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Coupled Catalytic Oscillators: CO Oxidation over Polycrystalline Pt

PATRICIA K. TSAI,* M. BRIAN MAPLE,* AND RICHARD K. HERZ†

**Department of Physics and Institute for Pure and Applied Physical Sciences, and †Department of AMES/Chemical Engineering, University of California, La Jolla, California 92093*

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We have observed unusual oscillations in the rate of CO oxidation over a polycrystalline Pt wire loop. In contrast to simple oscillations between states of low and high reactivity, the unusual oscillations occurred between low, intermediate, and high values of the reaction rate. Experiments were performed at atmospheric pressure in a gas flow reactor over a range of gas temperatures and CO partial pressures. The reaction rate was measured using a thermocouple spotwelded to the loop. For a given CO partial pressure, oscillations occurred over a range of gas temperatures. Oscillations were simple at high gas temperatures and became complex as the temperature was lowered. When we monitored two thermocouples on opposite sides of the loop, we found that oscillations on the two sides occurred in phase, but differed in details of shape and amplitude. When we cut the loop and separated the halves, the complex oscillations at lower gas temperatures disappeared, and oscillations on the half-loops occurred with different frequencies. Results obtained by varying the separation showed that coupling between the half-loops occurred primarily through the gas phase. When the loop was spotwelded back together, oscillations became resynchronized, and complex waveforms reappeared at lower gas temperatures. To our knowledge, this is the first experimental demonstration that coupling chemical oscillators can increase the parameter space over which oscillatory instabilities occur. © 1988 Academic Press, Inc.

INTRODUCTION

Coupling in nonlinear systems can result in a wide range of complex phenomena. In a spatially uniform system that is well-mixed and has constant input, coupling between processes can lead to oscillations in the state of the system. Several models in which reactants and products are coupled between elementary reaction steps describe oscillations in the rate of the Belousov–Zhabotinsky reaction in a continuously stirred tank reactor (CSTR) (*1–7*). In a study of a first-order exothermic reaction in a CSTR, Uppal *et al.* (*8*) showed that coupling between heat generation, heat transfer, and an activated rate constant can lead to stable limit cycles in conversion and temperature, and a variety of other types of dynamic behavior.

In systems that are initially uniform, coupling can cause spatial nonuniformities to develop. Complex spatiotemporal patterns develop in an unstirred solution of Belousov–Zhabotinsky reactants (*9*). In gas–solid reactions, spatial nonuniformity can develop on solid surfaces even when the surfaces have uniform properties. For example, recent experimental (*10–12*) and theoretical (*13, 14*) studies have shown that coadsorbed reactants can form "patches" or "islands" on smooth single crystal surfaces. Cox *et al.* (*15, 16*) observed the propagation of surface phase transitions on a Pt(100) crystal during oscillatory CO oxidation as a result of coupling between reactant adsorption and Pt surface structure. Ladas *et al.* (*17, 18*) found that an initially smooth Pt(110) surface can develop facets during CO oxidation as a result of similar coupling. In fact, increasing evidence suggests that the development of spatial nonuniformity in initially uniform systems may be a common occurrence rather than a special case.

In a system of coupled reacting units, spatial nonuniformity can develop even when the units are characterized by identi-

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cal properties. For example, the development of spatial structures as a result of statistical fluctuations in a ring of diffusively coupled biological cells has been proposed as a model for morphogenesis (*19*). In a model of a single reaction taking place over identical catalytic particles initially in the same state, Schmitz and Tsotsis (*20*) and Tsotsis (*21*) found that stable spatial variations in reaction rate appeared when the particles were diffusively and thermally coupled in linear and cyclic arrays.

When identical oscillators are coupled, spatially inhomogeneous oscillatory states, in which different oscillators have different limit cycles, can result. For example, Tyson and Kauffman (*22*) modeled the diffusive coupling of two identically oscillating Brusselators and found that the Brusselators can assume stable limit cycles that are different from each other and from the limit cycles that occur when they are decoupled. Raschman *et al.* (*23*) also found inhomogeneous oscillatory states when they coupled up to six Brusselators in series in linear and cyclic arrays. They found variations in the amplitudes and phases of the oscillations in the Brusselators and studied the symmetry of the solutions.

In contrast, Bar-Eli predicted (*24*) and confirmed experimentally (*25*) that coupling two oscillating CSTRs can lead to the cessation of oscillations under some coupling conditions.

Real systems in heterogeneous catalysis are inherently nonuniform in the sense that properties such as catalytic activity vary with position on local and system-wide scales. Coupling between nonidentical sections of a catalytic surface or between catalytic particles with differing properties can lead to interesting effects on the steady-state and dynamic properties of the systems. Chang (*26*) developed a domain model of catalytic surfaces to account for interior hysteresis loops found by some observers in the oxidation of ammonia (*27, 28*) and of CO (*29*) over Pt. Schmitz and co-workers (*30, 31*) studied the oxidation of hydrogen on Pt pellets that individually exhibited hysteresis between two stable steady states. When two or three pellets were strung together on a wire, the system conversion exhibited a complex bifurcation diagram with many stable steady states. They also used infrared thermography (*30, 32, 33*) to produce two-dimensional maps of the surface temperature of Pt foils, gauzes, and supported wafers and pellets during the oxidation of hydrogen. Spatial variations in temperature appeared even under conditions of steady-state catalytic activity. During oscillations on the foils, gauzes, and wafers, temperature gradients propagated across the catalyst surfaces.

