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Mechanism of the Kinetic Oscillations in the Oxidation of CO on Palladium Dispersed within a Zeolite Matrix

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Reaction rate oscillations of the oxidation of CO were studied on highly dispersed palladium embedded within a zeolite matrix under nonisothermal conditions. Transients and periodic oscillations are interpreted in terms of an oxidation–reduction cycle involving the Pd surface which moves the system between two kinetic branches of the reaction. The observation of aperiodic oscillations can be explained by the desynchronization of the catalyst surface. © 1989 Academic Press, Inc.

INTRODUCTION

Oscillatory behavior during the oxidation of carbon monoxide has attracted considerable attention during recent years. Theoretical and experimental studies of self-oscillations in this reaction have been reviewed by Razon and Schmitz (*1*). Several hypotheses have been developed to explain these phenomena. The results obtained by Ertl and co-workers (*2, 3*) and by Schwartz and Schmidt (*4*) under vacuum conditions showed that oscillations are associated with a surface phase transition from the hexagonal (hex) structure to the square (1 × 1) and $c(2 \times 2)$ structures during the reaction on Pt(100) single-crystal surfaces. Yeates *et al.* (*5*) observed oscillations on the Pt(100) surface at low pressure. They showed that under atmospheric conditions oscillations were observed on platinum single crystals of (111) and $(\underline{13}\ 1\ 1)$ as well as (100) orientation. Since platinum single crystals with (111) and $(\underline{13}\ 1\ 1)$ orientation undergo no CO-induced structural transformation the authors concluded that different mechanisms are responsible for the oscillations observed under low-pressure conditions and those observed at atmospheric pressure. Yeates *et al.* (*5*) suggested that the oscillations at atmospheric pressure are driven by a cyclic oxidation and reduction of the platinum surface.

Sales and co-workers (*6*) were the first to suggest that the formation of an oxide in the near-surface region of the catalyst and its reduction by CO led to the observed oscillatory behavior. Their work showed that oscillations in the CO oxidation rate on platinum wire had periods as long as 1 h. The observation of such oscillations proves that some slow processes play a significant role in the observed behavior (*7*). Such processes may be a slow modification of the surface, the dissolution of reactants in the near-surface region, and oxidation–reduction.

A large amount of experimental data concerning oscillatory behavior is available on CO oxidation on Pt catalysts. Relatively few studies have documented oscillatory behavior during CO oxidation on Pd catalysts, but these include Pd in the form of wire (*8*), Pd embedded within a zeolite matrix (*9, 10*) and supported Pd catalyst (*11, 12*). One of the best experimentally supported models to account for the oscillatory behavior of CO oxidation catalyzed by noble metals is the model including surface oxidation and reduction as the driving

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mechanism of the oscillations (*13*). Turner and Maple (*14*) showed that the time scales of these processes for Pd and Ir powder are similar to the oscillation periods. Highly dispersed noble metals are more susceptible to oxidation and reduction compared to larger crystals. This is why a palladium phase with a narrow size distribution of Pd crystallites supported within a zeolite matrix is a very good system for the study of self-oscillating regimes in the CO oxidation.

The purpose of the present work is to study the influence of the catalytic behavior and the state of Pd particles on the occurrence of oscillatory behavior and the properties of self-oscillations. Much attention will be paid to the conditions where regular oscillations appear and to their transformation into aperiodic ones.

EXPERIMENTAL

The reaction was carried out under nonisothermal conditions in a continuous flow reactor system. The catalyst (8 mg) was applied under shallow bed conditions on a frit in the glass reactor. The catalyst temperature was measured by a thermocouple positioned in the catalyst bed. Gases were preheated to reactor temperature before reaching the catalyst.

Supplied gases for reaction were a mixture of CO and N_2 (9.84% CO in N_2, 99.97% pure, Messer–Griesheim) and synthetic air (20/21% O_2 in N_2, impurities <0.1 vpm, Messer–Griesheim, total pressure $p = 10^5$ Pa).

The reaction mixture was fed into the reactor with a flow rate of 150 cm^3/min (weight hourly space velocity $\approx$1450 h^{-1}). The flow rates were controlled by thermal mass flow meters (HI–TEC ±1% precision). The catalyst could be subjected to H_2 pulse treatment by injecting hydrogen into the reaction mixture with a flow rate of 2 cm^3/min for 1–3 s.

The CO and CO_2 concentrations in the outlet of the reactor were continuously monitored by IR spectrometers (URAS 3G, Hartmann and Braun, FRG). Concentration changes with time could be resolved to within 1 s.

The calculations of a very small Peclet number has shown that the reactor cell behaved as CSTR for the small amount of catalyst and the flow rate employed in this study.

