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Catalytic oxidation of carbon monoxide under periodic and transient operation

Erdogan Gulari *, X. Zhou, Chien Sze

Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

Abstract

Periodic and transient operation of catalytic CO oxidation reactors has been studied more than any other reaction system. Large increases in global rates of reaction are observed with noble metal catalysts using forced cycling of the feed concentration between oxygen and carbon monoxide at frequencies between 0.02 Hz and 1 Hz. Smaller increases in rate of reaction are seen with metal oxide catalysts with much lower resonance frequencies. We review the past research in the area and outline the challenges and the unanswered questions for future research.

1. Introduction

Since the original publication by Douglas and Rippin [1] about the possible advantages of transient and periodic operation of chemical reactors over steady-state operation, numerous theoretical and experimental studies have been made. While experimental studies have led the way in recent years, rather detailed theoretical studies have appeared in the scientific literature. This review will be restricted to catalytic oxidation of CO which is the most researched reaction in periodic operation studies. The literature up to almost the end of 1991 has been summarized in two excellent reviews by Silveston [2,3]. We refer the reader who needs information on early publications to those reviews. Because of the short time period between the two reviews there is some unavoidable overlap of material. In those cases in which there have not been any new developments we will be referring the reader to the Silveston review and the references cited therein. In the remainder of the manuscript we will provide examples from important studies of CO oxidation using periodic operation or forced concentration cycling. In addition we will attempt to address the following important questions: Has it been conclusively shown that periodic operation is better than steady state for global increases in the rate and conversion? Under what general conditions will periodic operation achieve higher rates of reaction over that of steady state? What positive contributions did periodic and/or transient operation studies make to our understanding of CO oxidation? In order to understand the answers to these questions we will first describe periodic operation itself.

During steady-state operation of any chemical reactor our goal is to keep all the thermodynamic variables of the system as time invariant as possible. In periodic operation, however, we want to change one or more of the variables with time in a predetermined manner. The variables that can be changed as a function of time during operation

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* Corresponding author.

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of a catalytic reactor are: the flow-rates of the reactants, temperature of the reactor, and the reactor pressure. If we change any of these variables in a time dependent fashion we will be operating the reactor periodically. While changing the reactor temperature in a periodic fashion is possible with small laboratory reactors it is almost certainly impossible with large scale reactors. No experimental or theoretical study exists which has shown that varying the temperature periodically can lead to significant benefits over that of steady-state operation. Pressure swing adsorption and reaction has been used under certain conditions to achieve favorable separation of reactants and products ([4]) but it has not been used for rate or selectivity enhancement. Changing the flow-rates of the reactants, or more appropriately the concentration of the reactants in a periodic or transient manner has been the method of choice for laboratory studies of periodic operation of catalytic reactors. The most common industrial application of periodic operation, in which the catalyst is exposed to different reactive atmosphere in a periodic fashion, is the fluidized bed catalytic cracking reactor (FCCR). In FCCR a portion of the catalyst is continuously withdrawn from the reactor and exposed to an oxidizing atmosphere to burn off the coke deposit. This is equivalent to concentration cycling between a hydrocarbon feed and air feed into the reactor. Essentially all reactors in which the catalyst is periodically regenerated are periodically operated reactors even though they are not explicitly recognized as such.

2. Experimental

In the remainder of this manuscript we will focus solely on concentration cycling studies in catalytic CO oxidation. Fig. 1 introduces the variables we will be using to discuss periodic operation versus steady-state operation: τ represents the period of the concentration modulation, s is the duty fraction (also called cycle split ratio) or the ratio of the CO rich portion of the cycle to the period, cycle mode (sinusoidal, square wave etc.), and amplitude A of the change in concentration relative to the mean reactant composition. In addition to the variables shown in Fig. 1, phase lag, amplitude variation, and modulation at several frequencies simultaneously are other possible variables.

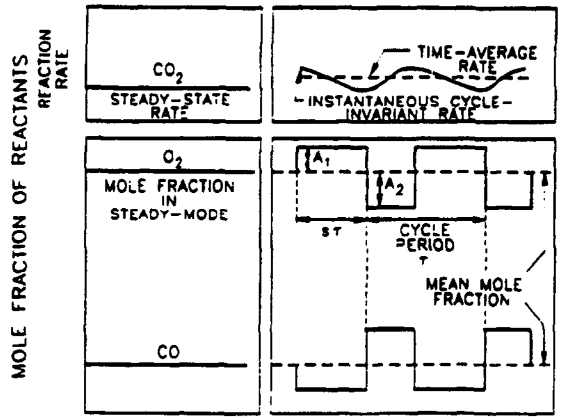

Fig. 1. Comparison of steady-state and periodic operating modes for the catalytic oxidation of CO. [Reprinted from Silveston [2] with permission of Can. J. Chem. Eng. All rights reserved.]

Fig. 2 shows an experimental reactor system used by Barshad and Gulari [5,6] and Zhou et al. [7] in their periodic operation studies of CO oxidation on supported platinum and palladium catalysts. While the exact details of the reactor systems used for concentration cycling studies by different investigators vary, Fig. 2 shows the basic setup. To vary the concentration of the reactants in a periodic fashion without changing the total flow-rate through the reactor, a flow control manifold equipped with computer controlled solenoid valves and mass flow controllers is employed. Other components include a low volume flow reactor with no unusual mixing properties; a high speed detection system for real time detection of the reactant and product profiles as a function of time, and a computer for the control of the reactor system as well as data recording and analysis. Normally the detectors used are either mass or IR (low volume non-dispersive) spectrometers or Fourier Transform IR spectrometers for high speed detection of the reactants and products. Under special circumstances gas chromatographs can also be used, but the long times required to complete an analysis usually precludes their use