Thus, in some cases (*24, 25*), coupling two oscillating units can stabilize the system, leading to the cessation of oscillations. In other instances, coupling destabilizes the system, resulting in the variety of complex phenomena discussed above. For CO oxidation over supported Pt, Sant and Wolf (*34*) maintain that the system will oscillate only when there is significant coupling between the individual Pt particles. In the present work involving CO oxidation over polycrystalline Pt, we have also found that coupling destabilizes our system.

In our experiments, we have studied the coupling and decoupling of oscillations on two sections of a Pt wire during CO oxidation over a wide range of gas temperatures and gas compositions. Our results demonstrate that coupling extends the temperature range over which oscillations occur by introducing complex oscillations, with more than one peak per cycle, at low temperatures.

To our knowledge, these are the first experiments to demonstrate that coupling two oscillating components can extend the range of parameters over which the system oscillates. One implication of this work is that coupling may lead to a reduction in the ignition temperature of a catalytic reactor through the introduction of oscillatory instabilities at low temperatures.

METHODS

The apparatus was a gas flow reactor which was operated at atmospheric pressure. The gases used were carbon monoxide (purity, 99.99%), oxygen (99.99%), and helium (99.999%). The CO gas was passed through an alumina trap which was heated above 300°C in order to decompose iron carbonyls; the O_2 and He gases were used without further purification. Gas flow rates were controlled by mass flow controllers. All components downstream from the gas manifold were bakeable, and copper gaskets were used on all sealing surfaces in this portion of the system. The reactor consisted of a quartz tube, which had an inner diameter of 22 mm, sealed at both ends to stainless-steel bellows, which were in turn welded to knife-edge vacuum flanges. Commercial furnace elements surrounded the quartz tube, and a thermocouple, connected to a programmable oven controller, was embedded in the coils. A turbomolecular pump or a cold-trapped mechanical pump was employed during bakeout before experiments were begun. During experiments, the total gas flow rate was 100 cm^3/min, corresponding to a linear flow velocity of 0.4 cm/sec. The O_2 flow rate was held constant at one-half the total flow rate, so that the oxygen partial pressure P_{O_2} was 0.5 atm. The gas composition was changed by varying the CO partial pressure P_{CO} up to 0.02 atm. Helium composed the remainder of the gas stream.

The catalyst was a polycrystalline Pt wire (purity, 99.99%) with a length of 2.5 cm and a diameter of 0.05 cm. The ends of the wire were spotwelded together to form a loop. The loop, which had been used in previous oscillatory experiments, was etched for approximately 20 min in hot aqua regia before use in this work. Chromel–Alumel thermocouple wires, which had a diameter of 0.013 cm, were guided down the reactor tube with a quartz boat. Two thermocouples were spotwelded at symmetrical locations on the loop, opposite each other and 90° from the spotweld that formed the loop. The catalyst was located at the center of the reactor tube, and the plane of the loop was held normal to the gas flow. The temperatures measured by the two catalyst thermocouples are designated T_r and T_l, where the subscripts signify the right and left sides. A third thermocouple situated upstream from the catalyst measured the gas temperature, T_g. The thermocouple readings were recorded on a continuous strip-chart plotter and by an HP-85 computer. Because CO oxidation is exothermic, the increase in catalyst temperature over the gas temperature could be used to measure the reaction rate in the vicinity of either thermocouple; for example, on the right side of the loop, the reaction rate was proportional to $T_r - T_g = \Delta T_r$. For a given CO partial pressure used in this experiment, the measured increases in catalyst temperature were smaller than the range of gas temperatures over which oscillations occurred for that value of P_{CO}.

RESULTS

Characterization of Oscillations on the Original Loop

In addition to simple oscillations that occurred as transitions between states of low and high reactivity, many oscillations observed in these experiments occurred between a low state and intermediate values of the reaction rate. In initial experiments, we monitored catalyst activity with the thermocouple on the right side of the loop. Examples of waveforms are given in Fig. 1. In Fig. 1A, recorded under the conditions P_{CO} = 0.005 atm and T_g = 264°C, the reaction rate oscillated between low, intermediate, and high values. The waveform has two square wave components that do not have a fixed phase relationship with each other. This waveform is representative of the first complex oscillations that we observed between multiple values of the reaction rate.

