JOURNAL OF CATALYSIS 88, 333–344 (1984)

Oscillations during CO Oxidation over Supported Metal Catalysts

I. Influence of Catalyst History on Activity

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Received August 1, 1983

The oxidation of CO over one (Pt–Pd)/Al_2O_3 and three Pt/Al_2O_3 catalysts was studied in a recycle reactor. The objective of the study was to investigate the occurrence of self-sustained oscillatory behavior during CO oxidation over supported metal catalysts. Oscillatory behavior was observed for all the catalysts studied; however, the oscillatory behavior and the stable steady-state activities were strongly affected by the history of the catalyst, i.e., prior treatment and reaction conditions. The influences of treatment and reaction conditions on oscillatory and catalytic behavior are described. Hydrogen and CO chemisorption, CO–O_2 titrations, and transmission electron microscopy were used to gain insight into the changes in metal surface area resulting from treatment and use.

INTRODUCTION

Numerous investigations of the catalytic oxidation of CO over group VIII metals have been carried out since the pioneering work of Langmuir over 60 years ago (*1*). During the past decade the occurrence of self-sustained oscillation during CO oxidation over supported (e.g., *2–7*) and unsupported (e.g., *8–12*) catalysts has received special attention. However, the nature of the oscillations and the conditions under which oscillations are observed vary widely among studies on apparently similar catalysts. Even repeat experiments on the same catalyst sample often yield irreproducible results under both oscillatory (*5, 6, 9, 11–13*) and nonoscillatory (*1, 14–16*) conditions.

Varghese *et al.* (*6*), e.g., report that no oscillatory behavior was observed during CO oxidation at 370 to 410 K over a fresh Pt/Al_2O_3 catalyst which had been pretreated in hydrogen and argon at 773 K followed by a 2-h oxygen pretreatment at 473 K. However, oscillatory behavior was observed on the same catalyst sample at 373 K after it had been used in CO oxidation runs at 473 K. This indicates that pretreatment at temperatures considerably above the subsequently used reaction temperature does not necessarily result in catalysts with stable activities. Pretreatments in oxygen or air at temperatures of 750 to 990 K, i.e., more than 200°C above the reaction temperature, have resulted in reproducible behavior (*10, 16–18*). Franck *et al.* (*12*) report that hydrogen pretreatment at 943 K for 1.5 h resulted in reproducible results for CO oxidation at 533 K over a bulk rhodium catalyst. Such severe pretreatment conditions can result in sintering of supported metal catalysts, and it is of interest to determine the changes in catalytic behavior which occur as a result of less severe pretreatment and reaction conditions.

In the present study we report changes of catalytic activity for supported Pt and Pt–Pd catalysts occurring during CO oxidation. Special emphasis is given to the influence of catalytic history on the occurrence of oscillatory behavior. Hydrogen and carbon monoxide adsorption measurements and transmission electron microscopy examinations of catalyst samples were done in addition to the activity studies in order to

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0021-9517/84 $3.00

TABLE 1

Properties of Catalysts Used in Study

Catalyst	Support area (m^2/g)	Metal and loading (mass %)	Hydrogen and carbon monoxide adsorption results		
			Treatment prior to adsorption[a]	Adsorption H/M	Uptakes CO/M
1	100	0.3% Pt	H_2, 300°C, 1 h	0.33	0.31
			H_2, 500°C, 1 h	0.41	0.29
			O_2, 550°C, 16 h; H_2, 500°C, 1 h	0.79	0.36
2	200	0.05% Pt	H_2, 500°C, 1 h	0.25	—
3	200	0.05% Pt	H_2, 300°C, 1 h	0.16	0.23
			H_2, 500°C, 1 h	0.18	0.22
			O_2, 550°C, 1 h; H_2, 500°C, 1 h	0.55	0.45
4A[b]	85	0.04% Pt and	H_2, 250°C, 1 h	0.51	0.16
		0.04% Pd	H_2, 500°C, 1 h	0.12	0.09
			O_2, 550°C, 1 h; H_2, 250°C, 1 h	0.38	—
			O_2, 550°C, 1 h; H_2, 500°C, 1 h	0.15	—
4B[b]			H_2, 250°C, 1 h	0.29	0.15
			H_2, 500°C, 1 h	0.07	0.09
4C[b]			H_2, 250°C, 1 h	0.18	0.18
			H_2, 500°C, 1 h	0.05	0.14
4D[b]			H_2, 250°C, 1 h	0.15	—
			H_2, 500°C, 1 h	0.02	—

[a] For H_2 adsorption, samples were degassed in flowing N_2 for 2 h at the H_2 treatment temperature; no degassing at elevated temperatures done prior to CO adsorption.

[b] Catalysts 4A, B, C, and D are GM converter catalyst after various stages of use: Cat 4A, fresh sample; Cat 4B, pretreated in air at 620 K for 12 h; Cat 4C, after use in CO oxidation at 393 K; Cat 4D, after use for runs shown in Fig. 5.

gain insight into possible changes brought about by pretreatment and reaction.