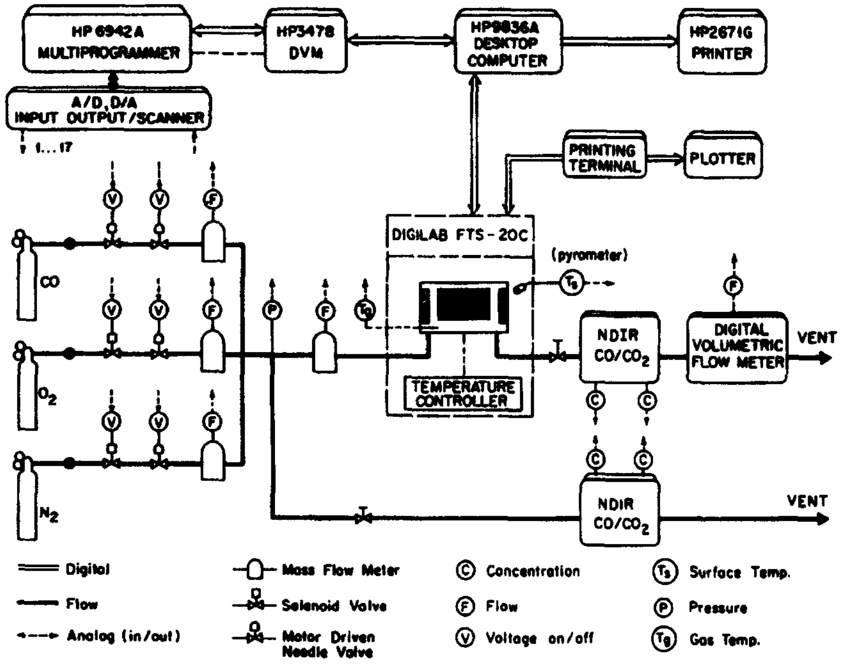

Fig. 2. Schematic drawing of the reactor system used by Barshad and Gulari [6] in their studies of periodic operation of catalytic CO oxidation reactors with noble metal catalysts. [Reprinted from Barshad and Gulari [6], J. Catal. Copyright 1985, Academic Press, New York. All rights reserved.]

in most cases. For studies of CO oxidation FT-IR or mass spectrometers are the ideal detectors. There are simpler but less flexible ways of changing the reactant concentration with time, the simplest being a two way valve switching between two premixed gas streams.

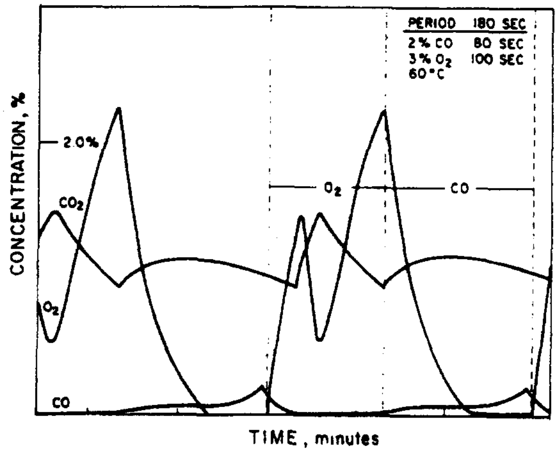

Fig. 3. Reactor outlet concentrations of CO_2, CO and O_2 over 0.5 wt.-% Pt/alumina catalysts at 60°C at a period of 3 min and a cycle split of 0.56. [Reprinted from Ref. [8], reproduced by permission of the American Institute of Chemical Engineers, copyright 1979. All rights reserved.]

3. Review of experimental systems investigated

CO oxidation at low temperatures can be catalyzed by noble metals supported on oxides of simple metals or reducible metal oxides, transition metals as well as metal oxides. Therefore, we will review the results of studies with these four distinct groups of catalysts separately.

3.1. Supported noble metal catalysts

3.1.1. Supported Pt and Pd catalysts

Using a recycle reactor, Cutlip [8] demonstrated that rate enhancements over supported platinum were possible by periodically exposing a 0.5 wt.-% Pt/Al_2O_3 catalyst to 2 vol.-% CO and 3 vol.-% O_2 in argon. Fig. 3, taken from Cutlip's paper, shows that for a cycling period of 3 minutes and duty fraction of 67% almost all of the CO is converted to CO_2 and that the concentration of CO_2 and oxygen exhibit double peaks per period. The first maximum in the oxygen trace can be explained by the recycle in the reactor. Because of recycle, even 30 seconds after the termination of the CO feed, some residual CO remains in the reactor. The residual CO prevents adsorption and reaction of oxygen fed to the reactor and, as a result, the concentration of oxygen in the gas phase builds up. When all of the gas phase CO is consumed, the adsorption of oxygen is not inhibited and the rate of adsorption as well as reaction increases dramatically, resulting in the first peak in CO_2 concentration. The same high adsorption and reaction rate consumes gas phase O_2 at a rate faster than supplied, causing the O_2 concentration in the outlet to decrease to a minimum. The second peak is due to the gradual slowing down of adsorption as the surface is saturated with oxygen. From this scenario, Cutlip deduced that the changes in surface coverage during periodic operation are the source of the activity improvement.

Cutlip's work with the γ-alumina supported platinum system was followed by investigations by the Waterloo researchers, Abdul-Kareem et al. [9,10]. In this study, the feed concentration was cycled around CO to O_2 time-average ratios of 0.36 and 0.86. One feature of the Waterloo studies was the symmetric switching of the time-averaged CO/O_2 ratios (as opposed to switching the CO and O_2 streams on and off). Both studies reported increased reaction rates over that under steady-state conditions. However, at the temperature they were operating (520 K), the improvements seen with 0.36 CO to O_2 ratio may have been due to crossing the ignition and extinction boundaries in the multiple steady-state region.

The use of a recycle reactor by Cutlip made good temperature control and composition uniformity possible, but precluded imposition of very steep concentration gradients and shorter cycling periods. Barshad and Gulari [5] used a packed-bed reactor, computer controlled high speed mass flow controllers and solenoid valves coupled with IR detection to extend Cutlip's studies to cycling periods as short as 5 seconds. By periodic switching of the reactants (CO in N_2 and O_2 in N_2), they observed marked increases in the rate of reaction over that of attainable under steady-state conditions. Fig. 4 shows the transition from steady state to periodic operation and the corresponding increase in the time-averaged rate of reaction. With the plug flow reactor Barshad and Gulari were able to observe rate enhancements as high as 15 times over that of the best steady-state rate at a given temperature, irrespective of the feed composition.

