 cm^3/min N_2, 12.0 cm^3/min CO, and oxygen programmed to decrease from 15.5 to 7.5 cm^3/min over a 45-min period. Shown in Figs. 5a and b are the *in situ* ir spectragrams for CO_2 (2360 ± 20 cm^{-1}), adsorbed CO (2070 ± 20 cm^{-1}) and average surface temperature (1310 ± 10 cm^{-1}). The programmed oxygen flow rate is also shown in Fig. 5b. Figures 5c and d show the response from the four surface thermocouples and a schematic showing their positions.

The CO_2 production and surface CO vary according to an inverse relationship in Fig. 5a, as is characteristic of the inhibition region. The surface thermocouple measurements show qualitatively similar regions as observed for Fig. 3. Initially, the catalyst temperature is increasing through a region marked by chaotic fluctuations, followed by a sharp decrease leading to quenching. The individual surface-temperature measurements however, deviate significantly from each other, indicating the occurrence of spatially distributed reaction rates in the inhibition region. The communication is apparently good in the direction perpendicular to flow, but there is considerable nonuniformity in the axial direction. Most noteworthy is the sharp decrease in local temperatures on one end which is mirrored by overshoots in temperature at the other end. This indicates that communication by mass and energy transfer is rapid, but localized hot spots can be sustained for time periods much longer than the time constants for mass and energy transfer. The average catalyst temperature (Fig. 5b) indicated by the ir band at 1310 cm^{-1} reflects more clearly the changes in CO_2 production, although a close inspection reveals that this average is steadily increasing in the first portion of the inhibition region where CO_2 begins to decrease and become unstable.

A clear indication of surface nonuniformity can be seen in Fig. 6. These oscillations were found at 200°C, with 200 cm^3/min N_2, 27 cm^3/min CO, and 14 cm^3/min O_2. The ir spectragrams for CO_2, adsorbed CO, and average catalyst temperature (Fig. 6a) are shown along with the four local-temperature measurements (Figs. 6b and c). The ir measurements are in agreement with the expected trends, showing average catalyst temperature and inverse CO coverage oscillations directly in phase with CO_2. However, the 15-min period of these oscillations reflects what appears to be a propagating nonuniform temperature wave in which low temperatures prevail at one end of the wafer while the opposite end axially is experiencing up to 100°C higher temperatures and vice versa. The four thermocouples provide information on this wave behavior since $T_{s,1}$ and $T_{s,3}$ are near one end of the wafer while $T_{s,2}$ and $T_{s,4}$ are near the opposite end in the axial direction. These results demonstrate that localized hot spots can indeed occur even under site-limited conditions, and lead us to believe that the inordinate temperature excursions in Figs. 2 and 4 are the results of similar localized events which also occur under reactant-limiting conditions.

The exact nature of the surface temperature wave cannot be determined from the temperature measurements alone. It may be a standing wave, an axially traveling wave moving backwards and forwards, or a wave always traveling in the same direction and restarting at the same edge. We have observed on at least 10 different wafers of both Pt/SiO_2 and Pd/SiO_2, that the inhomogeneities always travel in the axial direction even if the wafer is rotated 90° and the experiment repeated. This demonstrates that the wave direction is related to the direction of flow rather than some inhomogeneity in the wafer itself.

DISCUSSION

The major findings of this study can be summarized as follows:

1. Unstable and oscillatory behavior is observed when the system is within the high-to-low steady-state transition region where quenching begins to occur due to CO inhibition and competitive adsorption between CO and O_2.

2. The onset of oscillatory behavior shifts along with the onset of CO inhibition from near the stoichiometric ratio above 250°C, into the CO lean region and progressively toward lower CO/O_2 ratios for temperatures below 250°C.

3. A region of CO inhibition and oscillatory behavior can be systematically and reproducibly located by using transient reaction programming techniques. Starting at the high steady state, such regions can be found by using one of the following programming methods: (i) a *decrease* in the reactor temperature; (ii) a *decrease* in the O_2 partial pressure; (iii) an *increase* in the CO partial pressure.

4. Multiple surface-temperature measurements during the oscillations reveal the existence of local-temperature excursions which are vastly different and out of phase with the average temperature and CO_2 production measurements.