EXPERIMENTAL METHODS

Materials

The four catalysts used in this work are described in Table 1. Cat 1, purchased from Engelhard, consisted of 3.2 × 3.2-mm cylindrical pellets with the Pt located in a thin shell at the exterior portion of the pellets. The other three catalysts were in the form of 3.2-mm spherical pellets. Cat 4 is a General Motors, type 78925, converter catalyst.

The support surface areas were determined by the BET method, and X-ray diffraction measurements showed that all the supports were γ-Al_2O_3 (*19*). Cat 2 and 3 were prepared by impregnation of 3.2-mm γ-Al_2O_3 spheres with aqueous solutions of H_2PtCl_6. For Cat 2, the impregnation and drying was done in a beaker. This procedure resulted in a visually detectable uneven distribution of Pt among, as well as within the pellets. For Cat 3, the impregnation and drying steps were done in a rotating vacuum evaporator. This procedure resulted in a much more homogeneous Pt distribution.

Reactor and Associated Equipment

A schematic diagram of the reactor and auxiliary equipment is shown in Fig. 1. Feed mixtures (CO–N_2–O_2) of the desired compositions and flow rates were obtained with the feed metering and mixing devices shown in Fig. 1. The CO was obtained from a high pressure cylinder containing 11% CO in N_2. The flow rate was regulated with a needle valve, and was continuously monitored by a Matheson linear mass flowmeter.

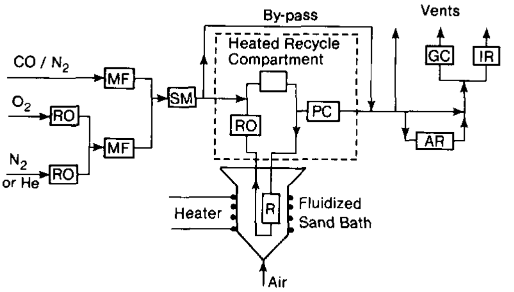

FIG. 1. Schematic diagram of equipment (AR, auxiliary reactor; GC, gas chromatograph; IR, infrared spectrophotometer; MF, linear mass flowmeter; P, metal bellows pump; PC, pressure controller; R, main reactor; RO, rotameter; SM, static mixer).

Oxygen and nitrogen flow rates were individually measured using calibrated rotameters, and the combined O_2 and N_2 flow rate was continuously monitored by another linear mass flowmeter. Linde Very Dry Grade N_2 (99.99%) and O_2 (99.96%) were used in most runs. Matheson Ultra High Purity O_2 (99.99%) was used in some runs to determine whether trace impurities affect oscillatory behavior (*6*). No effect of the impurity level of the O_2, which usually made up more than 80% of the feed, was observed. A static mixer, located after the metering section, was used to thoroughly mix the feed gases before they entered the recycle reactor system.

The reactor system consisted of a heated recycle compartment and a tubular reactor. External recycle was achieved by a metal bellows pump driven by a variable speed DC motor. The flow from the bellows pump, at 1800 rpm, was about 130 cm^3/s; this corresponded to recycle ratios greater than 10, and usually in the range 30–50, for the feed rates employed. The reactor was located outside the recycle compartment and was surrounded by a fluidized sand bath for temperature control. The tubular reactor, 160 mm long and 25-mm i.d., was made of 316 stainless steel. The total volume of the reactor and associated recycle equipment was 250 cm^3. Eight thermocouples were used to measure the temperature at various locations in the reactor; three in the catalyst bed, three on the reactor wall adjacent to the catalyst bed, and one above and another below the catalyst bed. Another thermocouple, located at the reactor inlet, supplied the input to the temperature controller which regulated the temperature of the fluidized sand bath. Excellent isothermality of the gas-phase temperature in the catalyst bed (variations <0.2 K) was achieved during all runs in which oscillations occurred. Exceptions to this isothermal operation were observed in some of the runs which are described later. The pressure in the reactor and recycle loop was regulated by a differential flow controller. The exit stream from the recycle compartment was routed to the chemical analysis equipment. The auxiliary reactor, shown in Fig. 1, was not used in the work reported in this paper. Its function will be described in a subsequent paper (*20*).

Experimental Procedure and Chemical Analysis

All catalyst samples were pretreated in dry flowing air at 620 K for 12 to 18 h before being placed into the reactor. With one exception (Cat 2), 20 g or less of pretreated catalyst was charged to the reactor. If less than 20 g of catalyst was used, then inert aluminum cylinders or spheres were added so that the total charge of catalyst plus diluent was 20 g.

The usual startup procedure consisted of flushing the reactor system with nitrogen while the reactor and recycle compartment were being heated to the desired temperature. The desired amount of O_2 was mixed with the N_2 during this heating period. The CO/N_2 flow was started when the desired temperature had been attained. The sequence of O_2 and CO introduction are important as the results below will show. Feed flow rates, temperatures, and CO_2 or CO product concentrations were continuously recorded during a run.

