

Oscillations during CO Oxidation over Supported Metal Catalysts

II. Effects of Reactor Operating Conditions on Oscillatory Behavior for a (Pt-Pd)/Al₂O₃ Catalyst

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The oscillatory behavior occurring during CO oxidation over a (Pt-Pd)/ γ -Al₂O₃ catalyst was studied in an isothermal recycle reactor. The effects of recycle ratio (0-50), gas phase temperature (373-423 K), feed composition (0.053-0.43 mole% CO, 50-99% O₂), feed flow rate (78-445 μ mol/s), and reactor pressure (0.1-0.2 MPa) were examined. Care was taken to ensure that the catalytic activity remained constant throughout the investigation. The results indicate that oscillations are caused by changes in the rate controlling step coupled with heating of the metal crystallites to temperatures above those of the support and gas phase. It is proposed that the rate controlling step changes from oxygen adsorption to surface reaction followed by rapid burn-off (ignition) of adsorbed CO and oxygen.

INTRODUCTION

The occurrence of self-sustained oscillations during the oxidation of CO over supported metal catalysts has been firmly established during the last decade. In a review article several years ago, Sheintuch and Schmitz (1) stated that there was a declining need for studies which simply demonstrate the existence of oscillatory behavior for reactions such as CO and H₂ oxidation. They also pointed out that there was a need for experiments which studied the causes of oscillatory behavior. Many reports of oscillatory behavior during the oxidation of CO have appeared since the review by Sheintuch and Schmitz (1), but most reports only confirm the existence of oscillatory behavior and do not give details regarding the influence of operating conditions (e.g., 2-4). A notable exception is the recent study by Rathousky and Hlavacek (5). These authors systematically investigated the effects of temperature, concentration, and amount of catalyst on the oscillatory

behavior for CO oxidation over a Pt/Al₂O₃ catalyst.

In this paper we report the results of a systematic study dealing with the influence of operating conditions on the oscillatory behavior occurring during the oxidation of CO over a well-characterized (Pt-Pd)/ γ -Al₂O₃ catalyst. The parameters investigated included external mass transfer, concentrations, temperature, total pressure and total feed rate. Great care was taken to ensure that the catalytic activity remained constant during these investigations since previous studies (6) showed that exposure to certain operating conditions causes significant changes in catalytic activity and oscillatory behavior. The objective of this study was to gain insight into the causes of self-sustained oscillations.

EXPERIMENTAL METHODS

Catalyst and Materials

The catalyst used in this work was a commercial 0.04 wt% Pt-0.04 wt% Pd on γ -Al₂O₃ catalyst (Cat 4 in Ref. (6)). The γ -Al₂O₃ support had a BET surface area of 85 m²/g, and the mean pore radius, determined by Kelvin condensation of nitrogen, was

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6.5 nm. The results of chemisorption and electron microscopy studies on this catalyst have been reported previously (6).

Prior to use for CO oxidation, the catalyst was pretreated in dry flowing air at 620 K for 12 h and exposed to five CO–O₂ pulse treatments at 423 K. It had been determined (6) that this type of pretreatment stabilizes the catalytic activity provided that the catalyst is not used for CO oxidation at temperatures above 423 K. A single 20-g charge of the catalyst was used for all results reported in this study. However, the behavior reported was reproducible with fresh catalyst charges as long as the above pretreatment was carried out. The sources of the reactants and diluents were the same as in the previous study (6).

Equipment

The recycle reactor, analytic instrumentation and other associated equipment have been described previously (6). However, an auxiliary reactor (designated as AR in Fig. 1, Ref. (6)) was added to the equipment. The auxiliary reactor was constructed from a stainless-steel tube, 250 mm long and 12-mm i.d., and contained 10 g of 4% Pt/Al₂O₃ catalyst. A resistance heater connected to a temperature controller was used to maintain the inside temperature of the auxiliary reactor at 500 K. The valving arrangement was such that the effluent from the main reactor could be passed through the auxiliary reactor or by-passed around it. In either situation, the gas stream could subsequently be sent to the ir and/or gc for analysis.