A few days after the results in Fig. 1A

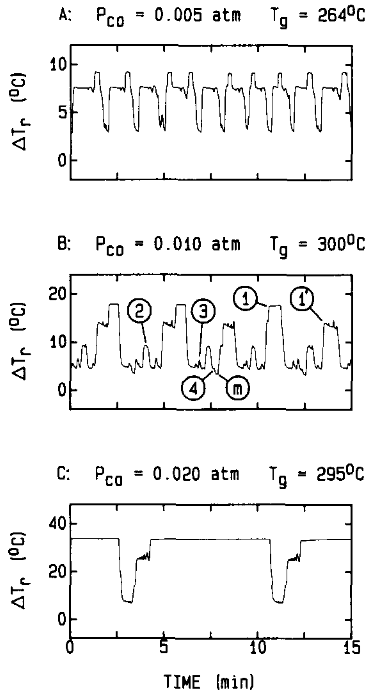


FIG. 1. Examples of waveforms observed during oscillations in the rate of CO oxidation over the original Pt loop for varying gas temperatures T_g and CO partial pressures P_{CO}. The oxygen partial pressure was P_{O_2} = 0.5 atm. The vertical scale gives the temperature difference between the Pt catalyst and the gas. This temperature difference is proportional to the rate of the exothermic reaction. (Original loop)

were obtained, the shape of the waveforms changed as a result of unknown changes in the Pt surface. The example in Fig. 1B, which was recorded for P_{CO} = 0.010 atm and T_g = 300°C, contains several types of peaks and is typical of the complex oscillations reported in the rest of this section and the next. In Fig. 1B, transitions occurred between six local extrema, marked 1, 1′, 2, 3, 4, and *m* in order of decreasing reaction rate. The rate values marked 1, 1′, 2, 3, and 4 indicate the amplitudes of five distinct types of oscillations. The largest oscillations, types 1 and 1′, are square waves. Oscillations of types 2 and 3 are more sinusoidal. Oscillations of type 4 are small fluctuations in reaction rate between the local minimum in most oscillations of types 1, 1′, 2, and 3, and the absolute minimum, marked *m*, attained under these reaction conditions. Some peaks appear to be superpositions of two types of oscillations. In Fig. 1C, oscillations for P_{CO} = 0.020 atm and T_g = 295°C are shown.

In order to characterize oscillatory behavior as a function of gas temperature, local extrema in the reaction rates were measured as T_g was varied slowly for a fixed CO partial pressure. Data obtained as T_g was decreased at the rate of 20°C/hr are plotted as a function of T_g in Fig. 2 for P_{CO} = 0.010 atm. For these scanning rates, we found that the results did not vary significantly when the direction of the scan was reversed. At high and low values of T_g, two branches of high and low reactivity are defined. In the case of ordinary oscillations, these would be the only states accessible to the system (*35*). In the present experiments, the structure of Fig. 2 shows six reaction branches, which are numbered in accordance with the waveform in Fig. 1B. Oscillations occur at gas temperatures from 266 to 366°C, where two or more branches overlap. At high temperatures within this range, only the high and low reaction branches are available to the system, and

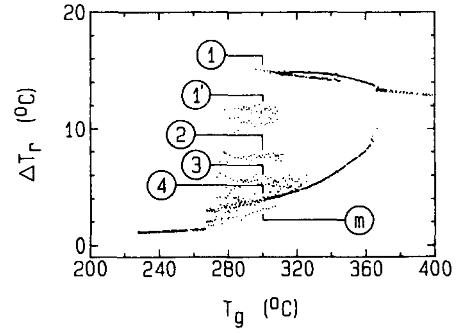


FIG. 2. Bifurcation diagram showing the gas temperatures at which oscillations were observed at P_{CO} = 0.01 atm and P_{O_2} = 0.5 atm. Oscillations occurred between 266 and 366°C. The horizontal branches, numbered in accordance with Fig. 1B, represent the extrema of the various types of oscillations. Below 266°C and above 366°C, oscillations in reaction rate did not occur and only one reaction branch was recorded. (Original loop)

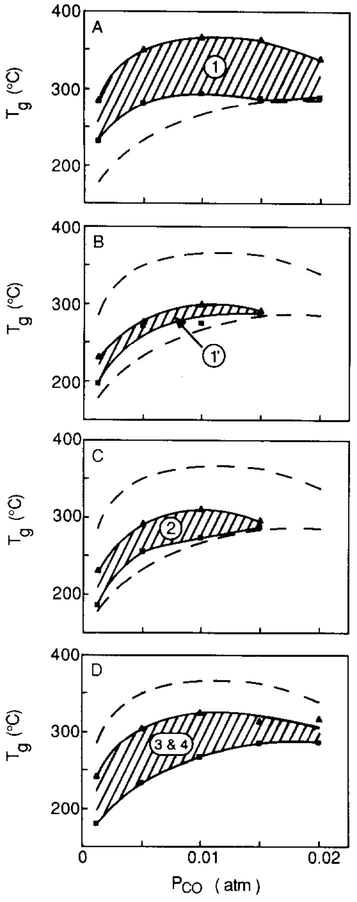


FIG. 3. The shaded areas show the ranges of gas temperature and CO partial pressure for the various types of oscillations (cf. Fig. 1B). (A) Type 1 oscillations. (B) Type 1' oscillations. (C) Type 2 oscillations. (D) Type 3 and type 4 oscillations. The dashed lines, which are the same in all three plots, indicate the range of T_g and P_{CO} over which oscillations of any type occurred. (Original loop)

type 1 oscillations occur as regular transitions between the two branches. At lower temperatures, more reaction branches become accessible and the waveforms become complex. As T_g approaches the minimum value within the range for oscillations, only oscillations with small amplitudes remain.