The CO_2 or CO concentration in the product stream was measured continuously with a Pye Unicam (Model SP3-200) ratio recording infrared spectrophotometer. The absorbances at 2355 or 2172 cm^{-1} were used for CO_2 and CO analyses, respectively. The data processor on the ir instrument was used for accurate placement of the monochromator for constant wave number scanning as well as for conversion of transmittance to absorbance. Absorbances of either CO_2 or CO were converted to CO conversions using absorbance–concentration curves. Usually CO_2 absorbances were used, since the CO_2 signal was about one order of magnitude more intense than the CO signal. The feed was routed through the reactor by-pass (see Fig. 1) for feed analyses. The CO concentration of the feed was determined by ir before and/or after each run.

Complete analyses of feed and product streams (CO, CO_2, O_2, and N_2) were obtained with a Hewlett–Packard Model 5734A gas chromatograph. A parallel, dual-column system was developed which allowed composition determinations of CO_2, O_2, N_2, CO, and H_2O mixtures from a single injection in less than 7 min with isothermal column operation. The gc analyses were used for the ir calibration and for spot-checking the calibrations of the feed flowmeters.

Catalyst Characterization

A dynamic pulse apparatus (*21*) was used to measure H_2 and CO adsorption and CO–O_2 titration uptakes. The H_2 used for adsorption and reduction was produced in a Matheson electrolytic hydrogen generator, and it was purified by passage through Pt/Al_2O_3 and molecular sieve beds. The other gases used in the adsorption and titration experiments were CO (99.99%), O_2 (99.99%), N_2 (99.9995%), and He (99.995%). The N_2 and He carrier gases, N_2 used for H_2 adsorption and He for CO and O_2 measurements, were further purified by passage through oxygen traps.

Samples of Cat 4 (Pt–Pd/Al_2O_3), after various stages of use and treatment were examined by transmission electron microscopy using a Philips EM400T microscope. TEM specimen were prepared by scraping small amounts of material from the surface of pellets, grinding the scrapings to a powder, suspending the powder in *n*-hexane, and placing a drop of the suspension onto a carbon-coated 400-mesh Cu grid. Images were recorded, using 100-kV accelerating voltage, at instrumental magnifications of 100,000 to 220,000. Metal crystallites were measured on photographic prints which had a threefold enlargement. Only metal particles with sizes greater than 1 nm were measured.

EXPERIMENTAL RESULTS AND DISCUSSION

Preliminary Investigations

Blank runs with the reactor empty, and the reactor filled with alumina spheres, showed that no CO conversion occurred at conditions comparable to, and usually more severe than, the conditions used with supported metal catalysts. Hence, all subsequently observed CO oxidation occurs on the noble metal.

Cat 1 was the first catalyst studied. Four different pretreated charges of this catalyst, containing 5, 2, 1, and 0.125 g of catalyst (each diluted to 20 g with inert alumina pellets), were successively placed in the reactor and used for CO oxidation. Although wide ranges of operating conditions were investigated, oscillatory behavior was never observed for 5, 2, or 1 g charges of catalyst. These charges of catalyst, however, displayed other interesting behavior which was useful in the interpretation of oscillations observed for other catalysts. All operating conditions resulted in either a low (<10%) or a high- (≈100%) conversion steady state. The high-conversion steady state was obtained if the reactor was flushed with O_2 before CO was introduced, while the low-conversion steady state resulted if the reactor was flushed with the CO–N_2 mixture before O_2 was introduced. A transition from a high- to a low-conversion steady state could at times be achieved by an abrupt step increase in CO feed concentration. This process was irreversible, since a similar abrupt step decrease in CO feed concentration did not result in a transition back to the high-conversion steady state. However, gradual increases in CO feed concentrations during high-conversion operations did not result in transitions to low conversions, but were accompanied by gradual increases in gas-phase temperatures with temperature gradients of up to 5 K across the 50-mm catalyst bed. The dependence of the steady-state conversion on the initial condition (i.e., initial O_2 versus CO coverage of the catalyst surface) indicates that under reaction conditions a sensitive balance between adsorption–desorption and surface reaction rates exists.

To eliminate the bulk temperature effects associated with the large rates of reaction when using the 0.3% Pt catalyst, a very small charge of 0.125 g of catalyst (3 pellets) was used in the reactor. For this charge it was possible, for the first time, to obtain steady-state conversions of less than 100% in the concentration region where the reaction displays positive order global kinetics with respect to the concentration of CO in the reactor. The global reaction rate behavior at 393 K for this small catalyst charge is shown in Fig. 2. For this, and all subsequent figures, the various operating parameters are summarized in Table 2.