5. Simultaneous, *in situ* FTIR measurement of CO_2 production and surface CO during self-sustained oscillations demonstrate that the two are related through an inverse correlation. However, each of these measurements represents an integral or average of the localized values which may be vastly different from point to point in the wafer as suggested by the surface-temperature measurements.

6. When the system is at either the high

or low steady state, the surface temperature, CO coverage, and CO_2 production appear to be spatially uniform throughout the catalyst wafer, whereas nonuniformity apparently prevails in the transition region.

The above results reveal that the oscillatory behavior in this system is characterized by two distinct conditions: (i) the onset of inhibition and (ii) the transition from spatially uniform reaction to a nonuniform, spatially distributed state in which localized hot spots of high reaction rate coexist with other regions of the catalyst that are locally much cooler because the reaction is inhibited by high CO coverage.

With the latest improvements in our ir-cell reactor, we have verified that spatial nonuniformity occurs along with inhibition whenever the reaction is programmed through the transition region. With the onset of inhibition, the spatial nonuniformity evidently arises because inhibition nucleates in one region of the catalyst while a hot spot is nucleating in another region (Fig. 5). It thus appears that the onset of a localized inhibition leaves more reactant available to be reacted in other portions of the catalyst to form a hot spot. This would explain why two of the thermocouples in Fig. 5 are much cooler while the other two are much hotter than the uniform average temperature that prevailed before entering the inhibition region.

The oscillations in Fig. 6 not only demonstrate the nonuniform spatial temperature distribution, but also demonstrate that the localized events can be dynamic and propagate throughout the wafer as a traveling wave. Apparently, this phenomena is similar to the traveling waves observed for CO oxidation in a fixed-bed reactor (*14*) and are related to the length of the bed and the axial geometry and flow pattern of the reactant gases.

Thus the ultimate pattern of the oscillations depends on the capacity of the system of individual oscillators (crystallites) to communicate with their immediate environment. This communication is apparently strongly linked to the geometry of the system through the patterns of gas flow and the mass and thermal transport rates that prevail within the catalyst pellet.

Clearly communication among regions at high steady state and regions of high CO coverage is not limited by diffusional transport of heat or mass since the time constant of these processes is far shorter (<5 sec) than the periods of the oscillations reported here (15 min to 1 h).

While the high degree of nonuniformity alone may account for the structure of certain oscillatory patterns, other factors must also be contributing to the ability of certain regions to sustain hot spots, as well as providing a hot spot with the ability to propagate along the catalyst pellet. One such factor could be the occurrence of coverage-induced and temperature-dependent surface phase transformations which have been observed for certain platinum crystal surfaces (*39–44*). The Pt(110) transformation has been found to occur below 25°C (*40, 41*), while the Pt(100) transition occurs in the range 180 to 250°C (*12*) depending on the coverage. Indeed the phase boundary between the two Pt(100) phases was shown to be a function of both CO concentration and temperature according to an Arrhenius dependence (*12*). The most recent results on this Pt surface (*17*) demonstrate that the phase transition indeed occurs during oscillations along with significant fluctuations in the local CO coverage. However, the exact picture in terms of differences in sticking coefficients and adsorption energies for CO and O_2 on the two surface phases is still incomplete. Some notable similarities between our own study and the UHV studies (*12, 17, 44*) include the inhibition behavior in which high CO coverage leads to the decreasing rate portion of the cycle while a drop in the CO coverage leads to the increasing rate. Also, the existence of spatial nonuniformity seems to occur even on the single crystals during the oscillations as evidenced by the apparent nucleation of isolated patches of the new phase as the transition occurs (*17, 44*). The LEED results during oscillations (*17*) indicate that spatial uniformity does not always exist over distances of the order of the 1-mm^2 area that the LEED beam samples.

The role of slow oxidation and reduction of a subsurface oxide (*23, 24*) does not seem to be responsible for the long periods of the oscillations in light of the severe spatial nonuniformity of the oscillating system. However, a slow modification of the surface does seem to occur over a 12- to 24-h induction period in which the initial system behavior upon entering the inhibition region is gradually modified. Initial instabilities most often appear as long transients or chaotic instabilities which over a time period of several hours develop into larger and more periodic oscillations which may become self-sustained or lead to quenching of the reaction. The time frame of this effect is more in line with the time constants resulting from measurement of the rate of oxidation of a platinum surface (*23*).