Three catalysts were used in this work and they are described in Table 1. An iron-free Na*X* with Si/Al = 1.2 was prepared by hydrothermal crystallization (*15*). Palladium was introduced in the form of its tetraammine ion complex from an aqueous solution of the chloride. The metal phase was precipitated by an autoreduction process during the decomposition of the ammine complex by heating a sample under argon in a fixed-bed reactor to 300°C (5°C min^{-1}). The metal phase was obtained with a narrow particle size distribution around 10 nm located within the zeolite matrix. For experimental details and electron microscopy results, see Refs. (*10, 16*). The oxidation of CO on the zeolite-supported Pd catalyst was studied in the temperature region 190–250°C. The inlet CO concentration in the synthetic air was varied from 0 to 3 vol%. Before each run the catalyst was oxidized for 16 h in streaming synthetic air at 330°C.

RESULTS

The dependence of the reaction rate on the CO concentration measured in the outlet of the reactor at 195°C for catalyst A is shown in Fig. 1. The maximum and minimum values of the rates during the oscillatory behavior are represented by the arrows. It must be pointed out that the actual or effective CO concentration is depicted

TABLE 1

Description of Zeolite-Supported Pd Catalysts

Catalyst	Pd loading (wt%)	Pd surface area (m^2/g catalyst)	Average size of zeolite crystals (μm)
A	4.6	2.2	50
B	4.6	2.2	5–7
C	2.3	1.1	5–7

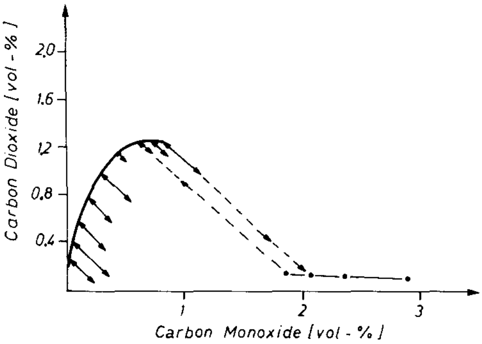

FIG. 1. Dependence of the reaction rate on CO concentration in the reactor at 195°C for catalyst A. Regions of self-oscillations are represented by arrows.

and not the inlet concentration. The CO inlet concentration can be derived from Fig. 1 and the other figures by adding the CO_2 concentration in the effluent to the effective CO concentration plotted on the abscissa. This can be done at the extrema of the oscillations represented by the arrows. The degree of conversion is then given by the ratio [vol% CO_2 (effluent)]/[vol% CO_2 (effluent) + vol% CO (effective)]. The effective CO concentration in the reactor has been plotted in order to visualize the shift during the oscillations as represented by the arrows. The reading of the thermocouple attached to the catalyst showed that the temperature in the high conversion oscillating region is 10–20°C higher than that in the low conversion region. This temperature difference is about one order of magnitude larger than the amplitude of the temperature oscillations which can be observed in synchrony with the oscillating rate of CO_2 production. Tracing the kinetic curve back from the low activity branch by lowering the CO concentration leads to ignition at a lower effective temperature of the catalyst bed and hence at a lower effective CO concentration. The small hysteresis shown in Fig. 1 may therefore be explained by nonisothermal conditions, i.e., by the variation of the average temperature of the catalyst during the kinetic measurements. The rate behavior under the same conditions for catalyst B is represented in Fig. 2. Catalysts A and B carry the same amount of Pd within the zeolite matrix. They differ, however, in the average size of the supporting zeolite crystals (Table 1). By comparison of Figs. 1 and 2 it can be seen that decreasing the crystallite size of the supporting zeolite leads to an increase in the average rate in the concentration region where the reaction rate displays positive order kinetics with respect to the CO concentration in the reactor. The maximum rate of the oxidation reaction corresponds to 100% conversion in Fig. 2 and to less than 100% in Fig. 1. At the same time the reaction rate decreases with the decrease of zeolite crystallite size for high CO concentrations in the reactor. Such observations can be expected if intraphase diffusion, e.g., in the channels of the zeolite support, can affect the catalytic activity. In this case for catalyst A in the region of first-order positive kinetics the observed rate constant ($k_{obs} = \eta \cdot k$) is smaller than the intrinsic rate constant k and the effectiveness factor η is less than unity. A decrease in the zeolite crystallite size leads to an increase in the effectiveness factor η and the observed reaction rate in the region of low CO concentration. In the region of high CO concentrations the effectiveness factor can be greater than 1 due to the onset of negative order kinetics. In this case the observed reaction rate of CO oxidation on the zeolite with the smaller crystallite size is also smaller.