It is seen (solid circles in Fig. 2 indicate experimental observations discussed in this section), that for low concentrations of CO in the reactor, the reaction rate increases essentially linearly with respect to the CO concentration, while for high concentrations of CO in the reactor, the reaction rate is very low and decreases as the CO concentration is increased. However, the behavior shown in Fig. 2 is not the intrinsic kinetic behavior for this catalyst as calculations show the existence of large mass transfer limitations. The maximum rates of CO mass transfer to the external surface of the pellets were estimated by the correlation of Petrovic and Thodos (*22*). The maximum external CO transfer rates fall between the two dashed lines shown in Fig. 2. These results clearly show that at low CO concentrations the rates of reaction are strongly influenced by mass transfer. A further observation made with this charge of catalyst was that oscillatory behavior could occur in the reaction region where large mass transfer resistances existed. The maximum and minimum reaction rates observed during the oscillations are indicated in Fig. 2 by the joining of two symbols by a line with arrowheads.

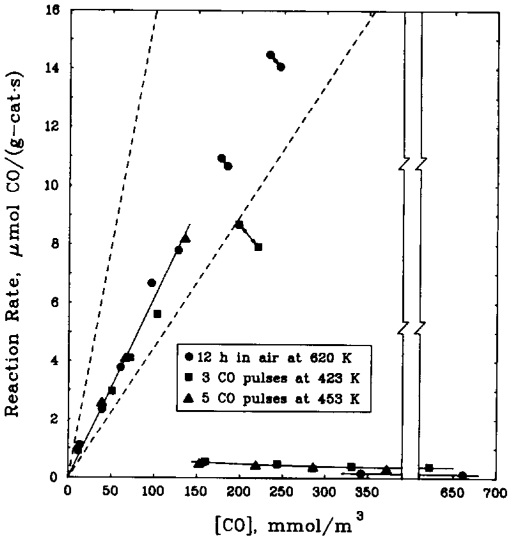

FIG. 2. Reaction rate behavior as a function of CO concentration in the reactor for Catalyst 1 (catalyst pretreatment indicated in legend).

The results for the various charges of 0.3% Pt catalyst suggest that for active catalysts with high metal loadings, for which large energy releases per unit mass of catalyst can occur, oscillations, other than those which are affected by transport limitations, are unlikely. For this reason, only catalysts containing lower metal loadings were used in subsequent experiments.

The next catalysts examined in these preliminary screening tests were Cat 2 and 3. Oscillations were observed for both of these catalysts, and typical CO_2 concentration oscillations are presented in Fig. 3. Although these catalysts displayed oscillatory

TABLE 2

Reactor Operating Parameters for Figs. 2 to 7

Figure	Catalyst[a]		Reactor temp (K)	Molar feed rate (μmol/s)	Feed composition (mol%)			Recycle ratio
	No.	Mass (g)			CO	O_2	N_2	
2	1	0.125	393	120–144	0.14–1.98	98.7–82.0	1.1–16.0	33–27[b]
3a	2	30	367	191	1.93	82.5	15.6	22
b	3	20	318	85	0.88	92.0	7.1	58
c	3	20	329	89	1.38	87.5	11.2	53
d	3	20	339	96	2.01	81.7	16.3	47
e	3	20	339	248	0.94	91.5	7.6	18
4a	4	5	413	90	0.79	92.8	6.4	42
b	4	20	413	96	0.61	94.5	4.9	39
c	4	20	403	87	0.68	93.8	5.5	44
d	4	20	403	86	0.55	95.0	4.5	45
e	4	20	403	88	0.64	94.2	5.2	44
5	4	20	393	127–136	0.11–0.74	99.0–93.3	0.9–6.0	31–29[b]
6	4	20	423	264–339	0.00–2.42	100.0–78.0	0.0–19.6	13–10[b]
7	4	20	393	114	0.31	97.2	2.5	34

[a] See Table 1 for description of catalysts.

[b] Lower values of recycle ratio correspond to higher values of feed rates (see column 4).

behavior, the ir signal was much noisier than the usual signal, especially for Cat 2 which had a very uneven distribution of Pt among the catalyst pellets. Furthermore, the oscillations were usually aperiodic. This behavior is attributed to the inhomogeneity of the Pt distributions (see Experimental Methods—Materials).

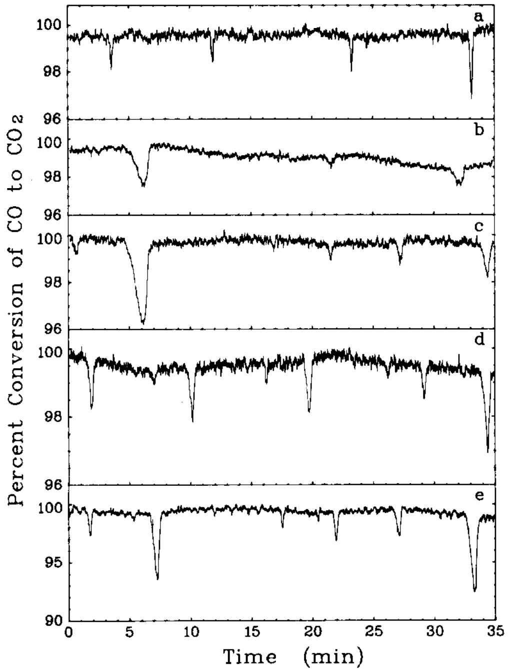

FIG. 3. Typical CO_2 oscillations for Cat 2 and 3.