Waveforms were monitored while the gas temperature was varied for several gas compositions. Complex oscillations with peaks of different amplitudes occurred for all CO concentrations studied, P_{CO} = 0.00125 to 0.020 atm. The ranges of T_g over which oscillations of types 1, 1', and 2 occurred are shown as the shaded bands in Figs. 3A, 3B, and 3C, respectively. The ranges of T_g for oscillations of types 3 and 4 are combined in the shaded band in Fig. 3D. In addition, the minimum and maximum gas temperatures which define the range of occurrence for oscillations of any type are plotted as dashed lines in each graph.

Oscillations were also monitored while the CO concentration was varied for a constant gas temperature. Reaction rates measured as P_{CO} was increased and decreased are plotted as a function of P_{CO} in Fig. 4 for T_g = 300°C. Again, no appreciable hysteresis occurred. Oscillations occurred over a range of CO concentrations, P_{CO} = 0.0025 to 0.015 atm. The maxima of the type 1 oscillations lie along the reaction branch labeled 1, which is approximately first order in P_{CO}. The minima of the oscillations lie along the reaction branch labeled *m*, which is roughly independent of the CO concentration. These two reaction branches correspond to the branches observed in a two-state oscillatory system (*35*). Oscillations of types 1', 2, 3, and 4 were present at this gas temperature for P_{CO} = 0.0075 to 0.015 atm,

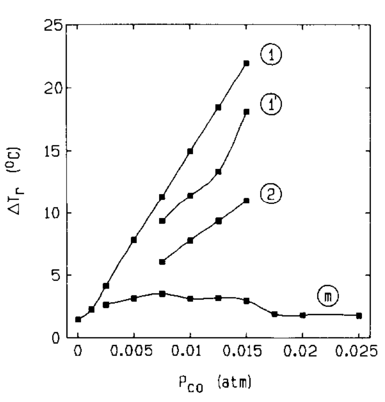


FIG. 4. Bifurcation diagram showing the CO partial pressures over which oscillations were observed at T_g = 300°C and P_{O_2} = 0.5 atm. Oscillations occurred for P_{CO} = 0.0025 to 0.015 atm. The branches are numbered in accordance with Figs. 1B, 2, and 3. (Original loop)

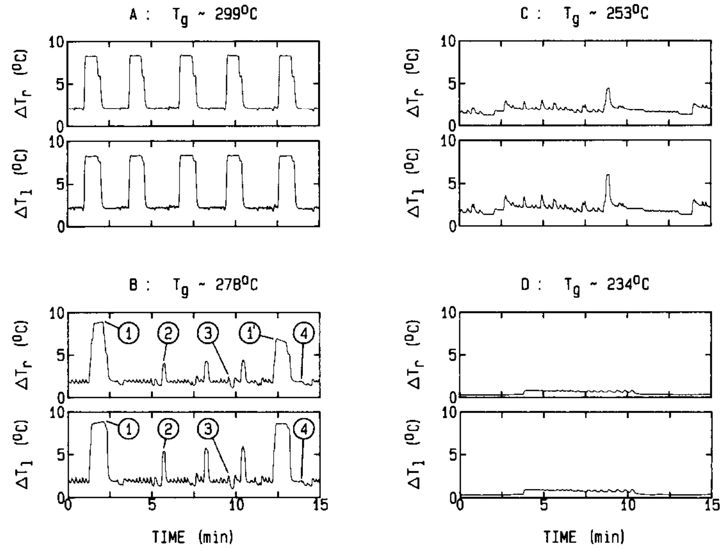


FIG. 5. Series of oscillations at $P_{CO} = 0.005$ atm, $P_{O_2} = 0.5$ atm, and four different gas temperatures in sets A through D. Two plots are shown in each temperature set: ΔT_r is proportional to the local reaction rate on the right side of the loop, and ΔT_l is proportional to the local reaction rate on the left side of the loop. (Original loop)

and the reaction branches associated with the maxima of oscillations of types 1′ and 2 are also approximately first order in P_{CO}.

In our observations of oscillations between multiple reaction branches, peaks with different amplitudes and shapes occurred somewhat independently of each other, resulting in a complex waveform that was not perfectly periodic. The polycrystalline structure of the catalyst suggested to us that oscillations could be occurring on patches having nonuniform catalytic properties on the wire surface. These patches could communicate thermally through the wire or gas, or through concentration changes on the wire surface or in the gas stream. Coupling between oscillations on the patches would give rise to the complex waveforms and the apparent number of reaction branches.

Oscillations at Two Locations on the Original Loop

In an effort to determine whether oscillations varied across the catalyst surface, we monitored the catalyst temperatures T_r and T_l on the right and left sides of the loop simultaneously. Each thermocouple gives a measure of the reaction rate in the vicinity of its spotweld to the catalyst, and Fig. 5 contains examples of waveforms recorded simultaneously at the two thermocouples for various gas temperatures. For these waveforms and the data presented in the remainder of this paper, the gas composition was $P_{CO} = 0.005$ atm. We found that oscillations at the two locations occurred at the same time within the resolution of our sampling interval (2 sec), but differed in details of shape and amplitude.