All the CO in the effluent from the main reactor was converted to CO₂ if the flow was routed through the auxiliary reactor. This conversion was desirable since the ir sensitivity for CO₂ concentration measurements was about an order of magnitude greater than that for CO. Thus, very sensitive determinations of low CO concentrations in the effluent from the main reactor could be made by measuring the difference between the concentrations of CO₂ in the

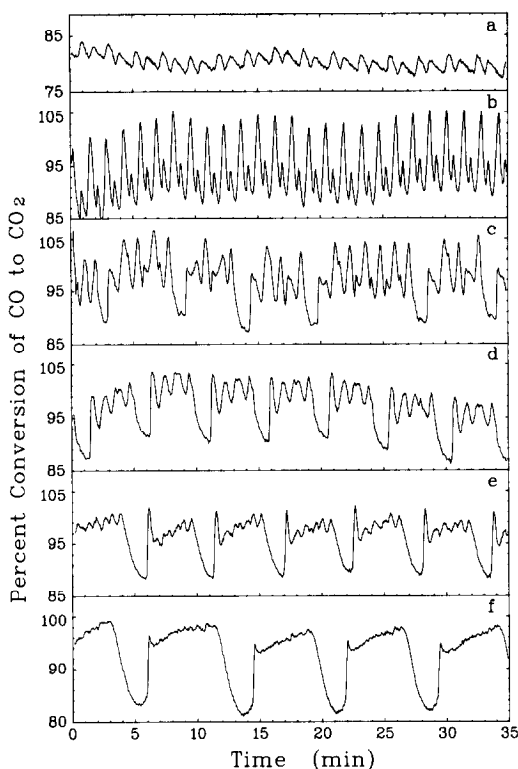


FIG. 1. Effect of recycle ratio, R , on CO₂ oscillations: (a) $R = 0$; (b) $R = 0.95$; (c) $R = 1.55$; (d) $R = 2.67$; (e) $R = 4.03$; (f) $R = 17.4$

effluents from the main and auxiliary reactors.

EXPERIMENTAL RESULTS AND DISCUSSION

External Mass Transfer Effects

The influence of external mass transfer effects for reactions carried out in a recycle reactor can be easily examined by observing the changes in reaction rates due to changes in the recycle ratio. Shown in Fig. 1 are the variations in CO conversion as a function of the recycle ratio with all other operating parameters held constant. For this and all subsequent figures, the pertinent reactor operating parameters are listed in Table 1.

It is seen in Fig. 1a that a small amplitude oscillation was observed in the CO₂ concentration in the main reactor effluent when the reactor was operated without recycle.

TABLE 1
Reactor Operating Parameters for Figs. 1-8

Figure	Reactor temp (K)	Reactor press (MPa)	Molar feed rate ($\mu\text{mol/s}$)	Feed composition (mol%)			Recycle ratio
				CO	O ₂	N ₂	
1	393	0.10	106	0.29	97.4	2.4	0-17.4
2	393	0.10	115	0.32	97.1	2.6	34
3	388-423	0.10	110	0.33	97.0	2.7	34
4a	393	0.10	88	0.43	96.1	3.5	46
4b	393	0.10	185	0.20	98.2	1.6	21
4c	393	0.10	295	0.126	98.9	1.0	13
4d	393	0.10	445	0.085	99.2	0.7	8
5	393	0.10	240-78	0.24	97.8	1.9	16-51
6	393	0.10	108	Figure caption	96.4-99.5	3.2-0.4	36
7	393	0.1-0.2	112	0.30	97.3	2.4	35
8	393	0.10	115	0.33	See figure caption		34

Careful examination of this oscillation reveals that there are two distinct peaks per cycle. This oscillatory behavior is not solely attributable to the kinetic mechanism of the reaction, since mass transfer calculations indicate that significant external transport limitations were present. External mass transfer coefficients were determined from the correlation of Petrovic and Thodus (7). It should be pointed out that even at high recycle ratios external mass transfer effects will always become important when the CO conversion approaches 100%. External temperature gradients, calculated using the *j*-factor analogy, were always negligible (<0.2 K for all runs).