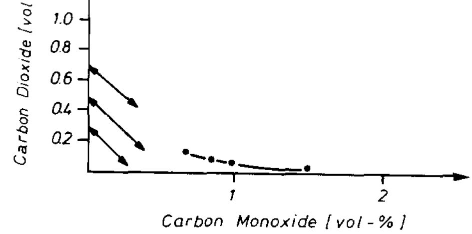

FIG. 2. Dependence of the reaction rate on CO concentration in the reactor at 195°C for catalyst B. Regions of self-oscillations are represented by arrows.

Figure 3 shows the oscillatory behavior observed on catalysts A and B at a temperature of 230°C and a CO inlet concentration of 2%. Oscillations for catalyst B with the smaller crystallite size are more regular and have a greater amplitude. The maximum rates for all oscillations observed for catalyst B always correspond to 100% conversion. The CO mass transfer rates to the external surface of the catalyst were estimated. The results obtained clearly showed that the rates of reaction are not influenced by mass transfer even in a 100% conversion state. To eliminate this high degree of conversion the catalyst C with a smaller Pd loading (2.3 wt%) was chosen for further kinetic studies. This catalyst had a small crystallite size (5–7 μm) of the zeolite support in order to eliminate the effect of intraphase diffusion upon the oscillatory behavior.

Catalyst C showed very low activity following the standard pretreatment (16 h in streaming air at 330°C). The kinetic studies on this catalyst at two temperatures are presented in Fig. 4. As can be seen from this figure the reaction rate diminishes with increasing temperature from 220 to 230°C and no oscillations are observed under these conditions. This oxidized state of the catalyst is not a stable one and if the catalyst is treated with the reaction mixture for a sufficient period of time very regular oscillations appear. Figure 5 shows the appearance of such oscillations at 200°C and 0.2% CO inlet concentration. Under this condition oscillations appear after 20 min. It is worth mentioning that the oscillations start in the manner of a hard excitation and that the amplitude is found to increase with time in a stepwise manner. Increasing the temperature and/or the CO concentration in the reaction mixture led to the decrease in this time. The treatment of the catalyst by short (3- to 10-s) pulses of hydrogen also decreased the time for the appearance of self-oscillations. This proves that during this long time a slow reduction of the cata-

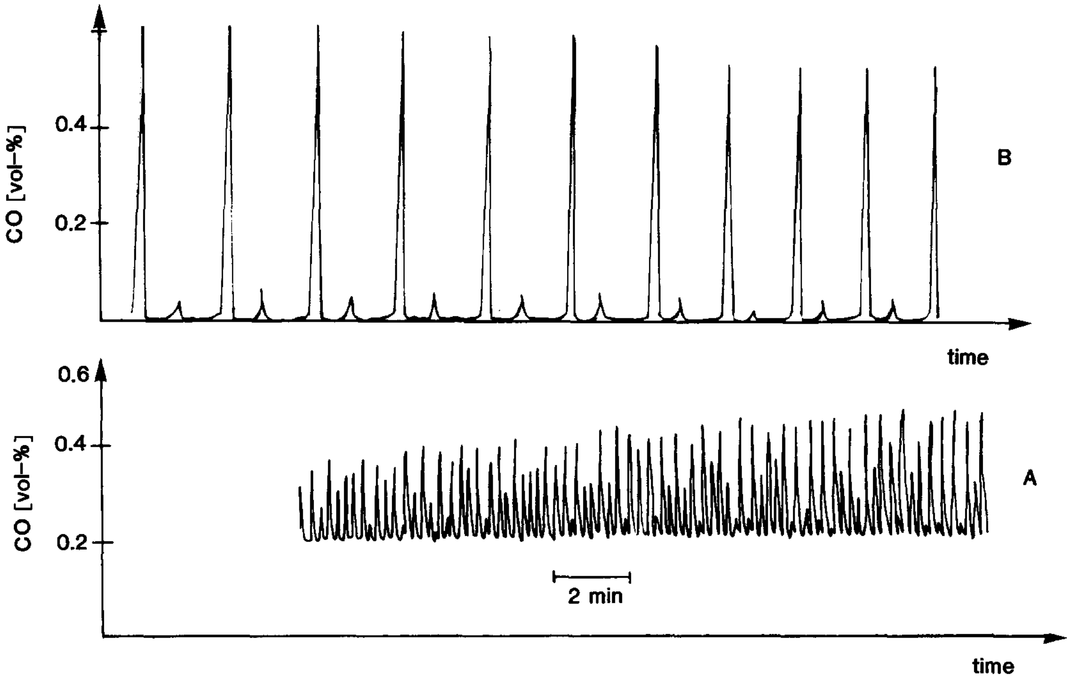

FIG. 3. Oscillatory behavior, observed for catalyst A and B at 195°C. CO inlet concentration, 2 vol%.