At high gas temperatures within the range of oscillatory behavior, type 1 oscillations occurred at both thermocouples. Figure 5A shows waveforms recorded at $T_g \simeq 299$°C. The square waves at the two locations have the same amplitudes, but the shoulders on the trailing edge occur at different reaction rates. At lower temperatures, oscillations became complex. Examples for $T_g \simeq 278$°C are given in Fig. 5B. The waveform recorded at the right thermocouple shows oscillations of types 1, 1′, 2, 3, and 4. The same five types of oscilla-

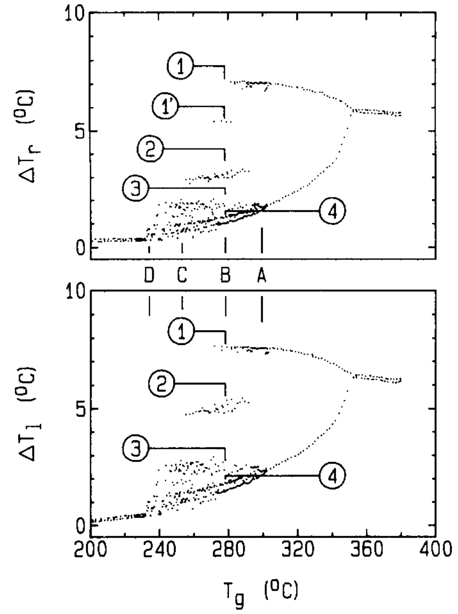


FIG. 6. Bifurcation diagrams showing the gas temperatures at which oscillations occurred on the right (top) and left (bottom) sides of the loop for the conditions of Fig. 5. The branches are numbered in accordance with Fig. 5B. (Original loop)

tions were present in the waveform in Fig. 1B, which was recorded at the same thermocouple for a higher CO concentration of $P_{CO} = 0.010$ atm. In contrast, the waveform recorded at the left thermocouple shows only four types of oscillations, with oscillations of type 1′ missing. The type 2 oscillations had somewhat larger amplitudes on the left side of the loop.

Figures 5C and 5D illustrate the oscillations at the two thermocouples as the gas temperature was lowered further. In Fig. 5C, recorded at $T_g \simeq 253$°C, oscillations of types 2, 3, and 4 are present. In Fig. 5D, at $T_g \simeq 234$°C, only the smallest amplitude oscillations of type 4 survive.

Measurements of the reaction rates at both thermocouples as a function of T_g are plotted in Fig. 6. At the right thermocouple, six reaction branches were present, corresponding to the five types of oscillations and the minimum rate branch. At the left thermocouple, there were only five branches. Oscillations occurred over the same range of gas temperatures, 232 to 351°C, at both locations on the loop. Oscillations of type 1 appeared above 282°C in ΔT_r, and above 272°C in ΔT_l.

These results demonstrate that local variations in reaction rate were present along the wire surface. Each thermocouple reading was proportional to a weighted average of the local rates over the surface of the wire, with areas or patches near the thermocouple weighted more than areas farther away. We suspect that the differences between the waveforms on the two sides of the loop were caused by variations in the catalytic properties of the surface in the vicinity of each thermocouple.

Oscillations on the Split Loop

In order to investigate how the oscillations would change when we eliminated direct coupling between the two halves of the wire, we cut the loop in two with the thermocouples centered on each half. Initially, with a small separation between the half-loops, complex oscillations were present, resembling oscillations on the original loop.

When we separated the half-loops by several millimeters, there were striking developments. All the oscillations became square waves, with fluctuations of high frequency and small amplitude superimposed on the high portion of the square waves, as shown in Fig. 7A. The square waves were type 1 oscillations, occurring between high and low reaction rates, at gas temperatures comparable to the temperatures for type 1 oscillations on the original loop. No complex oscillations occurred. These results show that coupling through the gas phase was responsible for the appearance of complex oscillations at low temperatures on the original loop. Oscillations on the half-loops differed in details of shape and amplitude, but maintained a fixed phase relationship. For a given gas temperature, oscillations had significantly lower frequencies than those on the original loop.

In an attempt to eliminate coupling through the gas stream, we placed a glass partition between the half-loops. Oscilla-

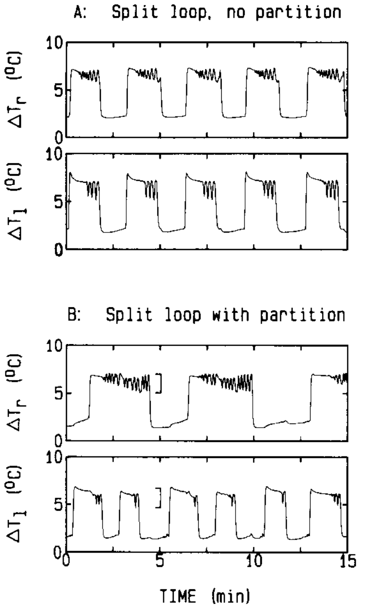


FIG. 7. Oscillations observed at $T_g = 328$°C on the split loop. The halves were separated by several millimeters. Waveforms were recorded (A) before and (B) after a glass partition was placed between the two halves. ($P_{CO} = 0.005$ atm; $P_{O_2} = 0.5$ atm.) (Split loop)

tions on the two halves occurred with different frequencies and no fixed phase relationship, as shown in Fig. 7B. Thus, gas-phase coupling was also responsible for synchronizing oscillations.