After the recycle pump was started and the recycle ratio was set at a value near unity, it is seen in Fig. 1b that the doublet nature of the oscillation was reinforced so that the oscillation is clearly seen to possess a two-peak per cycle character. The mass transfer calculations indicate that transport limitations were still present over much of the conversion region for which the oscillations occurred.

The recycle ratio was further increased (Fig. 1c) and it is seen that the oscillations are now interfering with each other. However, besides the sharp peaked oscillations

in the mass transfer limited region, it is seen that a second phenomenon characterized by a broad drop in the conversion, occurred in the conversion region ($\leq 90\%$) where mass transfer limitations were not large. In Figs. 1d and e it is shown that, upon further increases in the recycle ratio, the second type of phenomenon increasingly dominated the oscillations. Finally, in Fig. 1f, it is seen that the sharp peaked oscillations have essentially been reduced to the noise level in the high conversion regions. Mass transfer calculations indicate that the oscillations shown in Fig. 1f were occurring in the absence of significant external mass transfer limitations except for those parts of the cycle which were located in the region above about 98% conversion. Further increases in the recycle ratio to 35 did not alter the oscillatory behavior. Thus, these oscillations were a manifestation of the underlying kinetic behavior. It is unlikely that internal mass transfer limitations affected the behavior for cases where external transport effects were negligible since the catalytically active metal was located in a very thin layer at the external surface of the pellets. Internal temperature gradients, as is discussed below, probably play a very important role in the oscillatory behavior.

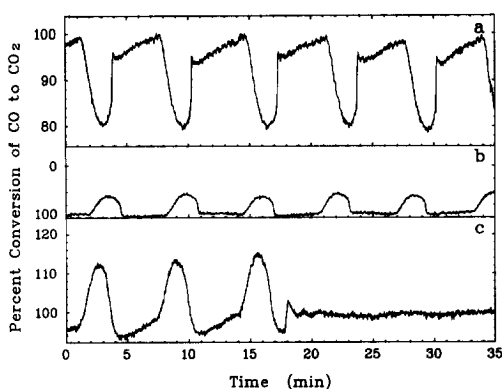


FIG. 2. Characteristic CO_2 , CO, and combined $\text{CO}-\text{CO}_2$ oscillations: (a) CO_2 from main reactor; (b) CO from main reactor; (c) CO_2 from auxiliary reactor (total of $\text{CO} + \text{CO}_2$ from main reactor).

Events Occurring during an Oscillatory Cycle

Shown in Figs. 2a and b are typical oscillations of CO_2 and CO concentrations in the effluent from the main reactor. These CO_2 and CO oscillations were not recorded simultaneously since the ir spectrophotometer could only monitor one frequency at a time. The slight mismatch in the oscillations is due to the sequential nature of the recordings. Shown in Fig. 2c are the oscillations which resulted when the effluent from the main reactor was passed through the auxiliary reactor so that all of the CO was converted to CO_2 . The approximately straight tracing in the rightmost part of Fig. 2c was the result of by-passing the feed stream around the main reactor so that it passed directly through the auxiliary reactor; this tracing represents the 100% conversion line. A comparison of Figs. 2a-c shows that there was no phase lead or lag between the CO and CO_2 concentration oscillations. The oscillations in Fig. 2c appear to be a direct combination of those in Figs. 2a and b once the differences in the ir sensitivities of CO and CO_2 are taken into account. Any phase lead or lag between the CO and CO_2 oscillations would show up in the form of local maxima, minima, and/or extra points of inflection in Fig. 2c. This absence of phase differences is a further in-

dication that the oscillations occurred in the absence of significant mass transport limitations.