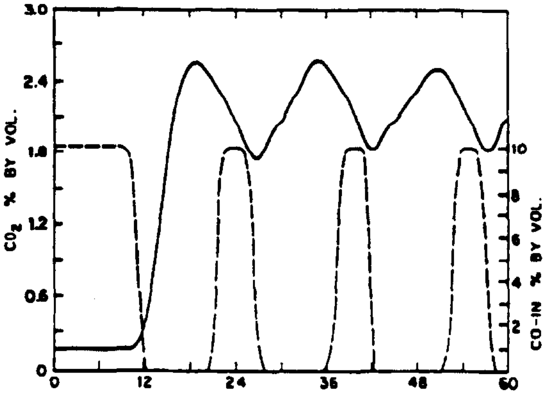

Fig. 4. Transition from steady-state operation to periodic operation. Note the very large increase in the CO_2 concentration and the decrease in the CO concentration immediately after the start of periodic operation. [Reprinted from Barshad and Gulari [5]. Reproduced by permission of the American Institute of Chemical Engineers, copyrighted 1985. All rights reserved.]

Barshad and Gulari [6], Zhou and Gulari [11], and Zhou et al. [7], extended the initial work on platinum to monolithically supported platinum and supported palladium catalysts. They were able to access cycling times as short as two seconds and also detect transients inside the reactor with high time resolution employing an FT-IR. Using their automated reactor system to advantage, exhaustive studies of cycle periods and CO duty fractions (cycle split) were performed to determine the optimum values for rate enhancement for each catalyst at a variety of temperatures. Fig. 5 and Fig. 6 below show the results of such an exhaustive study with the supported palladium catalyst.

There are several important features to be noted from these two figures. The optimal cycle time is strongly temperature dependent and is seen to decrease from 150 seconds to 20 seconds in going from 344 to 366 K. In addition, the time-averaged rate shows a steep increase with cycle period for times less than the optimum. Beyond the optimum

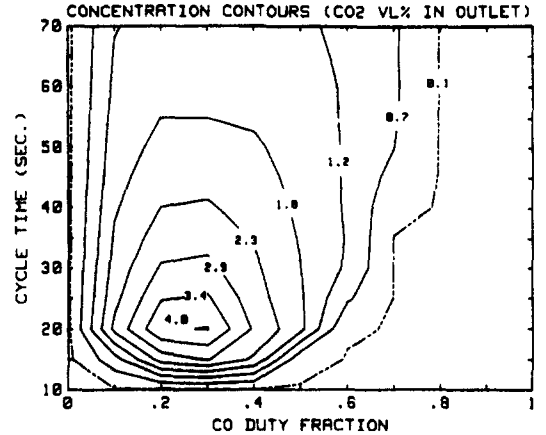

Fig. 5. A typical iso-concentration map showing the rate enhancement due to periodic operation. Each point on the map represents the time-averaged concentration of at least 100 cycle periods. The dashed line represents the best steady-state conversion achievable at the same temperature. Note that the maximum time-averaged rate is 44 times the best steady-state rate! At the optimum point 88% of the CO fed into the reactor is oxidized. Operating conditions: temperature 366 K, flow rate 0.7 dm^3 min^{-1}, feed is switched between 10 vol.-% CO and 15 vol.-% O^2 in nitrogen at atmospheric pressure. An NDIR detector was used to measure the outlet concentrations. [Reproduced with permission from Zhou et al. [7]. Copyright Pergamon Press, Oxford, 1986. All rights reserved.]

point, the dependence on cycle period is very weak. A similar dependence on the duty fraction (or cycle split) can be seen for duty ratios below the optimum. Combining these observations with transient response studies such as the ones shown in Fig. 7, Zhou et al. [7] argued that for the Pt and Pd catalysts the most important variable is the length of the oxygen pulse. If the length of the oxygen feed portion of the cycle is longer than the induction time observed before CO_2 is detected in the gas phase then there is significant rate enhancement. For shorter pulse lengths no rate enhancement is seen. Zhou and Gulari [12] also showed that on Pd the length of the induction period has an Arrhenius type of dependence on temperature with an activation energy of 92 kJ/mol. The weak dependence observed for long cycling times is simply due to over exposure of the catalyst surface alternately to CO and O_2 past the saturation point. An inverse dependence on the period is observed because essentially the same amount of total CO_2 produced per cycle is divided by longer and longer cycling periods to obtain the time-averaged conversion.

To delineate the surface processes leading to rate enhancement during periodic operation, Barshad and Gulari [6] and Zhou and Gulari [12] extended their studies to FT-IR detection of surface CO absorption spectra on Pt and Pd during periodic operation and steady state. Fig. 8a shows one set of time-averaged spectra as a function of cycling period along with the steady-state spectra. In this set of studies sharp increases in the oxidation rate were seen only for time periods longer than 25 seconds. In Fig. 8a we see that for time periods shorter than 25 seconds there is very little difference between the time-averaged IR absorbance spectra of surface CO species during periodic operation and the steady state. For longer time periods, however, there is a dramatic difference. The height of the CO band due to linearly adsorbed CO decreases dramatically on metallic Pt (the right-most peak), while on platinum oxide (the left-most peak) it increases. The most significant difference is in the intermediate range, where a new peak appears in the periodic operation spectra. Fig. 8b compares the intensities of the four bands as a function of CO_2 production rate and time period. By taking complete spectra every 0.6 seconds during a complete cycle of 40 seconds and deconvoluting the individual spectra as a sum of three Gaussians, Barshad et al. further showed

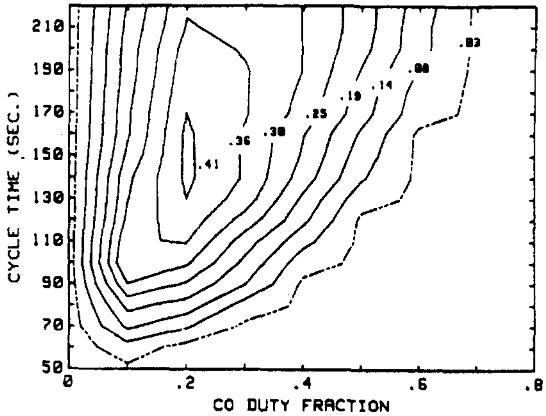

Fig. 6. Iso-concentration map of conversion at $T = 344$ K. At this temperature the shape of the conversion contours are different than those of Fig. 5. Flow-rate 0.5 dm^3 min^{-1}, cycling between 10 vol.-% CO in N_2 and 10 vol.-% O_2 in N_2. [Reproduced with permission from Zhou et al. [7]. Copyright Pergamon Press, Oxford, 1986. All rights reserved.]