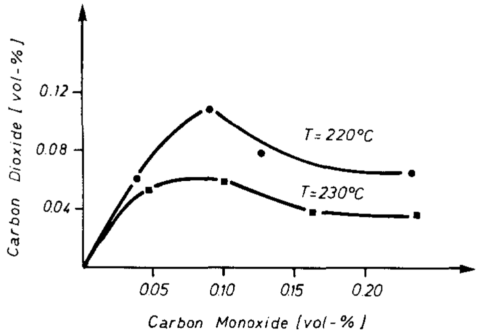

FIG. 4. Dependence of the reaction rate on CO concentration in the reactor for catalyst C following standard oxidation pretreatment of the catalyst.

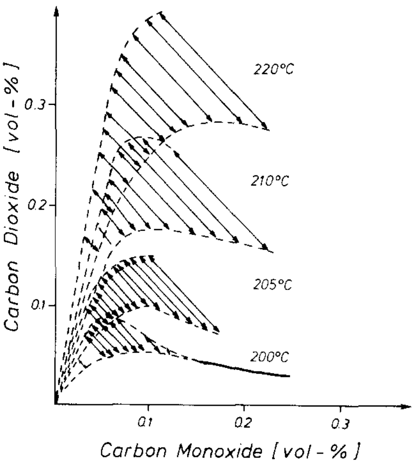

FIG. 6. Reaction rate at different temperatures as a function of CO concentration in the reactor. Regions of self-oscillations are represented by arrows.

lyst takes place which causes the increase in the activity of the catalyst and the appearance of regular reaction rate self-oscillations. The oscillatory state can also be reached starting with a catalyst fully reduced in a H_2 atmosphere. In this case the oscillating state is approached from a stationary state of higher activity. The regions where regular oscillations exist are represented in Fig. 6. The range of oscillations extends to higher CO concentrations at higher temperatures. An increase in the period of oscillations was observed with increasing CO concentration in the reactor, while the amplitude of oscillations at 200°C went through a maximum. At this temperature regular oscillations have been observed at CO concentrations smaller than 0.15% in the reactor. At higher temperatures the oscillatory behavior was observed at larger CO concentrations in the reactor, where the rate of catalyst reduction during the reaction may be appreciable. Figure 7 is an extension of the kinetic curve at 220°C depicted in Fig. 6 to higher CO concentrations.

For CO concentrations <0.3% the regular self-oscillations are observed. At higher CO concentrations the average activity of the catalyst increases and oscillations become less regular. Eventually the low activity branch of the reaction is established.

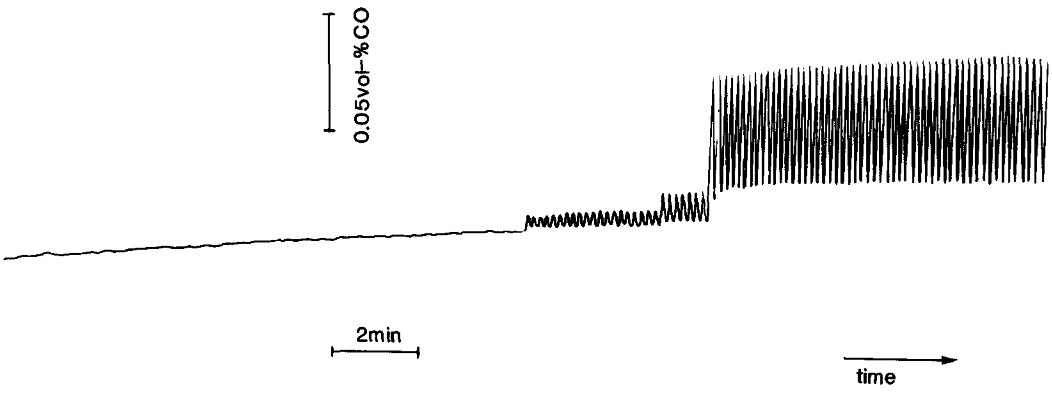

FIG. 5. Transient from steady state to limit cycle behavior at 200°C. CO inlet concentration, 0.2 vol%.