An additional factor which needs further investigation is the mechanism of energy dissipation in supported catalysts. Several theoretical studies have in the past, focused on the temperature rise of supported crystallites (*33–38*). The work of Steinbruchel and Schmidt (*37*) demonstrates that the mode of energy release, the size of the crystallites, and the thermal boundary resistance at the crystallite support interface are all important in determining temperatures. They predicted 150 to 300°C increases in crystallite temperature for a typical exothermic reaction using conservatively estimated parameters. Since the support temperature was assumed to be constant in these calculations, similar predictions for our system should be even higher since our observations of up to 150°C temperature excursions (Fig. 4) primarily represent the support temperature.

The mechanism of energy dissipation in the surface reaction itself is another area that could benefit from more theoretical and experimental work. Steinbruchel and Schmidt (*37*) point out that the products of exothermic surface reactions are most likely formed in excited states. However, the possibility that the product molecule desorbs from the surface without complete thermal accommodation was not considered. The assumption that the adsorbed reaction product releases its energy to the surface in several vibrational periods (10^{-12} sec) may not apply when the nascent product molecule is not trapped in an intermediate adsorbed state as is apparently true for CO_2 on platinum surfaces (*45*). Recently several studies have reported on the formation of hot CO_2 molecules on Pt single crystals and polycrystalline Pt foils in which excess energy was detected in the translational (*45–51*) as well as the vibrational and rotational modes (*52, 53*) of the desorbing CO_2 molecules.

In a previous publication (*32*) we described how such excited CO_2 molecules might contribute to the inordinate temperature excursions along with thermal nonuniformities by providing energy removal through deexcitation by radiation or collisions with other gas molecules. It now appears that the thermal nonuniformities are more severe than we at first thought and that the temperature reversals measured by the single thermocouple previously reported were partly due to localized inhibition on other parts of the catalyst. However, Fig. 5 demonstrates that the overheating can be observed at all four thermocouples at the onset of inhibition. Indeed, a gradual increase in the average catalyst temperature is observed before the uniformity of the reaction breaks down, suggesting that such an energy transfer process may have a role in nucleating a hot spot. While any role of excited states in our results is clearly unproven at this point, the occurrence of excited states is widespread in homogeneous oxidation reactions of hydrocarbon systems and has been well known for many years (*54*). These systems exhibit a wide variety of chemiluminescence in the ir, uv, and visible regions due to radiative deexcitation from excited states of nascent oxidation products. Indeed the chemiluminescence is widespread only in oxidation reactions much as is the case for oscillations in heterogeneous systems. The effects of high heat of reaction and energy removal are evidently common elements which make the homogeneous and heterogeneous oxidation reactions unique from other reacting systems that do not exhibit these types of behavior.

We have presented a variety of phenomena which may contribute to the self-sustaining nature of the oscillations reported here. It seems clear that future modeling efforts must take into account the spatially nonuniform regions which arise during oscillatory states as has recently been considered in the literature (*55, 56*). In addition rate expressions with lumped parameters will be inadequate to account for competitive adsorption and inhibition effects which vary spatially within the catalyst. Although the Langmuir–Hinshelwood mechanism has been convincingly shown to prevail for this system (*47, 49*), the assumption of a rate-limiting step may not be justified for any modeling attempt since the surface reaction may not be rate limiting for CO oxidation below 300°C, as is often assumed. Campbell *et al.* (*47*) have observed that the rate of CO_2 production on an oxygen-covered surface is limited by the adsorption rate for CO. As has been pointed out by Herz and Marin (*57*), CO adsorption-limited kinetics can fit the data very well at these temperatures. In fact our TPR and CPR results reported previously (*32*) and in Figs. 1 and 5 support that CO adsorption is indeed the rate-limiting step at the high steady state. This is evident since increasing the temperature above the value required for ignition during TPR does not affect the rate as would be expected if activation of the surface reaction step were rate limiting. Similarly, increasing the oxygen partial pressure above the value required for ignition does not lead to any increase in rate as would be expected if the oxygen adsorption were rate limiting. However, under all conditions on the high steady-state branch, increases in CO partial pressure produced a proportional increase in CO_2 production until the inhibition region was encountered. If CO adsorption is indeed the rate-limiting step at high steady state, then it is apparent that the rate-limiting step changes at the onset of CO inhibition since CO begins to accumulate. If we next consider the inhibited, low steady state, it is obvious that the surface supply of oxygen is rate limiting due to low availability of vacant sites for the dissociative oxygen chemisorption process. The occurrence of hot spots of locally high reaction rates seems to imply that the surface reaction rate is still not rate limiting during the conditions of inhibition and oscillation. Thus we can conclude that at the onset of inhibition the rate-limiting step shifts from being adsorption of CO to adsorption of oxygen which is hindered by accumulating CO.