The last catalyst examined was the General Motors converter catalyst (Cat 4). After investigating the behavior of this Pt–Pd catalyst at many sets of operating conditions, it was found that oscillatory behavior occurred at various operating conditions. Shown in Fig. 4 are some typical oscillations of the CO_2 concentration. In Fig. 4a, a very long period oscillation is shown which occurred when 5 g of catalyst (diluted to 20 g with inerts) were placed in the reactor. This oscillation was very regular over a period of several hours. It was found that the period and amplitude were quite sensitive to the concentration of CO in the feed, and it was possible to obtain oscillations with periods in excess of 1 h.

Studying the parametric sensitivity of an oscillatory phenomena with a period of an hour would be extremely time consuming, thus the operating conditions and the amount of catalyst in the reactor were var-

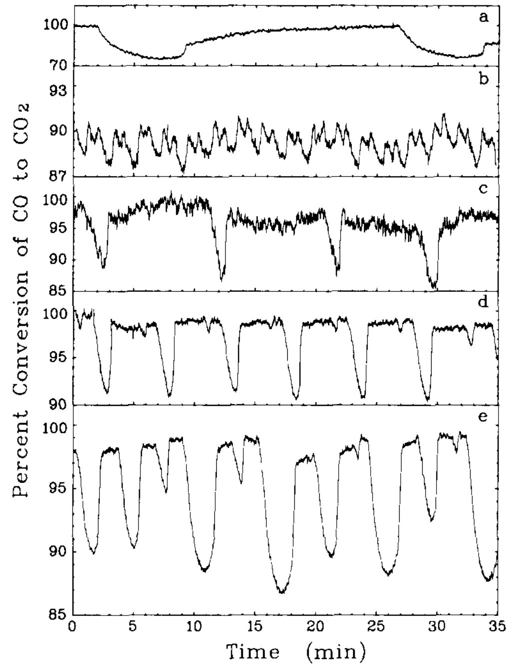

FIG. 4. Typical periodic and chaotic CO_2 oscillations for Catalyst 4.

ied in an attempt to obtain oscillations with shorter periods. Shown in Fig. 4b–e are oscillation which occurred when 20 g of catalyst were placed in the reactor (no dilution). It is seen that this catalyst is capable of displaying complex (multipeak and aperiodic), in addition to simple, oscillatory behavior.

During the preliminary work with this Pt–Pd catalyst it was observed that the long term oscillatory behavior was not reproducible as the catalyst activity was not constant. For example, despite comparable operating conditions, the oscillations shown in Figs. 3c and e are very dissimilar. A detailed examination of the reaction history of the catalyst charge revealed that increases in catalyst activity occurred when the catalyst was subjected to "severe" reaction conditions (high temperature coupled with large reaction rates). To determine the details of this effect, a series of experiments were carried out in which a fresh pretreated catalyst charge was systematically exposed to a series of severe reaction conditions.

Effect of Catalyst History on Activity

A fresh charge of 20 g of Pt–Pd catalyst was pretreated as previously described. The reaction rate behavior for this catalyst was determined at 393 K and it is shown by the lower curve in Fig. 5. As with the previous catalysts, it was possible to determine low conversion reaction rates in the region where the global kinetics display negative order dependence on the CO concentration. However, when the feed concentration was decreased so that the concentration of CO in the reactor fell below 78 $mmol/m^3$, the system abruptly switched to a total conversion steady state. It was not possible to obtain any steady-state behavior for which the CO concentration in the reactor was significantly different from zero but less than 78 $mmol/m^3$.

After the initial reaction rate curve was determined, the reactor was purged with O_2, and the reactor temperature was raised to 423 K (from 393 K). Once the reactor temperature had stabilized, and all residual CO_2 production had ceased, the reactor was subjected to the "CO pulse treatment" shown in Fig. 6. The numbers of the following points refer to the labeled locations in Fig. 6.

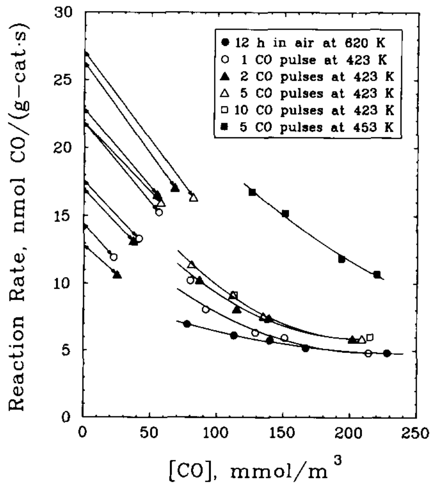

FIG. 5. Effect of CO pulse treatments on the reaction rate behavior of Catalyst 4 (catalyst pretreatments indicated in legend).