A detailed examination of the dynamic behavior of CO_2 , CO, and combined CO_2-CO shown in Fig. 2 yields valuable insight into the phenomena occurring during oscillations. The oscillation at about 10–17 min in Fig. 2 will be used as an illustration. Observations for the above oscillation, which are similar to those for other oscillations, are summarized in Table 2. The observations in Table 2 can be phenomenologically explained by assuming that the adsorption rate for O_2 is less than half that for CO, and that large temperature differences exist between the metal crystallites and the bulk phases when the reaction rate is large. These assumptions are not unfounded;

TABLE 2
Description of Oscillation Shown in Fig. 2

Region	Time (min)	Figure Part	Behavior of bulk CO_2 , CO, and CO plus CO_2 concentrations
1	10–10.5	a	Very rapid increase in CO_2 concentration
		b	Very rapid decrease in CO concentration to zero
		c	Combined CO plus CO_2 in product decreases from greater than to less than amount of CO in feed
2	10.5–14.5	a	Gradual increase in CO_2 concentration
		b	No CO in product
		c	Combined CO plus CO_2 in product less than CO in feed
3	14.5–16.5	a	Fairly rapid decrease in CO_2 concentration
		b	Fairly rapid increase in CO concentration
		c	Combined CO plus CO_2 in product exceeds amount of CO in feed

Engel and Ertl point out that the incorporation of oxygen into ordered adsorbed structures is slow (8), and experimental evidence has been reported that significant local temperature differences can exist on the surfaces of catalysts during adsorption and reaction (9-11).

Based on the above two assumptions, the following events are postulated to occur during an oscillatory cycle (see Table 2 and Fig. 2 for description of regions). In region 1 essentially all CO and oxygen on the catalyst surface react to form CO₂. Due to the rapidity of the reaction, the temperature of the metal crystallites rises substantially above that of the bulk phases. In region 2 all CO entering the reactor adsorbs on the surface, however this CO does not all react as the reaction is limited by the adsorption of O₂. Essentially all of the O₂ that adsorbs immediately reacts thus the surface temperature remains above that of the bulk phases. Due to the differences between the adsorption rates of CO and O₂, accumulation of CO on the surface occurs. At the beginning of region 3, the CO accumulating on the surface increasingly inhibits the rate of O₂ adsorption. Since the overall reaction rate is primarily limited by the O₂ adsorption rate, the reaction rate begins to decrease. A decrease in reaction rate leads to a decrease in surface temperature which further decreases the reaction rate. This feedback effect causes the surface temperature and the reaction rate to rapidly drop. As the surface temperature drops, the overall reaction rate ceases to be limited by O₂ adsorption (surface reaction becomes limiting), and oxygen begins to accumulate on the surface. Eventually a point is reached at which the decrease in reaction rate due to decreasing temperature is offset by the increase in reaction rate due to the increasing value of the product of the surface concentrations of oxygen and CO. An increasing reaction rate leads to an increasing surface temperature and this autothermal effect causes the reaction to ignite, thus completing the cycle.

The output from the auxiliary reactor was particularly useful in elucidating the above sequence of events. In region 2 it is clearly seen that CO is accumulating on the surface as the output from the auxiliary reactor shows that only about 95-98% of the CO entering the reactor leaves as CO or CO₂. This accumulation of CO can be quantitatively determined from Fig. 2c by finding the amount of CO₂ production in excess of 100% conversion in regions 1 and 3. This calculation shows that approximately 4 μ mol of CO accumulates on the surface. This means that about 25% of the available sites are occupied by CO during part of the oscillatory cycle (based on measured CO/M of 0.14; also see Table 1 in Ref. (6)). This was not the maximum CO accumulation which could occur during an oscillatory cycle; for other operating conditions as much as 13 μ mol of CO accumulated during a cycle.

In the following sections the effects of various reactor operating conditions on the oscillatory behavior are presented. In each case an examination will be made of the consistency of the experimental observations with the preceding phenomenological description of the oscillatory cycle.

Bulk Temperature Effects

The influence of bulk temperature on the conversion of CO to CO₂ is shown in Fig. 3. The reactor operated at a low to intermediate conversion stable steady state if the temperature was ≤ 388 K. As the temperature was raised above 388 K, the reactor ceased to operate at a stable steady state and instead oscillatory behavior was observed. As the temperature was further increased, the frequency and amplitude of the oscillations decreased and the oscillations became less regular. This erratic nature of the oscillations in Figs. 3d and e was probably due to a coupling of mass transfer and kinetic effects, as significant mass transfer limitations existed when the conversions exceeded 98%.