This work presents several new and definitive results concerning oscillatory states during CO oxidation on Pt/SiO_2. A systematic method for finding such states via temperature and concentration programming shows that they occur in the transition region between high and low steady states. Surface oscillations in both coverage and temperatures are clearly observed. The spatially average nature of the ir measurements is shown in contrast with the localized nature of temperature excursions, a point not experimentally demonstrated before. We anticipate that the temperature fluctuations are related to similar wavelike inhomogeneities in CO coverage. In order to elucidate the true nature of the inhomogeneities, a new series of experiments are underway in which selected area FTIR measurements will be used to determine if the temperature waves can be correlated with similar wavelike behavior in CO coverage.

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REFERENCES

1. Hugo, P., and Jakubith, M., *Chem.-Ing.-Tech.* **44,** 383 (1972).
2. Beusch, H., Fiegith, P., and Wicke, E., *Chem.-Ing.-Tech.* **44,** 445 (1972).
3. Dauchot, J. P., and Van Cakenberghe, J., *Nature Phys. Sci.* **246,** 61 (1973).
4. McCarthy, E., Zahradnik, J., Kuczynski, G., and Carberry, J. J., *J. Catal.* **39,** 29 (1975).
5. Varghese, P., Carberry, J. J., and Wolf, E. E., *J. Catal.* **55,** 76 (1978).
6. Cutlip, M. B., and Kenney, C. N., *Proc. 5th Int. Symp. Chem. Reaction Eng., Houston, ACS Symp. Ser.* **65,** 475 (1978).
7. Plichta, R., and Schmitz, R. A., *Chem. Eng. Commun.* **3,** 387 (1979).
8. Keil, W., and Wicke, E., *Ber. Bunsenges. Phys. Chem.* **84,** 377 (1980).
9. Wicke, E., Kummann, P., Keil, W., and Schiefler, J., *Ber. Bunsenges. Phys. Chem.* **84,** 315 (1980).
10. Sheintuch, M., *AIChE J.* **27**(1), 20 (1981).
11. Turner, J., Sales, B., and Maple, M., *Surf. Sci.* **103,** 54 (1981).
12. Ertl, G., Norton, P., and Rustig, J., *Phys. Rev. Lett.* **49**(2), 177 (1982).
13. Liao, P., and Wolf, E. E., *Chem. Eng. Commun.* **13,** 315 (1982).
14. Rathousky, J., and Hlavacek, V., *J. Catal.* **75,** 122 (1982).
15. Elhaderi, A., and Tsotsis, T. T., *ACS Symp. Ser.* **196,** 77 (1982).
16. Schmitz, R. A., D'Netto, G. A., Razon, L. F., and Brown, J. R., "Proceedings, NATO Workshop on Chemical Instabilities." Austin, Texas, March 14–18, 1983.
17. Cox, M. P., Ertl, G., Imbihl, R., and Rustig, J., *Surf. Sci.* **134,** L517 (1983).
18. Sheintuch, M., and Schmitz, R. A., *Catal. Rev.-Sci. Eng.* **15**(1), 107 (1977).
19. Slinko, M., and Slinko, M., *Catal. Rev.-Sci. Eng.* **17**(1), 119 (1978).
20. Hlavacek, V., and Vortruba, J., "Advances in Catalysis," Vol. 27, p. 59. Academic Press, New York, 1978.
21. Eigenberger, G., *Chem.-Ing.-Tech.* **50**(12), 924 (1981).
22. Lagos, R. E., Sales, B. C., and Suhl, H., *Surf. Sci.* **82,** 525 (1979).
23. Vayenas, C. G., Lee, B., and Michaels, J., *J. Catal.* **66,** 36 (1980).