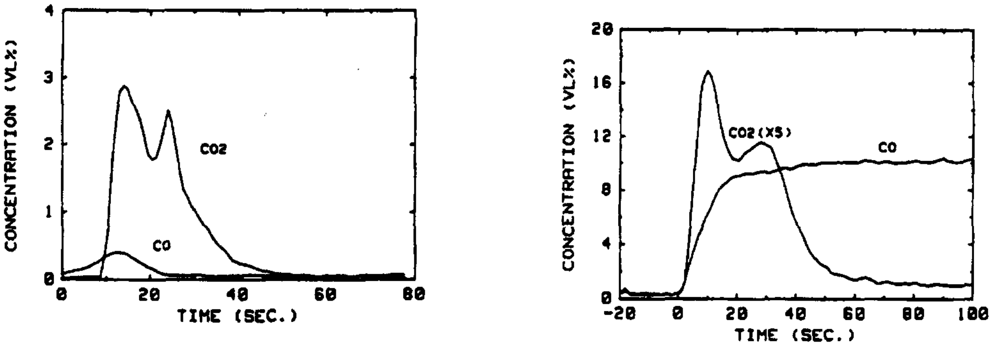

Fig. 7. CO and CO_2 transient responses of: (left) the CO pretreated palladium catalyst to a step up of 10 vol.-% oxygen in N_2 after pretreating the catalyst for 3 min with 10 vol.-% CO in nitrogen and (right) the oxygen pretreated catalyst to a 10 vol.-% CO in N_2 step up after a pretreatment with 10 vol.-% O_2 in nitrogen for 5 min. Both pretreatments were followed by a short nitrogen purge to clear the gas phase. Conditions: temperature 376 K, flow-rate 0.5 dm^3 min^{-1}. Inside the reactor detection with FT-IR. With this type of detection the volumetric concentrations observed are slightly more than half the concentration detected at the outlet. Note that in the left-hand side of the figure some CO is desorbed since this CO is not detected in the outlet it must be re-adsorbed again. [Reproduced with permission from Zhou et al. [7]. Copyright Pergamon Press, Oxford, 1986. All rights reserved.]

that the CO molecules adsorbed on oxidized platinum (2123 cm^{-1} band) are spectator species and do not react, even during prolonged oxygen exposure. CO molecules adsorbed linearly on metallic platinum (2073 cm^{-1} band) react only after a significant induction time and that the new species giving rise to the band in the middle (2093 cm^{-1} band) react with oxygen with no induction time [28]. One other interesting piece of information provided by the FT-IR studies of the surface spe-

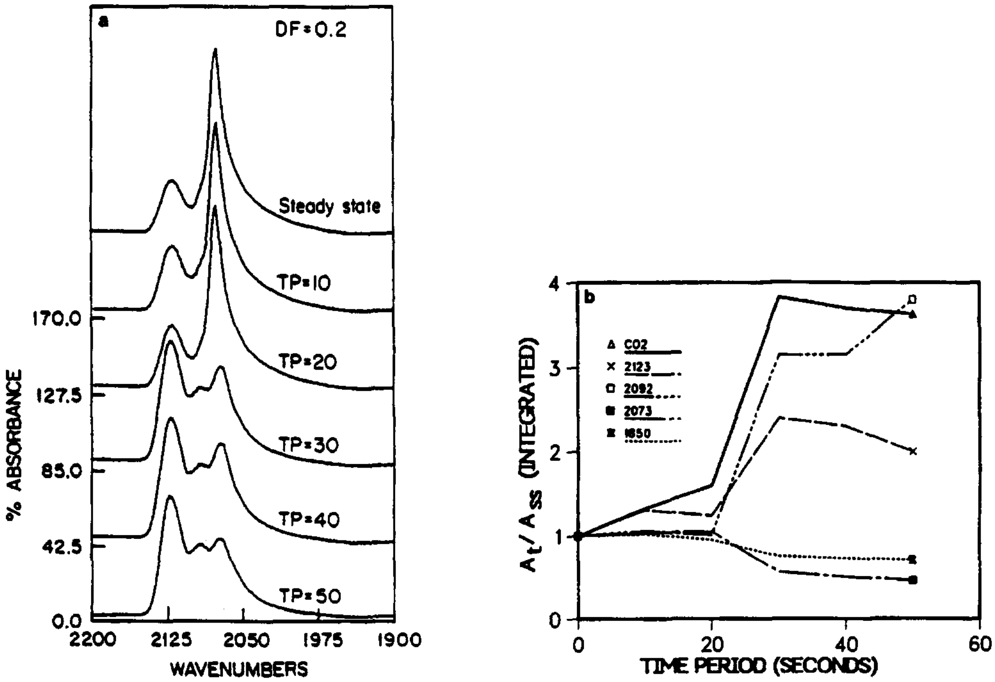

Fig. 8. (a) Time-averaged IR spectra under steady state and periodic operation. The steady-state feed is 2 vol.-% CO and 12 vol.-% O_2 in N_2. Periodic operation consisted of switching between 10 vol.-% CO and 15 vol.-% O_2 in N_2 with a duty fraction of 0.2, resulting in exactly the same time averaged gas phase composition as the steady state. (b) Plot of the integrated peak areas for the various CO bands during periodic operation ratioed to their steady-state values. Also shown is the time averaged CO_2 production rate. The curve shown for the 1850 cm^{-1} band is a ratio of peak heights and not of areas. [Reproduced with permission from Barshad et al. [30]. Copyright 1985, Academic Press. All rights reserved.]

cies was that, even during periodic operation, the catalyst surface is never completely free of chemisorbed CO. There was ample (but unreactive) CO on the surface even at the end of a thirty second oxygen pulse with no gas phase CO present!