In Fig. 8, reaction rates on the half-loops in the presence of the partition are plotted as a function of gas temperature. Type 1 oscillations occurred over different temperature ranges on the two catalyst sections: from 284 to 358°C on the right half, and from 299 to 365°C on the left half. Three reaction branches are present. The brackets in Figs. 7B and 8 indicate the amplitudes of the high-frequency fluctuations on the high branch of the square waves and show that the branch of intermediate reactivity is associated with the minima of these high-frequency oscillations.

Several details of the data suggest that some communication between the two halves of the loop occurred through the gas in spite of our attempts to isolate them with the glass partition. First, at gas temperatures from 284 to 299°C and from 358 to 365°C, oscillations present on only one half were mirrored by small variations in catalyst temperature on the other half. Second, in Fig. 7B, two or three oscillations occurred on the left half for every oscillation on the right half. This is consistent with the theoretical prediction (*36*) that two weakly coupled oscillators will have periods τ_1 and τ_2 related by $n_1\tau_1 = n_2\tau_2$, where n_1 and n_2 are integers. Finally, Fig. 7B also shows that for every large amplitude transition on on one half-loop, there was a perturbation in the reaction rate on the other half-loop.

An independent experiment provided a measure of the thermal communication through the gas in the presence of the glass partition. When only one half-loop was placed in the reactor, and the gas temperature on the other side of the partition was monitored, an oscillation with an amplitude

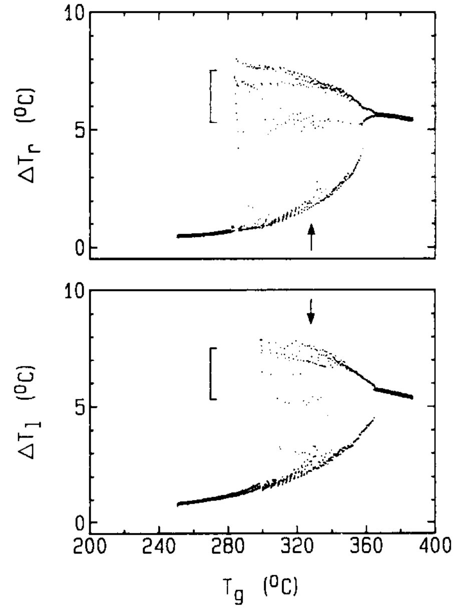


FIG. 8. Bifurcation diagrams for the right (top) and left (bottom) separated halves of the original loop in the presence of the partition. The arrows indicate the gas temperature at which the waveforms in Fig. 7B were recorded. The brackets, which correspond to the brackets in Fig. 7B, show the amplitude of the high-frequency fluctuations on the high reaction rate branch. (Split loop with partition)

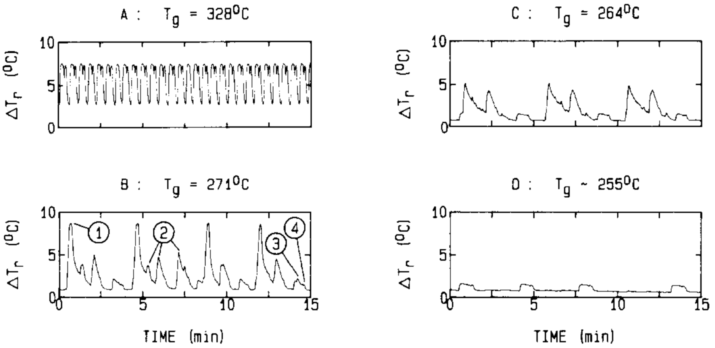


FIG. 9. Oscillations observed on the rewelded loop. (P_{CO} = 0.005 atm; P_{O_2} = 0.5 atm.) (Rewelded loop)

of 10°C on the half-loop caused a temperature rise of 0.5°C at the gas thermocouple on the other side of the partition. We believe that the small thermal communication through the gas with the partition in place did not significantly affect the results.

Oscillations on the Rewelded Loop

For the final phase of our experiments, we spotwelded the loop back together in order to observe the effect of restoring the direct coupling between the two halves. Whereas small differences between ΔT_r and ΔT_l occurred on the original loop, the thermocouple readings on the two sides of the rewelded loop were nearly identical over the entire range of gas temperatures. Thus only data from the thermocouple on the right side of the rewelded loop are shown in Figs. 9 and 10.

Figure 9 shows that, in contrast to the square wave oscillations on the split loop, complex waveforms reappeared on the rewelded loop. The high-frequency components that were present on the split loop were eliminated when the two halves were recoupled. At a given gas temperature, the oscillatory frequencies on the rewelded loop were significantly higher than on the split loop, and slightly higher than on the original loop.