24. Sales, B. C., Turner, J. E., and Maple, M. B., *Surf. Sci.* **114,** 381 (1982).
25. Pikios, C. A., and Luss, D., *Chem. Eng. Sci.* **32,** 191 (1977).
26. Jensen, K. F., and Ray, W. H., *Chem. Eng. Sci.* **35,** 2439 (1980).
27. Jensen, K. F., and Ray, W. H., *Chem. Eng. Sci.* **37,** 1387 (1982).
28. Berman, A. D., and Krylov, O. V., *Int. Chem. Eng.* **20**(2), 313 (1980).
29. Reikert, L., *Ber. Bunsenges. Phys. Chem.* **85,** 297 (1981).
30. Cusumano, J. A., and Low, M. J., *J. Catal.* **17,** 98 (1970).
31. Kember, D. R., and Sheppard, N., *J. Chem. Soc., Faraday Trans. 2* **77,** 1321 (1981).
32. Kaul, D. J., and Wolf, E. E., *J. Catal.* **89,** 348 (1984).
33. Luss, D., and Amundson, N. R., *AIChE J.* **15,** 194 (1969).
34. Luss, D., *J. Chem. Eng.* **1,** 311 (1970).
35. Chan, S. H., Low, M. J., and Mueller, W. K., *AIChE J.* **17,** 1499 (1971).
36. Ruckenstein, E., and Petty, C. A., *Chem. Eng. Sci.* **27,** 937 (1972).
37. Steinbruchel, C., and Schmidt, L. D., *Surf. Sci.* **40,** 693 (1973).
38. Dagonnier, R., and Nuyts, J., *J. Chem. Phys.* **65,** 2061 (1976).
39. Salmeron, M., and Somorjai, G. A., *Surf. Sci.* **91,** 373 (1980).
40. Ferrer, S., and Bonzel, H. Pl, *Surf. Sci.* **119,** 234 (1982).
41. Jackman, T. E., Davies, J. A., Jackson, D. P., Unertl, W. N., and Norton, P. R., *Surf. Sci.* **120,** 389 (1982).
42. Lang, B., Joyner, R. W., and Somorjai, G. A., *Surf. Sci.* **30,** 454 (1972).
43. Comsa, G., Mechtersheimer, G., and Polesema, B., *Surf. Sci.* **119,** 159 (1982).
44. Thiel, P. A., Behm, R. J., Norton, P. R., and Ertl, G., *Surf. Sci.* **121,** L553 (1982).
45. Engle, T., and Ertl, G., *in* "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (D. A. King, Ed.), Vol. 4, pp. 73–93. Elsevier, New York, 1982.
46. Becker, C. A., Cowin, J. P., Wharton, L., and Averbach, P. I., *J. Chem. Phys.* **67,** 3394 (1977).
47. Campbell, C. T., Ertl, G., Kuipers, H., and Segner, J., *J. Chem. Phys.* **73,** 5862 (1980).
48. Campbell, C. T., Ertl, G., Kuipers, H., and Segner, J., *Surf. Sci.* **107,** 207 (1981).
49. Barteau, M. A., Ko, E. I., and Madix, R. J., *Surf. Sci.* **104,** 161 (1981).
50. Matsushima, T., *Surf. Sci.* **127,** 403 (1983).
51. Segner, J., Campbell, C. T., Doyden, G., and Ertl, G., *Surf. Sci.* **138,** 505 (1984).

52. Mantell, D. A., Ryali, S. B., Halpern, B. L., Haller, G. L., and Fenn, J. B., *Chem. Phys. Lett.* **81,** 185 (1981).
53. Bernasek, S. L., and Leone, S. R., *Chem. Phys. Lett.* **84,** 401 (1981).
54. Shlyapintokh, V., Karpukhin, O., Postnikov, L., Tsepalov, V., Vichutinskii, A., and Zakharov, I., "Chemiluminescence Techniques in Chemical Reactions." Plenum, New York, 1968.
55. Sheintuch, M., and Pismen, L. M., *Chem. Eng. Sci.* **36,** 489 (1981).
56. Jensen, K., *Chem. Eng. Sci.* **38,** 855 (1983).
57. Herz, R. K., and Marin, S. P., *J. Catal.* **65,** 281 (1980).