While Pt had low reactivity surface CO species under the reaction conditions studied, Zhou and Gulari [10] found that on supported Pd, all of the surface CO is converted into CO_2 during a long oxygen pulse. They further observed that during the CO 'on' portion of the cycle, a new short lived surface CO species is formed. They were able to show a linear relationship between the concentration of this new species and the instantaneous rate of CO_2 production for that portion of the period. This new species was assigned to CO chemisorbed in islands of mixed 2×2 structured CO and oxygen.

Based on their FT-IR studies Zhou et al. provided the following explanation for the observed rate enhancements of CO oxidation on supported Pt and Pd catalysts during periodic operation: (1) Forced cycling of the feed composition between CO and O_2 prevents formation of large reactant islands which store surface species. Since surface reaction occurs between the chemisorbed yet mobile CO and chemisorbed but stationary O atoms the reaction rate is proportional to the length of the perimeters of CO and O islands. Periodic operation creates many smaller islands which results in large increases in the perimeter length and therefore the reaction rate. (2) During periodic operation new and much more reactive surface CO species are generated, which lead to further increases in the rate of reaction. This explanation is schematically shown in Fig. 9 below.

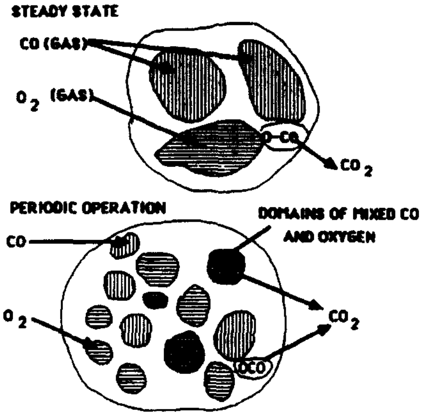

Fig. 9. Schematic drawing of the surface coverage by CO and oxygen illustrating the differences between steady state and periodic operation. The formation of new surface structures containing highly energetic CO and O in equal surface coverage and the numerous but smaller CO islands formed during periodic operation are believed to be responsible for the enhanced rates. During steady state large areas of the surface are covered with CO, resulting in low reaction rates. [Reproduced with permission from Zhou et al. [7]. Copyright Pergamon Press, Oxford, 1985. All rights reserved.]

CO oxidation on supported Pt catalysts has also been investigated under transient and forced cyclic concentration conditions by Herz and coworkers. Herz and Shinouskis [13] showed that CO reacts with two types of oxygen on supported Pt catalysts, chemisorbed oxygen which is highly reactive and oxygen which is bound more strongly to platinum in the form of platinum oxide. The reactivity of surface chemisorbed oxygen was found to be much higher than that tied up in the oxide. Racine et al. [14] used two different supported platinum catalysts, one derived from the usual chloride precursor (chloroplatinic acid) and another from tetraamine-platinum-nitrate. Their TPD and reaction studies showed that the nitrate based sample interacted with CO much more strongly. Their transient response experiments produced double peaked CO_2 responses similar to those observed by Barshad and Gulari [5]. During periodic concentration cycling they saw 'extra' CO_2 production that could not be accounted for by the instantaneous reaction rate calculated from a knowledge of steady-state kinetics. Fig. 10 below shows one such result for both types of catalysts. It is interesting to note that the catalyst made from the nitrate precursor had a lower steady-state activity and stronger interaction with CO and produced significantly more CO_2 due to transient processes occurring during cycling.

Racine and Herz [15] later modeled their experimental observations by taking into account intrapellet diffusion resistance and site heterogeneity. They concluded that single site Langmuir–Hinshelwood models failed to predict the steady state and dynamic observations made in their system. They used an elementary step model with a

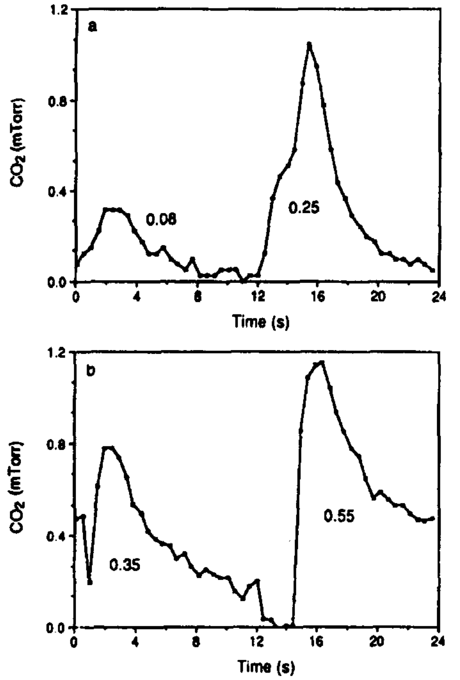

Fig. 10. 'Extra' CO_2 production for the 24 second period and 50% duty fraction cycling experiment at 145° C and 330 mTorr O_2 for (a) the chloride sample and (b) the nitrate sample. The number on each peak refers to the amount of extra CO_2 produced in the peak in units of 'monolayers'. [Reproduced with permission from Racine et al. [12]. Copyright 1991, Academic Press, New York. All rights reserved.]

bimodal distribution of active sites to successfully predict the behavior of both of their catalysts. Fig. 11 shows the success of their model in predicting the dynamic response of the nitrate and chloride based platinum catalysts.

In one of their experiments, Barshad and Gulari [5] cycled only the CO feed into a steady stream of oxygen with different duty fractions and observed time-averaged rates of reaction higher than the maximum attainable by 180 degree out of phase cycling of oxygen and carbon monoxide. This observation has been verified and supplemented by a very detailed study by Graham and Lynch [16], who showed that by varying the phase angle it was possible to achieve a global maximum in the time-averaged rate of reaction. Fig. 12 below shows the importance of 'phase lead' in their reactor system.

Graham and Lynch used Pt surface reconstruction between the hex phase and 1 × 1 phase, as a function of surface CO coverage, to model their system's response to changes in the gas phase. By using a large difference in the oxygen sticking probability and the surface reaction rate they were able to reproduce the majority of their observations. Fig. 13a and b compare the predictions of the model with experimentally observed results. Clearly, even with the adjustable parameters the predictions are very good.