In Fig. 3 it is seen that, as the tempera-

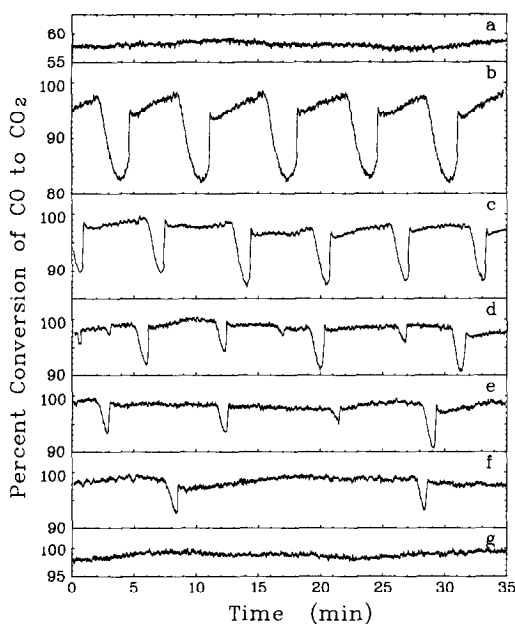


FIG. 3. Bulk temperature effects on CO_2 oscillations: (a) 388 K; (b) 393 K; (c) 398 K; (d) 403 K; (e) 408 K; (f) 413 K; (g) 423 K.

ture increased, the average conversion in the high conversion region (region 2 in preceding section) increased, thus leaving less unreacted CO to accumulate on the surface. Due to the lower rate of CO accumulation, the inhibition of the O_2 adsorption with subsequent lowering of the surface temperature takes longer to occur. Hence the oscillatory cycle stays in the high conversion region for increasing lengths of time. This is the main cause of the lengthening of the period with increasing temperature.

The decrease in the amplitude of the oscillation with increasing temperature is caused by an increasing value of the surface reaction rate constant. As previously hypothesized, the cycle will remain in the low conversion region until sufficient oxygen accumulates to provide high reaction rates with subsequent ignition of the reaction due to surface temperature increases. As the bulk temperature increases, less oxygen accumulation is necessary to provide ignition. Thus, the amplitude of the oscillation will decrease since the time between reaction

inhibition and ignition will decrease due to the decreasing time necessary for oxygen accumulation.

Effects of Total Molar Feed Rate

The effects of varying the total molar feed rate to the reactor while maintaining a constant molar feed rate of CO are shown in Fig. 4. It is seen in Fig. 4a that at a low feed rate (high CO concentrations in feed) the reactor operated at a stable intermediate conversion steady state. However, when the total feed rate was increased (with a concomitant decrease in the CO feed concentration) a periodic oscillation replaced the stable steady state. Upon further increases in the total feed rate it is seen that the amount of time spent in the high-conversion part of the oscillation was initially unaffected (cf. Figs. 4b and c) and then subsequently increased slightly (cf. Figs. 4c and d). Since the CO feed rate was constant, the amount of time to accumulate a fixed amount of surface CO should be independent of the total molar feed rate as long as the conversions in the high-conversion region did not differ significantly. In all three cases, the amounts of CO accumulated on the surface were approximately equal, since from the auxiliary reactor it was determined that about 25% of the available sites were occupied by CO during the

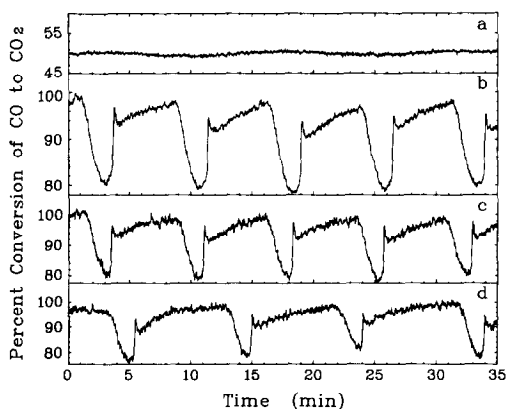


FIG. 4. Effect of total molar feed rate (constant CO molar flow) on the CO_2 oscillations (see Table 1 for pertinent parameters).