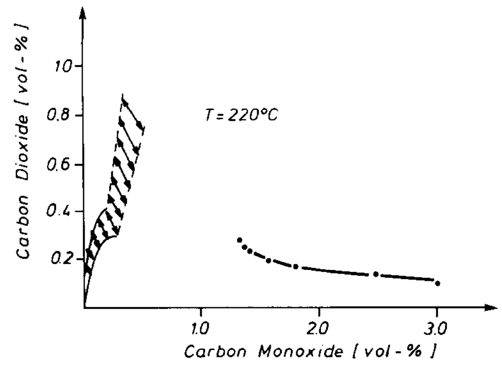

FIG. 7. Dependence of the reaction rate on CO concentration in the reactor for catalyst C at 220°C. Regions of self-oscillations are represented by arrows.

The discontinuity in Fig. 7 is due to the plot of the effective CO concentration in the reactor on the abscissa.

Figure 8 (curve a) illustrates the change in the character of the oscillations with the addition of only 0.02% CO in the inlet reaction mixture. In this sensitive region of CO concentrations in the reactor the reaction rate falls immediately after the addition of even such a small amount of CO. Then, after a period of time, the reaction ignites and oscillations of a different character appear. As the CO concentration was further increased the oscillations became more and more aperiodic. The reaction rate at 220°C

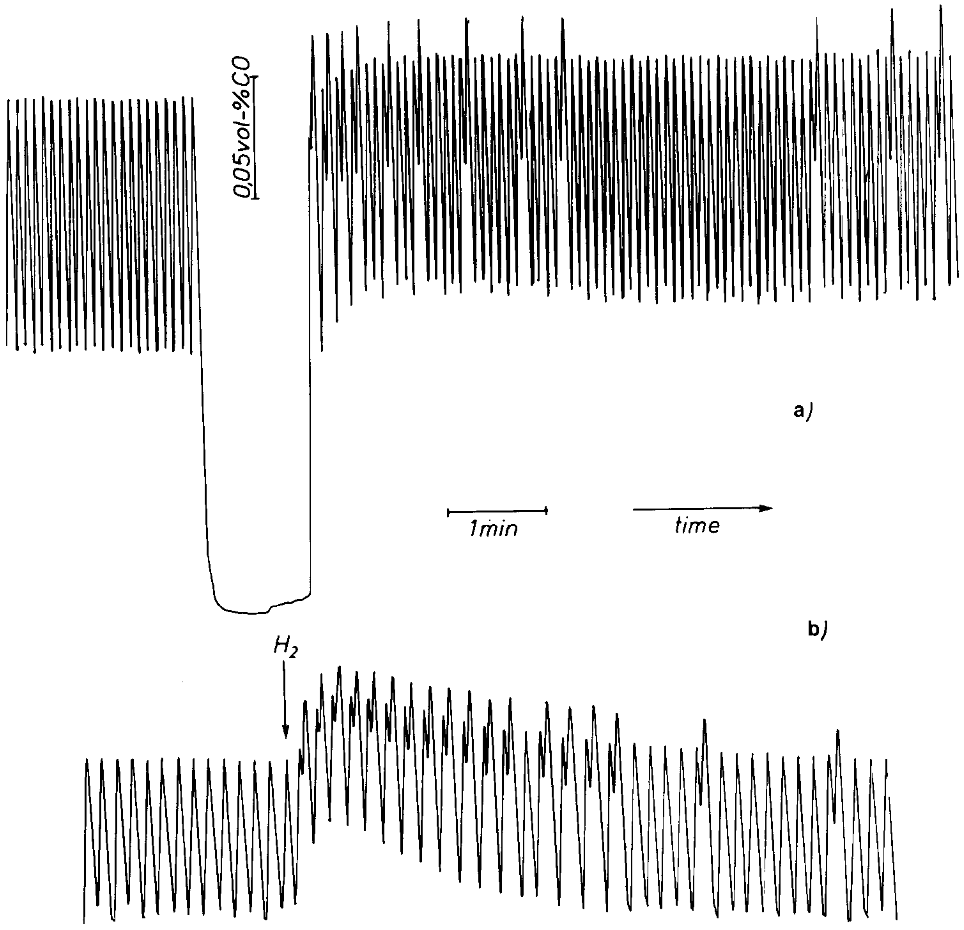

FIG. 8. Curve a: Evolution of oscillatory patterns with time after the addition of 0.02 vol% CO in the inlet reaction mixture. Temperature, 220°C; CO inlet concentration, 0.3 vol%. Curve b: Evolution of oscillatory patterns with time after the third hydrogen pulse treatment of the catalyst surface. Temperature, 205°C; CO inlet concentration, 0.26 vol%.

also went through a maximum; however, the breakdown was observed at a higher CO concentration in the reactor compared to that at 200°C.