The waveforms in Fig. 9 for the rewelded loop differed in shape from those in Fig. 5 for the original loop. However, the waveforms on the original and rewelded loops showed a similar degree of complexity and similar behavior as the gas temperature was varied.

In Fig. 10, measurements of the reaction rates as a function of gas temperature show five reaction branches: 1, 2, 3, 4, and the minimum rate branch. The same number of branches appeared on the left side of the original loop. On the rewelded loop, oscilla-

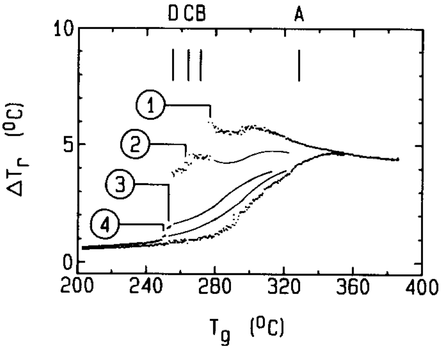
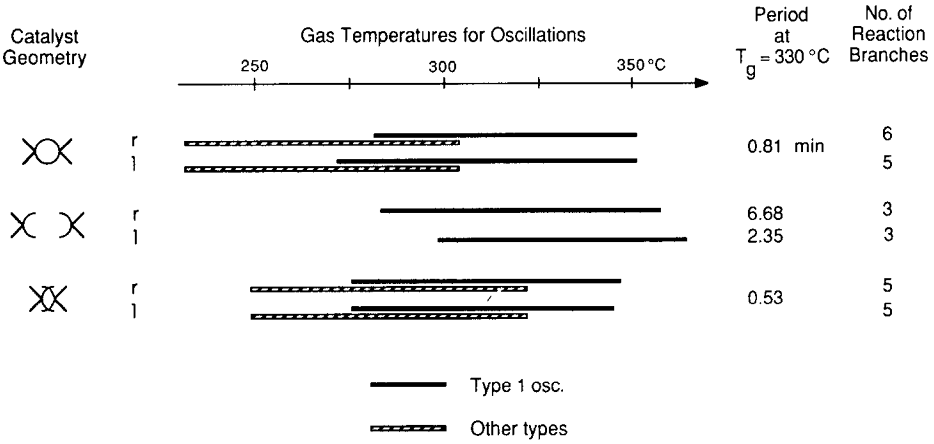


FIG. 10. Bifurcation diagram for the rewelded loop. The reaction rate branches are numbered in accordance with Fig. 9B. The dots represent the minimum and maximum reaction rates detected by the computer during discrete sampling periods as the gas temperature was varied slowly. Because the computer sampling period was long relative to the periods of oscillation, only the maxima of the largest amplitude oscillations that occurred in a given sampling period were recorded by the computer. The solid lines at intermediate ΔT_r indicate the ranges of gas temperatures for oscillations of types 2, 3, and 4 as determined from visual inspection of waveforms on a continuous strip-chart graph recorded simultaneously with the discrete computer sampling. (Rewelded loop)

TABLE 1

Oscillatory Characteristics



Catalyst Geometry		Period at T_g = 330 °C	No. of Reaction Branches
	r	0.81 min	6
	l		5
	r	6.68	3
	l	2.35	3
	r	0.53	5
	l		5

tions occurred from 249 to 346 ± 1°C, a range of gas temperatures comparable to the original range. Type 1 oscillations appeared on the rewelded loop above 276°C, at gas temperatures comparable to the temperatures for type 1 oscillations on the original loop and the split loop.

Summary

Oscillatory characteristics for each catalyst configuration are summarized in Table 1. These results were recorded for a fixed CO concentration of P_{CO} = 0.005 atm (P_{CO}/P_{O_2} = 0.01). The ranges of gas temperatures for type 1 oscillations and for all other types are diagrammed as solid and dashed lines, respectively. Type 1 oscillations occurred between branches of low and high reactivity; the other types occurred between branches of low and intermediate reactivity. Also shown in the table are the period of the oscillations at a constant gas temperature of 330°C and the total number of reaction branches that appeared over the entire range of gas temperatures for oscillations.

Oscillations on the two sides of the original loop occurred in synchrony, but exhibited small differences in the details of the waveforms.

After the loop was split, complex oscillations persisted for small separations between the half-loops. When the separation was increased, only oscillations of type 1 occurred. Frequencies of oscillations were substantially lower than those on the original loop. Results in Table 1 were obtained when the half-loops were further isolated with a glass partition, causing differences to develop in the temperature ranges and frequencies of oscillations on the two halves.

When the loop was rewelded, oscillations became resynchronized, and complex oscillations reappeared. Differences in oscillatory characteristics between the original and the rewelded loops were probably caused by changes in the nature of the catalyst surface with time and differences in the coupling at the spotwelds between the two halves.