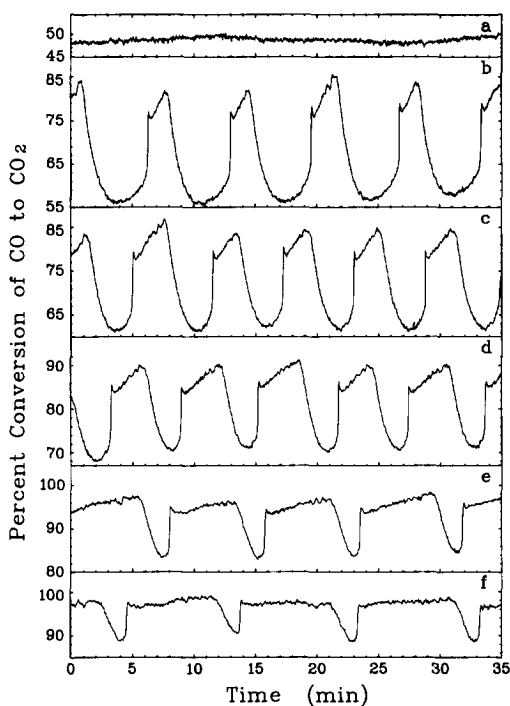


FIG. 5. Effect of total molar feed rate (constant composition) on the CO₂ oscillations: (a) 240 $\mu\text{mol/s}$; (b) 199 $\mu\text{mol/s}$; (c) 165 $\mu\text{mol/s}$; (d) 141 $\mu\text{mol/s}$; (e) 97 $\mu\text{mol/s}$; (f) 78 $\mu\text{mol/s}$.

accumulation phase for any of the oscillations shown in Fig. 4. In each of Figs. 4b–d it is seen that the amplitude of the oscillations are approximately constant. This is to be expected since the amount of O₂ adsorption needed to remove the accumulated CO is the same in each case.

Displayed in Fig. 5 are the effects of varying the total molar feed rate with the overall feed composition held constant. It is seen that, consistent with the preceding results, the time spent in the high-conversion region increased as the rate of CO entering the reactor decreased. This was due to the increasing times needed to accumulate sufficient CO to inhibit O₂ adsorption when the CO molar feed rate became small. The large decrease in the amplitude of the oscillations as the feed rate was decreased is due to the additional CO which continues to adsorb while the surface oxygen begins to accumulate (after the reaction is extin-

guished). At low CO molar flow rates, the CO which is eliminated by reaction cannot be quickly replaced. Thus, the inhibiting influence of the adsorbed CO can be quickly neutralized leading to short times between reaction extinction and ignition with commensurate small amplitudes. At high CO molar flow rates, the surface CO which is eliminated by reaction is largely replaced from the large CO flow entering the reactor, thus the inhibiting influence is maintained for long periods of time. This results in large amplitude oscillations.

Effects of Feed Composition

The effects of variation of the feed concentration with the total molar flow rate held constant are shown in Fig. 6. It is seen that, at high CO concentrations in the feed, the reactor operated at a stable intermediate conversion steady state, while at low concentrations a stable high-conversion steady state was reached. At intermediate concentrations, the reactor effluent compo-