While the results of the Graham and Lynch [16] and Racine and Herz [15] models are impressive, there are still significant questions that remain unanswered about CO oxidation on supported catalysts. The gradientless reactor system used by Graham and Lynch is very satisfactory

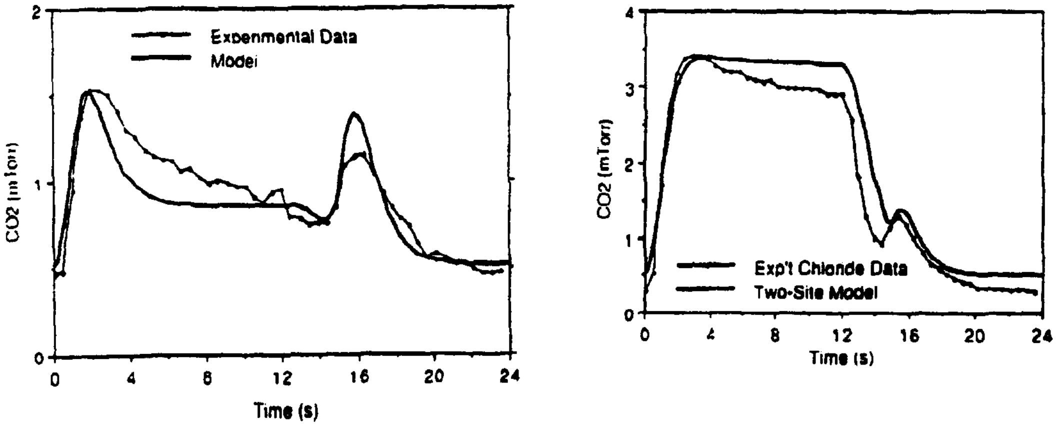

Fig. 11. (Left) comparison of simulated dynamic response of the two-site model to the experimental CO_2 response for the nitrate sample. (Right) comparison of simulated dynamic response of the two-site model to experimental CO_2 response for the chloride sample. [Reproduced with permission from Racine and Herz [13]. Copyright 1992, Academic Press, New York. All rights reserved.]

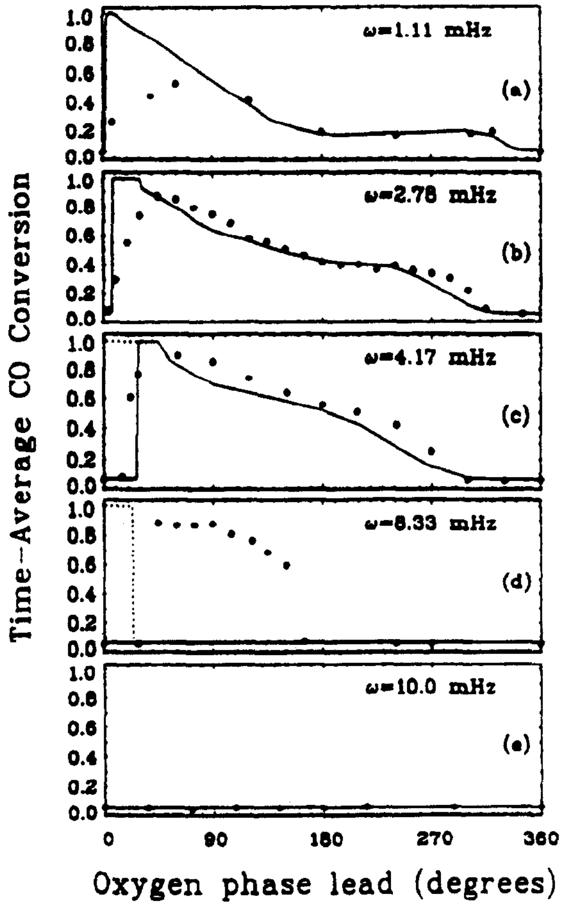

Fig. 12. Effect of phase angle between CO and O_2 feed streams on the time-average conversion during forced cycling. Experimental conditions external recycle CSTR, 14.6 g of 0.5 wt.-% Pt/Al_2O_3 catalyst, flow-rate of 2.05×10^{-4} mol/s, reactor volume of 190 cm^3, 90°C operating temperature. [Reproduced by permission from Graham and Lynch [16]. AIChE J., all rights reserved.]

from a temperature control and modeling point of view, but its residence time of almost 30 seconds makes the concentration gradients and the response times very sluggish. Hence some behavior observable only with the imposition of sharp concentration gradients are, most likely, not observable in such a reactor.

Supported rhodium catalysts

Transient and steady-state behavior of CO oxidation on supported rhodium has also been studied in recent years. Li and Gonzales [17] nperformed transient response experiments similar to those on supported Pt and Pd catalysts, described above. They observed that the induction times for the oxygen step-up transient with a CO covered catalyst surface was significantly shorter on silica-supported rhodium than is the case on Pt and Pd. It was noted that the linearly and bridge adsorbed CO reacted very rapidly with oxygen. Yao and Gonzales explained their results by suggesting the formation of a mixed carbon monoxide and oxygen adlayer, unlike the separate islands of reactants observed on Pt.

Prairie et al. [18] studied CO oxidation in steady state, transient and forced cycling experiments with an IR pellet reactor. They studied the possibility of rate enhancement as a function of cycling frequency. The time-averaged rates of reaction were seen to increase with decreasing cycle time but not to levels significantly above steady-state values in the frequency range they were cycling. Table 1 below summarizes their results. It was pointed out that the system involved exhibits significant external and internal mass transfer limitations. Since the primary mechanism through which concentration cycling increases time-averaged reaction rates is by elimination of CO inhibition, it is not surprising that concentration cycling has no effect when the limitation in the reaction rate is due to mass transfer.

3.2. Reducible metal oxide supported noble metal catalysts

Vaporciyan et al. [19] studied the performance of a supported $Pt–SnO_2$ catalyst during forced concentration cycling. Along with rate enhancements they also observed complex resonances showing as many as three characteristic resonance times of approximately 3500 seconds, 240 seconds and a cycle time of 20 seconds. Similar experiments carried out with a Pt/Al_2O_3 catalyst under identical conditions revealed the existence of only the two short time scales. The longer time scale was tentatively assigned to the oxidation/reduction of tin, while the intermediate time scale can be due either to reduction of platinum oxide (similar results were obtained by Herz and Shinouskis [13] or other surface phenomena associated with the platinum component of the catalyst.