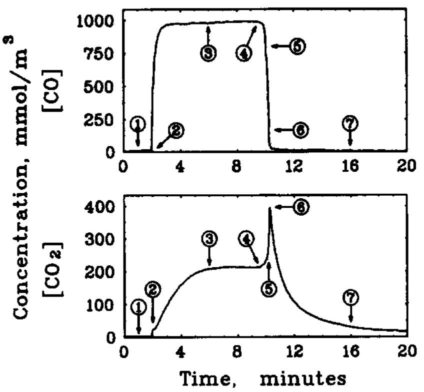

FIG. 6. CO pulse treatment of Catalyst 4 (see text for details).

1. The reactor feed composition consists of pure O_2. No CO_2 is being produced, and the reactor temperature is 423 K.

2. The reactor feed composition is abruptly changed so that it now contains a large amount of CO in O_2. The initial virtually instantaneous rise in the CO_2 concentration results from the rapid reaction of the incoming CO with the oxygen adsorbed on the catalyst surface.

3. After the oxygen surface layer is removed, the CO covers the surface, and the reactor operates at a low conversion (≃10–20%) steady state. This behavior is similar to that observed with the other catalysts whenever a large abrupt increase was made in the feed CO concentration.

4. After the CO and CO_2 concentrations in the reactor approach constant values, the feed stream composition is abruptly changed to 100% O_2.

5. The CO concentration in the reactor decreases due to the purging effect of the pure oxygen feed. The production of CO_2 begins to increase as the CO concentration drops.

6. Instead of continuing to decrease exponentially (expected from mixing effects), the CO concentration in the reactor decreases rapidly to zero. The CO_2 production almost instantaneously rises to a maximum as all the CO on the surface is removed by reaction with O_2. A small bulk temperature rise (≃0.5 K) is observed during this period of high reaction rate, implying the possible existence of a large temperature rise on the metal crystallites.

7. The CO_2 concentration in the reactor approaches zero as the pure O_2 feed purges the system. No further CO_2 is produced as all carbon monoxide has either reacted or been flushed from the reactor.

After this CO pulse treatment at 423 K, the reactor temperature was lowered to 393 K and the reaction rate behavior was determined for the second time. This is shown by the second curve in Fig. 5 (open circles). It is seen that, in the high CO concentration region, the low conversion reaction rates are now larger than before the CO pulse treatment, i.e., the catalyst activity has increased. However, in the low CO concentration region (below 80 mmol/m^3), the system does not pass to a total conversion steady state as before, but rather oscillations now occur. The maximum and minimum values of the rates during the oscillations are shown by the lines connecting the open circles to the rate axis. It is worth noting that the maximum rates for all of the observed oscillations always corresponded to a 100% conversion state. No steady states with less than 100% conversion were observed in the low CO concentration region.

Clearly the catalyst activity has been substantially changed by subjecting it to the CO pulse treatment at 423 K. The catalyst was then subjected to further CO pulse treatments at 423 K to determine if additional activity changes were possible. After each pulse treatment, the reaction rate behavior was examined and the results are shown in the upper curves in Fig. 5. It is seen that the reaction rate continues to increase after each CO pulse treatment until the catalyst has been treated a total of five times. Further CO pulse treatments did not result in measurable activity changes.

Once the catalyst activity had been stabilized by the above procedure, the reproducibility of the oscillatory behavior was exam-

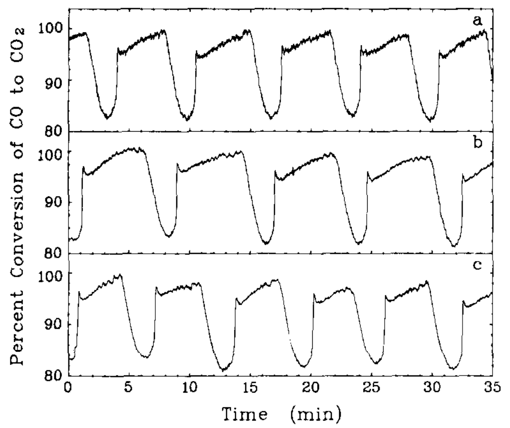

FIG. 7. Reproducibility of the oscillatory behavior for Catalyst 4: (a) stabilized fresh catalyst; (b) after 150 h of use; (c) after 250 h of use.

ined. Shown in Fig. 7a are oscillations at 393 K which were observed shortly after the catalyst activity had stabilized. This catalyst was then used for approximately 150 h of operation with various feed conditions. However, the reactor temperature was never raised above 423 K during this 150-h period. The reactor operating conditions were reset to those used in Fig. 7a, and the resulting oscillations are shown in Fig. 7b. It is seen that the oscillatory behavior was very reproducible. Shown in Fig. 7c, for the same set of operating conditions as in Fig. 7a, are oscillations which were observed after the catalyst had been used for approximately 250 h after the CO pulse treatments. This oscillatory behavior is thus shown to be reproducible over long periods of time.