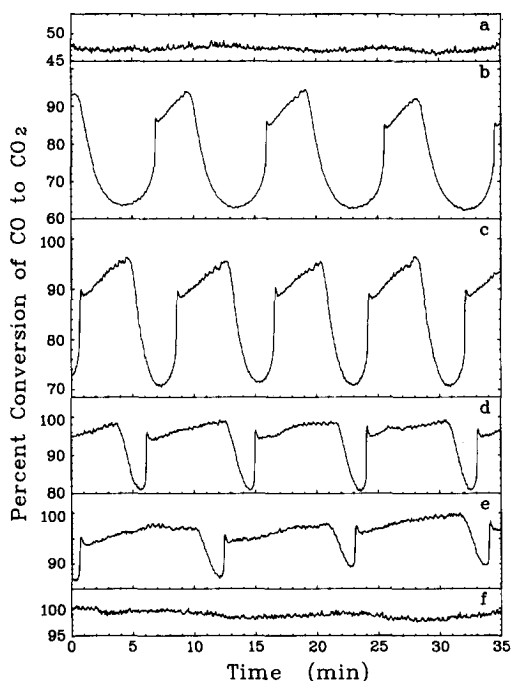


FIG. 6. Effect of feed CO concentration on the CO₂ oscillations: (a) 0.40% CO; (b) 0.37% CO; (c) 0.32% CO; (d) 0.27% CO; (e) 0.22% CO; (f) 0.053% CO.

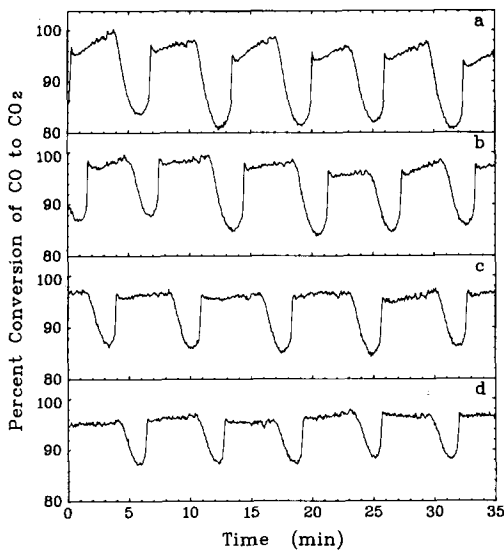


FIG. 7. Effect of reactor pressure on the CO_2 oscillations: (a) 0.10 MPa; (b) 0.13 MPa; (c) 0.17 MPa; (d) 0.20 MPa.

sition oscillated, and the explanation of the variations in the period and the amplitude is identical to that given in the preceding section. The explanations are identical because in both Figs. 5 and 6 the molar flow of CO to the reactor continually decreases in going from parts a to f, and this apparently is the most important variable in dictating the characteristics of the oscillations.

Effects of Reactor Pressure

The importance of the molar feed rate of CO is further emphasized in Fig. 7 in which the effects of the reactor pressure on the oscillatory behavior are depicted. It is observed that the amount of time spent in the high-conversion part of the oscillations was independent of the pressure. This is consistent with the preceding explanations since this amount of time appears to be solely related to the molar flow of CO into the reactor which was constant for the four cases. The decreasing amplitudes of the oscillations as the pressure was increased is attributed to increasing rates of O_2 adsorption at the higher pressures. Larger rates of O_2 adsorption after the reaction has extinguished result in more rapid neutralizations

of the inhibiting effects of the adsorbed CO with resulting decreases in the amplitude of the oscillations.

Effects of N_2 and He Diluents

The influences of N_2 and He diluents on the oscillatory behavior are displayed in Fig. 8 where oscillations of the CO concentration in the main reactor effluent are shown. At point A in Fig. 8, about one-quarter of the O_2 in the feed was replaced with N_2 . It is seen that the resulting decreased rate of O_2 adsorption during the low-conversion part of the cycle causes the oscillation to increase both in amplitude and in time between extinction and ignition.

At point B in Fig. 8, the N_2 diluent was replaced with an equal amount of He diluent. It is seen that the effects of the He are almost the same as those of the N_2 . This implies that heat transfer from the metal crystallites to the gas phase must not be the predominant mode by which the energy released by reaction is dissipated. The primary mode of heat transfer is probably by conduction to the bulk support.