DISCUSSION

In our experiments, oscillations in the rate of CO oxidation on a Pt wire loop were monitored with two thermocouples spotwelded to the wire surface. The thermocouples, which were located on opposite sides of the loop, provided a measure of the local activity at two areas of the catalyst surface. For all catalyst geometries, some differences were observed between waveforms recorded simultaneously by the thermocouples. These differences confirm other observations (*30, 32–34, 37, 38*) of spatial inhomogeneities in oscillations and suggest that the catalyst surface was composed of individually active areas interacting with each other. In our system, coupling occurred primarily through the gas phase. On the basis of this work, we cannot discriminate between coupling mechanisms involving heat and mass transfer.

We believe that the most significant result of our experiments is the demonstration that coupling between areas on a catalyst surface, each exhibiting somewhat different oscillatory properties, can extend the range over which oscillations occur to lower temperatures. New types of oscillations occurred at the lower temperatures, and the resulting complex waveforms were composed of peaks of varying amplitudes. We believe that this is the first experimental demonstration that coupling chemical oscillators can increase the parameter space over which oscillatory instabilities occur.

In a few investigations, oscillations have been generated by coupling units that would not oscillate if decoupled. In experiments involving CO oxidation over wafers of Pt/SiO_2, Sant and Wolf (*34*) found oscillations in the catalyst temperature only for sufficiently small separations between Pt particles. In modeling heart cell activity, Krinskii *et al.* (*39*) showed that the interaction between two cells individually under nonoscillatory conditions could produce a finite train of "echo waves" traveling between the cells. Tyson (*40*) used a similar approach and predicted that two Oregonators initially in stable steady states could oscillate under a delicate range of parameters when coupled. A cellular automaton model suggested by Dress *et al.* (*41*) has been developed (*42, 43*) to account for the fractal-like waveforms observed by Jaeger *et al.* (*44*) in the oxidation of CO over zeolite-supported Pd. In this model, the reactivity of an individual crystallite would remain in steady state if it were isolated from its neighbors. When crystallites are coupled on the model catalyst, their behavior is synchronized by heat transfer, yielding the fractal-like waveforms and the propagation of spatiotemporal structures.

At temperatures below the range over which the fractal-like oscillations occurred in Ref. (*44*), a region of "multistable aperiodic behavior" was characterized by irregular fluctuations between three different conversion states of the catalyst. These irregular fluctuations are suggestive of the complex oscillations which appeared in our work at low temperatures on the original and rewelded loops.

Jaeger *et al.* (*45*) studied thermal coupling between three areas of an alumina-supported Pd catalyst during oscillations in the oxidation of ethanol. In contrast with our observations, they found that the complexity of some of the waveforms measured on each area increased as the coupling was decreased.

Some studies have shown that when individual components of a system are oscillating with simple waveforms, the integrated output of the system can have a complex waveform. Ravi Kumar *et al.* (*46*) modeled the coupling of two parallel CSTRs, each oscillating under different steady-state conditions. When the CSTRs were weakly coupled, the total output had a complex oscillatory behavior. In their "fuzzy wire" model, Jensen and Ray (*47*) used a bulk wire covered by protrusions to simulate the structure of a catalytically etched surface. Each protrusion oscillated with a frequency dependent on its size. With as few as two or three different protrusion sizes, complex oscillations in the temperature of the wire could be generated. In experiments involving CO oxidation over silica-supported Pt wafers, Kaul and Wolf (*38*) found that simple oscillations measured with thermocouples located on the four quadrants of their catalyst had different phases and amplitudes. In contrast, when the average temperature of the wafer was measured by IR, the oscillations were complex, with two peaks per cycle. These studies demonstrate that the shape of the waveforms can depend on the portion of the system sampled. While illustrating that complex oscillations can result from combining individual oscillators, these results differ from our own in that the complex waveforms were not observed on the individual parts of the system, but appeared only in the output of the entire system.

In other investigations, coupling between oscillators with simple waveforms has resulted in complex oscillations occurring on a local scale. In their model of coupled Brusselators discussed in the Introduction, Raschman *et al.* (*23*) found that some of the Brusselators in their linear and cyclic arrays developed double-peaked oscillations. In experiments coupling two BZ tanks held at different temperatures, Marek and Stuchl (*4*) found differences in the waveforms in the two reactors. Under certain conditions, irregular splitting of some oscillations resulted in peaks similar to those in Fig. 9A. Quasi-periodic variations in oscillatory amplitudes also occurred when the coupling was high and the oscillations in the two tanks were nearly synchronized. These studies show that the shape of oscillations occurring locally in a coupled system can be influenced by coupling between portions of the system.

In the investigations discussed in the preceding two paragraphs, combining units oscillating with simple waveforms resulted in the appearance of complex oscillations. Other studies have found that coupling oscillating units can inhibit oscillations (*24, 25*) or decrease their complexity (*45*). In our experiments, complex oscillations occurred on the original and rewelded loops at temperatures at which no oscillations occurred on the split loop.

CONCLUSION

Our work shows that coupling two catalysts can cause oscillations to occur at lower temperatures than those on the individual catalysts. Thus, coupling destabilizes the system by extending the region over which instabilities occur. In our experiments, the instabilities occurred as oscillations; in practical systems, coupling could have implications in the design of catalytic reactors with lower ignition temperatures.

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