To determine if the catalyst activity had reached its maximum value, the catalyst was subjected to five CO pulse treatments at 453 K. The reaction rate behavior at 393 K for this catalyst is given by the upper curve in Fig. 5. Clearly there has been a further large increase in the catalyst activity. Also, oscillations were no longer observed in the low CO concentration region, but rather the system would always go to a total conversion steady state.

The above described CO pulse treatment procedure was also carried out on Cat 1 for which the rate behavior was presented in Fig. 2. It was found that CO pulse treatments at 423 K and 453 K had very little effect on the activity of the catalyst in the low CO concentration region, as is shown in Fig. 2. However, catalyst activity changes in the low CO concentration region would be very difficult to detect due to the large transport limitations. In the high CO concentration region, the catalyst activity approximately doubled after the CO pulse treatments, cf. circles with triangles and squares in Fig. 2 at CO concentrations above 150 mmol/m^3.

Catalyst Characterization Results

Hydrogen and CO adsorption uptakes were measured on the catalysts after various treatment and reduction conditions to determine whether adsorption capacities are correlated with observed changes in catalytic activity. The results of these measurements are summarized in Table 1. For Cat 1 and 3, reduction temperature (300 or 500°C) had only a small effect on H_2 and CO uptakes, but high temperature O_2 treatment resulted in increased adsorption uptakes. Hence, the doubling of activity at high CO concentrations for Cat 1 as a result of CO pulse treatments shown in Fig. 2 is believed to be due to an increase in Pt surface area brought about by the CO pulse treatments. Usually treatment temperatures above 550 K in O_2 are required to significantly increase Pt surface areas for Pt/Al_2O_3 catalysts (*23, 24*), but CO pulse treatment at 453 K results in activity increases, probably due to Pt area increases. This suggests that the CO pulse treatment causes local increases in temperature which are responsible for Pt redispersion.

The effect of reduction temperature on the adsorption behavior of Cat 4 was quite different than that observed for Cat 1 and 3. Hydrogen, and to a lesser extent CO, adsorption uptakes decreased markedly when the reduction temperature was increased

TABLE 3

$CO–O_2$ Titration Uptakes at 120 and 155°C for Catalyst 4 after Various Treatments[a]

Run	Treatment	Titration temp (°C)	CO and O_2 titration uptakes (CO/M and O/M)[b]							
			C1	O1	C2	O2	C3	O3	C4	O4
1	O_2, 4 h, 120°C	120	0.33	0.12	0.13	0.14				
2	O_2, 16 h, 155°C	155	0.35	0.09	0.17	0.16	0.17	0.18	0.18	0.18
3	O_2–CO pulses at 155°C[c]	155	0.31	0.10	0.21	0.21	0.21			
4	O_2, 14 h, 366°C[d]	155		0.28	0.29	0.34	0.32	0.34	0.33	
5	O_2–CO pulses at 155°C[c]	155	0.32	0.33	0.33	0.35	0.30	0.34	0.32	

[a] All measurements and treatments done consecutively on the same sample.

[b] Ci and Oi are CO and O_2 titration uptakes for the *i*th titration in molecules CO and atoms of oxygen per metal atom.

[c] Pure O_2 and CO pulses of 5 min duration were alternatively passed over the catalyst (3 O_2 and 2 CO pulses).

[d] CO reductions carried out at O_2 treatment temperature before cooling to titration temperature.

from 250 to 500°C (see Table 1). It had been hoped that the higher activity of Cat 4D compared to Cat 4C (see Fig. 5); Cat 4D data corresponds to solid squares and Cat 4C to solid circles) would be reflected in the adsorption uptakes. This, however, was not the case. In order to obtain further information on the state of the metal in Cat 4 after various treatments, unreduced and reduced samples of Cat 4 were examined by conventional transmission electron microscopy (CTEM).

The CTEM results clearly showed that exposure to different reaction conditions and reduction at elevated temperatures causes changes in the state of the metal. No metal particles larger than 1 nm were detected in unreduced samples of Cat 4A and B. Metal particles, in the 1- to 6-nm size range, were detected in unreduced samples of Cat 4C and D, as well as in samples of Cat 4A and D which had been reduced in H_2 at 500°C. The main difference between catalysts in which metal particles were detected was the concentration of metal particles. The two samples reduced in H_2 at 500°C contained at least three times as many metal particles as the unreduced samples, and the unreduced Cat 4C had a higher metal particle concentration in the 1- to 3-nm range than unreduced Cat 4D.