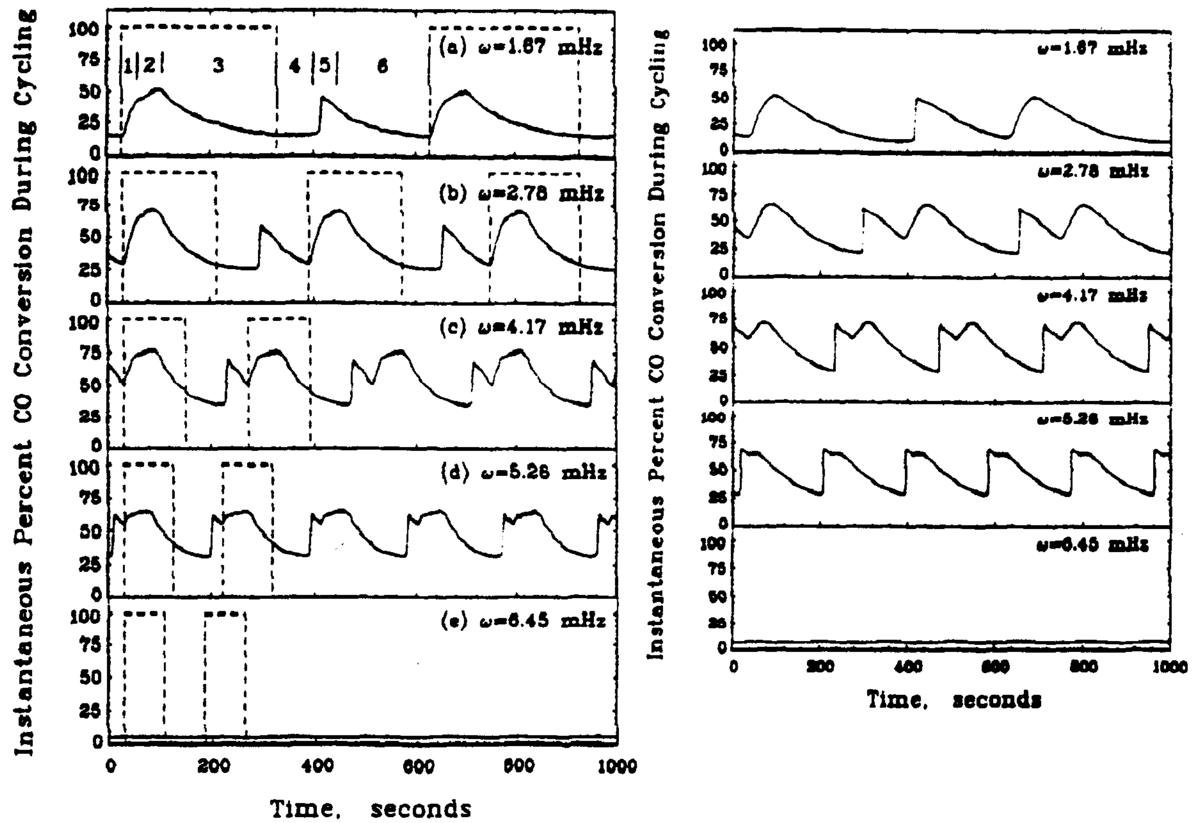

Fig. 13. (Left) instantaneous CO conversion during 180 degrees out of phase forced cycling data. Dashed lines indicate the timing of step changes in the feed CO concentrations with oxygen step-changes 180 degrees out of phase. (Right) predicted transient CO conversion for forced concentration cycling for the experimental case given in (a). Experimental conditions are the same as those of Fig. 12. [Reproduced by permission from Graham and Lynch [16]. AIChE J., all rights reserved.]

The Pt–SnO_2 system displayed increasing rate enhancements with temperature and duty fractions as high as 0.6 for the maximum time-averaged conversions under periodic operation. The lower rate enhancements seen during periodic operation at low temperatures may be due to the significant contribution from the tin component of the catalyst to steady-state conversion.

Table 1

Time-averaged results from cycled feed stream experiments (periods 2,4, and 8 seconds) and calculated from asymptotic theory for periods approaching zero and infinity[a]

Period (s)	Time-av. CO2 production rate (μmol/s)	Approximate time-av. CO coverage (monolayer)
0	10.8	0.78
2	10.8	0.55
4	10.4	0.44
8	10.0	0.38
∞	9.2	0.39

[a] Taken from Prairie et al. [15].

Haruta et al. [20–22] discovered that reducible metal oxide based gold catalysts had extremely high reactivities for CO oxidation at very low temperatures when air is used to oxidize low amounts ($\leq 1\%$) of CO in an excess of O_2. Despite much work in this area (Haruta et al. [20–22] and Gardner et al. [23]) our knowledge of these catalysts and how they function is very primitive in comparison to the platinum catalysts. The operating assumption has been that the metal component and the oxide support work in a synergistic manner. CO molecularly adsorbs on gold and diffuses to the perimeter of the gold crystallite to react with chemisorbed oxygen (possibly present as O_2^-) giving rise to a bicarbonate species which subsequently decomposes to CO_2. This hypothesis has not yet been put to a critical test. Sze and Gulari [24] attempted to study the performance of gold supported on iron oxide under concentration cycling. The extremely high steady-state activity exhibited by these catalysts (complete conversion at room temperature) rendered concentration cycling of little value. Recently, steady-state rate expressions for reducible metal oxide supported gold catalysts were determined by Haruta et al. [22]. The dependence on CO concentration was found to be of zero order for Au/TiO_2, Au/Co_3O_4, and $Au/\alpha\text{-}Fe_2O_3$. The dependence on oxygen concentration was found to be of zero order for the $\alpha\text{-}Fe_2O_3$ supported catalyst, and ca. 0.2 for the other two systems. The activation energies were also unusually low, 8.2, 8.4, and 3.9 kcal/mol for the TiO_2, $\alpha\text{-}Fe_2O_3$, and Co_3O_4 supported gold catalysts, respectively. These results indicate that there is no inhibition by either reactant. If there are no reactant inhibition effects we do not anticipate these catalysts to exhibit rate enhancements during periodic operation. This prediction is also supported by two recent Monte Carlo models of these two component catalysts (Brosilow et al. [25] and Herz et al. [26]).