At point C in Fig. 8, the amount of He in

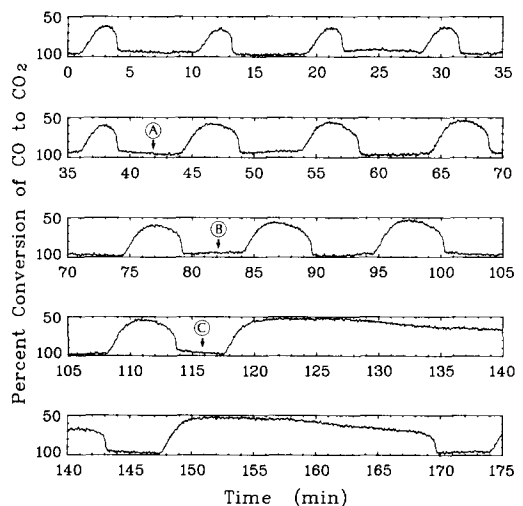


FIG. 8. Effect of N_2 and He diluents on CO oscillations: Before A—97.0% O_2 , 2.7% N_2 ; after A—70.2% O_2 , 29.5% N_2 ; after B—70.2% O_2 , 2.7% N_2 , 26.8% He; after C—50.1% O_2 , 2.7% N_2 , 46.9% He (see text for details).

the feed was increased so that the O₂ concentration was about one-half of that existing before point A. It is seen that the amplitude of the oscillation increased slightly, but that the period increased dramatically. As before, this increase in the time necessary for the reaction to proceed from extinction to ignition is attributed to the decreased rate of O₂ adsorption resulting from the dilution of the feed stream. Further increases in the diluent concentration resulted in the disappearance of the oscillatory behavior with the system passing to a stable low- to intermediate-conversion steady state. It is worth noting that, despite the large increase in the total period of the oscillation, the time spent in the high-conversion region of the oscillations was essentially independent of the use of the diluents. This reaffirms that it is the CO accumulation on the surface which determines the time spent in the high-conversion part of the cycle.

The same catalysts charge had been used for about 250 h at reaction temperatures ≤ 423 K for obtaining the results reported above. Previously reported results (Fig. 7, Ref. (6)) showed that the catalytic activity remained constant throughout these experiments. The catalyst charge was subsequently used at 433 K and high CO concentrations. Attempts to reproduce the oscillatory behavior at 393 K reported in Figs. 2-7 were unsuccessful since the exposure to higher temperature had resulted in an increase in catalytic activity. This is in agreement with the previously reported effects of treatment and use on the catalytic activity of the Pt-Pd/ γ -Al₂O₃ catalyst.

SUMMARY AND CONCLUSIONS

The results presented on the influence of operating conditions on the oscillatory behavior during CO oxidation over a supported Pt-Pd catalyst suggest that the oscillatory behavior is caused by changes in rate-controlling steps coupled with significant temperature differences between metal particles and bulk phases. During the

high-conversion part of a cycle, the temperature of the metal particles is initially much higher than the support and gas-phase temperatures, and the rate-determining step is oxygen adsorption and possibly mass transfer. The rate-limiting oxygen adsorption results in a decrease in the reaction rate which causes the metal temperature to decrease. CO is accumulating on the metal surface during this stage. When the rate has decreased sufficiently, the surface reaction between adsorbed oxygen and CO becomes rate controlling, and the concentrations of adsorbed CO and oxygen increase. Finally, the stage is reached where increases in the concentrations of adsorbed species result in an increased reaction rate which brings about increases in the metal particle temperatures. This causes a rapid burn-off of the adsorbed species, and the system is returned to the high-conversion state. All of the observations are in agreement with this proposed sequence of events.

Dagonnier and co-workers (12, 13) have proposed a model in which variations in surface temperature are responsible for oscillations in concentrations of adsorbed species. They did not include variations in bulk phase concentrations which, according to our results, have a significant influence on oscillatory behavior. We have developed a general model based on the phenomenological observations reported in this paper. Preliminary predictions of this model have shown semiquantitative agreement with the experimental observations (14). A variety of complex behavior is predicted by the model, but the complexity of the model (six coupled highly nonlinear first-order ordinary differential equations containing 15 independent parameters) has precluded detailed exploration of the parameter space. Even a reduced version of the model, which replaces the heterogeneous recycle reactor by a homogeneous mixed reactor and only consists of three differential equations, presents a formidable numerical problem (15). It should be noted that even this reduced model can pre-

dict the occurrence of very complex dynamical behavior, such as chaos, in certain parameter regions. Work on the general model is continuing; the main deficiency is the lack of reliable values of adsorption and surface reaction rate constants as functions of temperature.

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