These results show that a significant fraction of the metal in unreduced catalysts is present in subnanometer particles. The observation that Cat 4D contained less detectable metal than Cat 4C is in agreement with the higher catalytic activity observed for Cat 4D. The observation that high-temperature reduction in H_2 causes formation of large metal particles explains why the chemisorption results are not correlated with catalytic activity, i.e., chemisorption uptakes, measured after high-temperature reduction, do not reflect the metal surface area existing under reaction conditions. To circumvent this problem, $CO–O_2$ titration measurements were done on Cat 4 after various treatments.

A fresh, untreated sample of Cat 4 (8.8 g) was placed into a quartz U-tube sample holder which was then attached to the dynamic adsorption apparatus. Uptakes of CO and O_2 at 120 or 155°C were measured after various treatments by injecting pulses of CO or O_2 into the He carrier gas. At temperatures of 120 to 155°C, adsorbed O_2 (or CO) reacts readily with adsorbed CO (or O_2). The $CO–O_2$ titration results after various treatments are summarized in Table 3.

Since the overall titration reaction is $CO + \frac{1}{2}O_2 \rightarrow CO_2$ then the CO/M to O/M ratios (i.e., ratio of molecules of CO to atoms of oxygen consumed) should be 1 : 1 if no (or equal amounts) of CO and O_2 desorb between successive titrations. Hence, titration uptakes cannot be used to determine amounts of CO and O_2 adsorbed. Ratios approximately equal to unity were obtained for all titrations except for the first CO (C1) and O_2 (O1) uptakes for Runs 1 to 3. The high C1 values for Runs 1 to 3 are due to bulk oxidation of the metal during the O_2 treatments prior to measuring C1. The low O1 values are due to incomplete reduction during the first CO adsorption measurement. A low value of O1 compared to O2 is not observed if the sample is reduced in CO at elevated temperatures prior to measuring O1 (see Run 4).

The results in Table 3 show that O_2 and CO treatments at temperatures up to 366°C increase CO and O_2 titration, and hence adsorption, uptakes by a factor of about 2.5 (cf. C2 and O2 for Run 1 with C2 and O2 for Runs 4 and 5). These increases in CO and O_2 uptakes are in good agreement with the two- to threefold increase in activity brought about by CO pulse treatments in the reactor (see Fig. 5). Hence, thermal treatment and use, even under relatively mild conditions, can cause significant changes in the metal surface area. These changes are reflected in changes in catalytic activity and stability behavior (oscillatory versus stable).

SUMMARY AND CONCLUSIONS

Oscillatory, as well as stable, behavior during the oxidation of CO was observed for each of the four catalysts investigated. The stability and rates of oxidation were not only dependent on reactor operating conditions, but were strongly affected by prior treatments and use. Exposure of the catalysts to conditions which result in high rates of CO oxidation, e.g., CO–O_2 pulse treatments, results in increases in metal surface area and activity. The increases in metal surface area are due to disintegration of small metal particles (redispersion). At high oxidation rates, the temperature of the metal particles is believed to be much higher than that of the bulk support and gas phases; hence, redispersion occurs at relatively low bulk temperatures. Fukushima and Katzer (*25*) have observed, by EXAFS, that disintegration of small Pt crystallites occurs as a result of O_2 adsorption even at room temperature.

We believe that oscillatory behavior at low reaction rates, i.e., in the absence of mass transfer effects (results for Cat 2, 3, and 4) is due to the temperature difference between metal particles and the bulk phases. The oscillations at high reaction rates, observed for Cat 1, on the other hand, are largely due to mass transfer effects (see Fig. 2). The increases in stable steady-state activity at low reaction rates for Cat 1, as well as the increases in activity for Cat 4 (see Fig. 5), as a result of treatments are due to increases in metal surface areas. Catalyst characterization studies showed that treatment and use of catalyst cause significant changes in metal areas. It should be pointed out, however, that chemisorption uptakes, especially for catalysts containing small amounts of metal, do not necessarily reflect the metal surface area existing under reaction conditions since the usual pretreatments required for chemisorption measurements may result in changes in metal surface area.

One of the objectives of studying oscillatory behavior is the determination of the mechanism responsible for the oscillatory behavior. The testing of proposed mechanisms or models requires comparison of model predictions with experimental results obtained at various operating conditions. If significant changes in the activity of the catalyst occur during the experiments used to determine the influence of operating conditions, then comparison of experimental results and model predictions becomes meaningless. In this paper we have shown that large changes in the type of rate behavior and the catalytic activity can occur for CO oxidation on supported metal catalysts. In the following paper (*20*) we report experimental results for the oxidation of CO over supported Pt–Pd (Cat 4), which shows the effects of reactor operating conditions on oscillatory behavior for a catalyst with constant activity.

ACKNOWLEDGMENT

We acknowledge the support of this research by the Natural Sciences and Engineering Research Council of Canada.

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