3.3. Other metal catalysts

Since the last review by Silveston [2] there has not been any significant new results on CO oxidation by other metal catalysts with the exception of supported silver, which was observed to have a high activity for CO oxidation for low levels of CO in an oxidizing atmosphere [23]. However, the only transient and concentration cycling experiments that exist are still the ones reviewed by Silveston and we refer the interested reader to the 1991 review.

3.4. Metal oxide catalysts

Compared to the number of studies performed with noble metal based catalysts, there is a dearth of experimental concentration cycling studies on metal oxide catalysts. To date, the only published experimental results are those of the Waterloo group. In their study of CO oxidation over a potassium promoted vanadia catalyst, Abdul-Kareem et al. [9,10] observed rate enhancement with cycling period when they cycled the reactor feed between CO rich and O_2 rich streams. Fig. 14 below shows the interesting behavior exhibited by their catalyst.

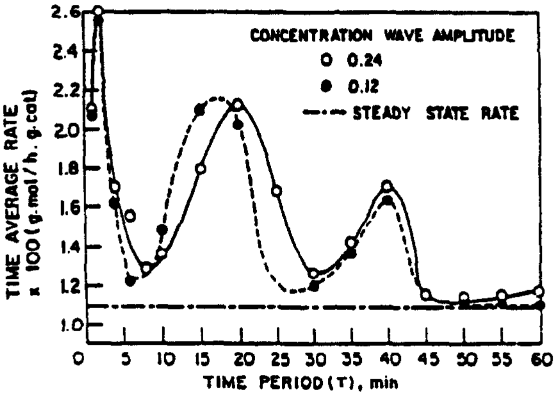

Fig. 14. Variation of the time averaged rate of CO oxidation with cycling period at $P_{CO}/PO_2 = 0.86$ and 440°C. [Reprinted with permission from Abdul-Kareem et al. [9]. Copyright 1980, Pergamon Press, Oxford. All rights reserved.]

Based on these results, the supported vanadia catalyst warrants further study to elucidate the reasons for the observed multiple resonances.

A recent observation by Haruta [27] that cobalt oxide itself is an excellent CO oxidation catalyst in oxidizing atmospheres when the moisture in the feed stream is below ppm levels opens the way for the intriguing possibility of CO oxidation rate enhancement on reducible transition metal oxides by periodically drying the catalysts.

Apart from noble metals supported on reducible metal oxides, Hopcalite, a mixed copper oxide manganese oxide catalyst is also very active for CO oxidation at low temperatures and is being used commercially in air purifiers. Hopcalite catalyst would certainly be an interesting system to study as a high activity oxide catalyst. However, thus far no experimental concentration cycling studies of this system have been made.

4. Discussion

Based on experimental evidence accumulated to date, we can now conclude that periodic operation leads to time-averaged rates of reaction higher than that possible under steady-state operation conditions for supported Pt and Pd catalysts [28] and Yadav and Rinker [29]). These experimental observations are also supported by the theoretical modeling work of Graham and Lynch [16] and Racine and Herz [15]. However, based on the experiments to date, we can not distinguish a priori between the two proposals explaining the rate enhancement, i.e., formation of more reactive species in smaller reactant islands or adsorbate induced surface reconstruction. Through the use of concentration cycling with supersonic molecular beams on single crystal surfaces under UHV conditions, it may be possible to image the surface with a high concentration of reactants present. This would be comparable to operation under atmospheric pressures, and could be used to differentiate between the two mechanisms.

Data also indicate that periodic operation will achieve higher rates of reaction over that of steady state in reaction systems in which there is strong inhibition of the rate by one of the reactants. By this measure, all of the catalytic reaction systems exhibiting a negative order dependence on reactants or products would make good candidates for future periodic operation studies. Experimentally, strongly peaked responses in the reaction rate to step changes in concentration of reactants is indicative of a system in which rate enhancements may be possible through concentration cycling. We should, however, note that mass transfer resistance may indeed lower the enhancements attainable. We suspect that in many experiments, mass transfer resistance can mask the rate increases. This is especially true for catalysts pressed into the form of IR pellets. Experiments done by the authors indicate that the rate enhancement achieved with IR transmitting pellets were at least a factor of two to three worse than those achieved on monolithically supported catalysts.

It is clear that results from periodic operation studies have led to a critical review of the standard Langmuir–Hinshelwood model of CO oxidation on supported noble metals as well as to additional transient response and high vacuum studies of CO oxidation catalysts to elucidate the underlying factors involved in the experimentally observed rate enhancements. The net outcome of these studies has been a better understanding of the mechanism of CO oxidation on Pt and Pd. Similar studies are needed to critically examine CO oxidation mechanisms proposed for metal oxides and other supported metal catalysts.

5. Conclusions and recommendations for further study

It is perhaps paradoxical that the interest in periodic operation of catalytic reactors has been wanning in recent years, just as the number of interesting systems is expanding and as experimental apparatus with higher species and time resolution are becoming more readily available. Just considering CO oxidation, the following systems are among those that warrant future study:

(1) *NO reduction and CO oxidation on supported platinum group metals.* In this reaction strong NO adsorption at low temperatures is believed to impact both the rate of reaction and the selectivity between the products of N_2 and N_2O. This reaction system appears ideal for studies on selectivity.

(2) *CO oxidation on reducible metal oxides.* Further clarification of the interesting resonance phenomena observed by Abdul-Kareem et al. and Vaporciyan et al. is necessary.

(3) *Novel supported gold catalysts.* This new class of systems provides an interesting contrast to the platinum based CO oxidation catalysts if the conversion levels can be lowered to the differential reactor regime. Periodic operation studies can shed light on the mechanism of CO oxidation proposed for the supported gold catalysts. All of these mechanisms involve relatively weak adsorption of CO only on gold and of oxygen on the oxide support.

(4) *CO oxidation on other supported noble metals (i.e., Rh and Ru).* These are known to chemisorb CO both molecularly and dissociatively and could shed new light on the role played

by both atomic surface carbon and oxygen deposited through the dissociation of chemisorbed CO. In addition, new experiments are needed to clarify the conclusions of some previous work in which mass transfer limitations may have played a role [30].

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