In order to support the hypothesis that the change in the character of the oscillations is connected with the reduction of the surface of the catalyst, the following experiments with hydrogen pulse treatment of the catalyst were carried out. Regular oscillations were obtained at 205°C and a CO inlet concentration of 0.26%. Under these conditions the reduction of the catalyst due to the reaction was found to be very slow. Once the oscillations had been established, the catalyst was subjected to the hydrogen pulse treatment. Following the first and second pulses of H_2 the average activity of the catalyst increased and the amplitude of the oscillations decreased. After some time the original oscillations were reestablished. The effect of the third pulse is shown in Fig. 8 (curve b). After the catalyst surface was treated with H_2 for the third time oscillations changed their shape and assumed a more complicated waveform. Subsequent pulses of hydrogen led to further complications in the oscillations and finally aperiodic oscillations could be seen.

The reduction of the catalyst during the reaction leads to the apparent hysteresis phenomenon shown in Fig. 9. Curve a presents the kinetic results obtained during the increase in CO concentration in the reactor up to 0.56%. At this CO concentration the low conversion steady state was obtained. The average activity of the catalyst at this state slowly increased due to the reduction of the catalyst (Fig. 9, curve b) and after 35 min regular small amplitude oscillations could be observed. The decrease in CO concentration led to an increase in the reaction rate and the appearance of aperiodic oscillations with large amplitudes (Fig. 9, curve c). The observed phenomenon does not represent a true hysteresis, because if one comes back to the zero concentration of CO in the reactor and begins to increase its value again, only kinetic curve c and aperiodic oscillations will be observed. The constants of pseudo first order can be obatined at low CO concentration for curves a and c. Comparison of these values shows that in this region the average activity of the reduced catalyst is more than five times higher.

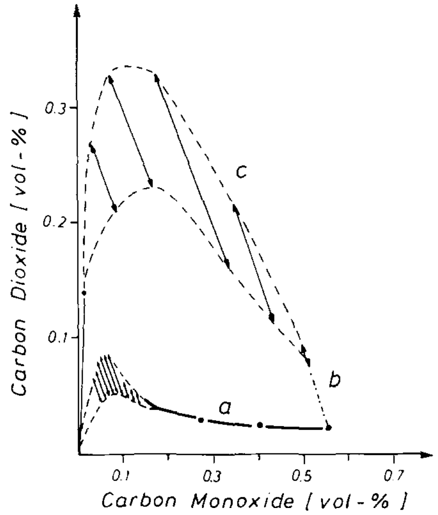

FIG. 9. Dependence of the reaction rate on CO concentration in the reactor for catalyst C at 200°C for increasing CO concentration (curve a) and for decreasing CO concentration (curve c). Increase of catalyst activity during 35 min due to the catalytic reaction (line b, [0.56 vol% CO in the feed]). Regions of self-oscillations are represented by arrows.

Figure 10 shows another kind of complicated dynamic behavior which has been observed at temperatures between 200 and 205°C in the region of a CO concentration in the reactor where the transition from the high to the low activity kinetic branch takes place. The figure shows regular oscillations during the slow decrease in the average catalyst activity. At some critical value of the catalyst activity the self-oscillations disappear abruptly and about 15 min is needed until they appear again at a slightly higher level of catalyst activity than the point of extinction of the reaction. The average level decreases again during the oscillating regime until the next extinction of the reaction rate.

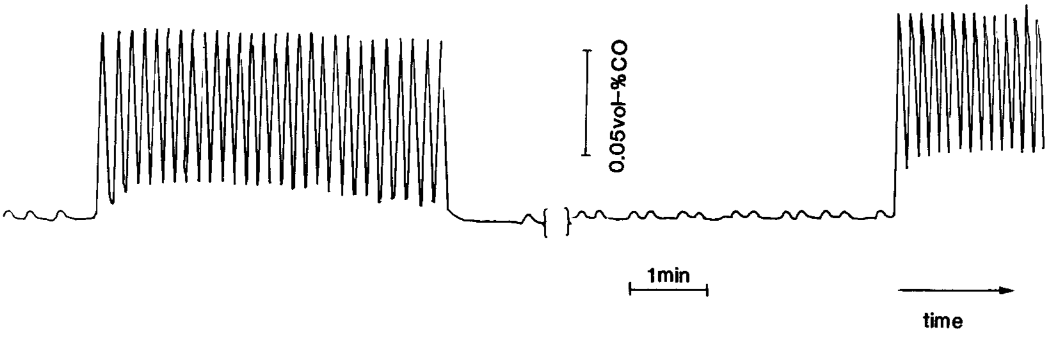

FIG. 10. Complicated dynamic behavior observed for catalyst C. Temperature, 205°C; CO inlet concentration, 0.325 vol%.

DISCUSSION

The experimental results presented in the previous sections show that the observed oscillations during CO oxidation on Pd-zeolite catalysts depend greatly upon catalyst pretreatment and activity. A transient steady state is observed before self-oscillations start on a catalyst following the standard pretreatment. Figure 5 demonstrates the process of initiation of self-oscillations over an oxidized catalyst. An appreciable time is needed before the appearance of the oscillations. The process can be accelerated with a higher CO feed concentration or by hydrogen pulses, which proves that the slow process which gradually changes the activity of the catalyst is the reduction of the catalyst. It can be concluded that a defined state of the Pd catalyst and of its activity must be established for the observation of self-oscillations.

The study of oscillatory behavior in the CO oxidation on Pd-zeolite catalysts was carried out under conditions where external diffusion problems were eliminated. Intraphase diffusion was found to influence amplitude and period of the self-oscillations (see Fig. 3). The regular self-oscillations have been observed on catalyst C, where the influence of intraphase diffusion upon the reaction rate was negligible. The observation of such regular oscillations requires the synchronization of Pd crystallites embedded in the zeolite matrix. The variation in partial pressure is discussed as a dominant synchronizing force in Ref. (*4*). A mathematical model for the synchronization of oscillating centers has been developed on the basis of a cellular automaton (*17*).

The results obtained reveal that the maximum amplitude of oscillations is observed in the region where the reaction rate reaches its maximum. It was shown by several authors (*18, 19*) that under this condition the surface coverage may change from predominantly adsorbed oxygen to predominantly adsorbed CO. Figure 8 demonstrates that in this region the addition even of very small amounts of CO can cause the breakdown of the reaction rate. The observation of such ignition–extinction phenomena can be explained by the existence of a steady-state multiplicity of the reaction rate.

From early work of Matsuura and Kato (*20*) and Beusch *et al.* (*21*) it is known that the combination of Langmuir-type kinetics with a transport process characterized by a straight line can give rise to multiple steady states (r_c in Fig. 11). The study of oscillatory behavior was carried out under conditions where problems of external diffusion were eliminated. At the same time for the regular oscillations observed on catalyst C in the kinetic range of the catalytic reaction the influence of intraphase diffusion upon the reaction rate was found to be negligible. Hence, the process which in combination

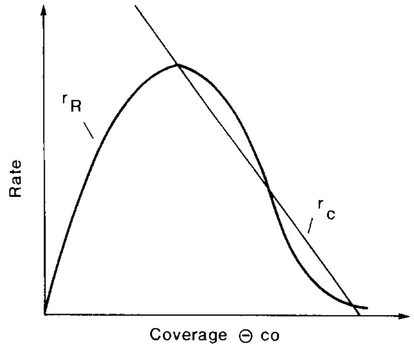

FIG. 11. Multiple steady states due to the combination of reaction rate curve r_R and chemisorption line r_C.

with the reaction rate is needed for the occurrence of multiple steady states must be CO chemisorption. Following the approach of Wicke and co-workers (*22*), multiple steady states can be obtained by the combination of Langmuir-type kinetics with the rate of CO chemisorption. This relation is shown in Fig. 11. The physical reason for the occurrence of rate multiplicity is the competitive chemisorption of CO and O_2. It has been suggested that a system which exhibits bistability would be capable of oscillations when subjected to an appropriate feedback (*23*). This feedback must be based on the strong dependence of the reaction rate upon the free active sites of the catalyst (*24*). A periodic succession of ignited and extinguished states is possible if there is a side process in the system which provides empty sites after the reaction is extinguished and which consumes empty sites after an ignition has taken place. In the last decade three hypotheses concerning the nature of this side process have been proposed in an attempt to explain oscillatory behavior in the CO oxidation reaction. According to the first hypothesis, suggested by Eigenberger (*25*), the reversible adsorption of an inert species can play the role of a buffer step and switch the ignited and the extinguished steady state by the slow provision or consumption of empty sites. Second, Sales, Turner, and Maple (*13*) proposed that the periodic oxidation and reduction of the catalyst surface may play the role of the side process. The active site blocking effect is connected with a platinum oxide. Third, Burrows *et al.* (*19*) and Collins *et al.* (*26*) developed the idea that the oscillations in the CO oxidation are due to deactivation/activation cycles. Deposited carbon is suggested to be the cause of the oscillations. Mathematical models based on each of these hypotheses contain similar equations and it is very difficult to discriminate between the different mechanisms.

The formation of carbonaceous deposits and their removal by the adsorption of oxygen on carbon and subsequent oxidation is not considered in view of the widely different length of period and shape of the oscillations reported in Refs. (*19, 26*), the high conversion, and the excess oxygen in our experiments.

The results obtained clearly indicate that periodic oxidation and reduction of Pd particles in the zeolite matrix is the driving mechanism of the observed oscillations. When the reaction proceeds in the high conversion state, the local temperature of the Pd crystals might increase considerably. The Pd surface is covered with chemisorbed oxygen and the hot surface of the catalyst provides a good condition for the oxidation of Pd. This process leads to the decrease in catalyst activity and the subsequent cooling of the catalyst surface. Carbon monoxide accumulates on the catalyst surface and the system reaches a low state of conversion. After the reaction rate has decreased and the surface is covered with CO, the reduction of the catalyst begins and the activity and the temperature of the catalyst increase. As a consequence the desorption of CO accelerates and the system returns to the high rate of CO oxidation. This mechanism would account for the observable temperature oscillations with an amplitude of between 1–2°C. Temperature therefore plays an important role in the mechanism of the observed oscillations.

This hypothesis is supported by the observation that the activity of the oxidized catalyst can even decrease with the increase of temperature (see Fig. 4). The experimental data also show that the reduction of the catalyst leads to an increase in its activity and in the local temperature, which in turn causes the acceleration of the reaction rate due to CO desorption.

The observation of the complicated behavior shown in Fig. 10 might be interpreted by the assumption of two kinds of oxidation–reduction processes in the studied system. Regular single-peak relaxation oscillations at low temperatures indicate the presence of two time scales. The "fast" time scale belongs to steps of adsorption, desorption, and reaction. The "slow" time scale is associated with the oxidation–reduction process of the first kind. This kind of oxidation–reduction process moves the system from one kinetic branch to another. The presence of the third time scale process increases the complexity of the observed oscillatory behavior. This process slowly modifies catalyst activity and changes the positions and intersections of the reaction rate curve and the adsorption line in Fig. 11. The existence of a second type of oxidation–reduction process leads to the superposition of fast high-frequency oscillations (attributable to the fast oxidation–reduction cycle) on a relaxation-type low-frequency process (attributable to the slow oxidation–reduction cycle). The nature of the two kinds of oxidation–reduction cycles must be established in future work. One suggestion would be that there are two types of palladium oxides, differing in the rates of their formation and reduction, e.g., a surface and a bulk oxide.

Another interesting feature which must be accounted for is the marked difference between regular oscillations for an oxidized catalyst and aperiodic oscillations for the reduced catalyst. This observation could be understood in terms of a desynchronization of the catalyst surface for reduced catalysts and might be connected with the average concentration of palladium oxide and its distribution across the catalyst surface. The spatial propagation of oscillatory behavior is indeed affected by the separation of active centers, as has been shown by Sant and Wolf by *in situ* selected-area FTIR spectroscopy for the CO oxidation on Pt/SiO_2 (*27*).

As derived from previous experiments (*9, 10*), concentration waves of surplus CO spreading from particles which had just undergone a phase transition to PdO (and therefore are no longer reactive) are assumed to be the synchronizing mechanism for macroscopically visible reaction rate oscillations. Such a concentration wave will drive neighboring and still active Pd particles to an enhanced reaction rate and in this way increase their tendency to form PdO due to the locally heightened heat production.

This is supported by experiments aimed at the impact of an external periodic variation of the CO inlet concentration (*28*) on autonomous oscillations. It could be verified that the concentration waves are able to synchronize aperiodic behavior of the autonomously oscillating reaction leading to strictly periodic behavior of the forced system.

If there are only small patches of inactive PdO surface sites surrounded by a large number of active Pd particles, CO concentration waves will die out in the vicinity of their triggering center, which means that their synchronizing effect is constricted to a limited area of the catalyst surface. This could lead to spatially nonuniform reaction rates, locally oscillating regions, and waves traveling on the surface of the catalyst as observed by Brown *et al.* (*29*) and Kaul and Wolf (*12, 30*) by *in situ* measurements of the temperature and the CO coverage.

The low activity of the oxidized catalyst should be attributed to a high concentration of palladium oxide particles, which generates a rather continuous distribution of inactive sites. Therefore CO concentration waves may spread across larger areas of the catalyst surface before reaching active sites, thus causing an enforced synchronization among locally acting catalyst regions.

A far more convincing explanation is the coupling of differently acting surface areas. With slowly changing constraints (it should be pointed out that Fig. 5 shows transient behavior) the differently acting regions of the catalyst might reach their own oscillatory state, thereby increasing the overall amplitude of the oscillations in a stepwise manner by means of synchronization (entrainment) and resonant behavior.

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