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Concentration Forcing of Catalytic Surface Rate Processes

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Periodic feed switching between carbon monoxide/argon and oxygen/argon mixtures to a gradientless reactor has been found to significantly increase the average reaction rate as compared to the steady state rate, when the time averaged feed concentrations in both cases are stoichiometric. The rate enhancement achieved during periodic reactor operation is attributed to the attainment of more desirable surface concentrations on the platinum catalyst which dramatically increase the surface rate processes leading to carbon dioxide production.

Part I. Isothermal Carbon Monoxide Oxidation Over Supported Platinum

SCOPE

Most studies of chemical processes are made with the tacit assumption that steady state operation is optimal. Several researchers, notably Douglas (1972) and Bailey (1973, 1977) and their co-workers, have championed the potential benefits from the deliberate periodic or unsteady operation of chemical processes such as chemical reactions. Successful periodic operation capitalizes on the nonlinear nature of the process. Good candidates for periodic operation are catalytic reactions where increases in reaction rates and selectivities may occur when some combination of reactor temperature, feed concentration, or flow rate is varied. Increasing attention is being given to the fundamental surface rate processes in recent experimental studies into the periodic forcing of catalytic reactions.

In this work, the catalytic oxidation of carbon monoxide by a supported platinum catalyst was studied under isothermal conditions, where the reactor feed was alternated between an oxygen/argon mixture and a carbon monoxide/argon mixture. Gradientless reactor operation was used to eliminate potentially undesirable heat and mass transfer resistances so that the effects of the feed cycling on the intrinsic surface rate processes could be clearly observed.

CONCLUSIONS AND SIGNIFICANCE

Significant rate enhancement at constant temperature has been obtained for carbon monoxide oxidation over a supported platinum catalyst by the periodic introduction of the individual reactants to a gradientless reactor. This rate increase can be qualitatively explained by reference to the elementary surface steps commonly associated with this reaction, where the periodic feed forcing achieves surface coverages of adsorbed species which lead to increased rates of surface reaction.

For stoichiometric carbon monoxide and oxygen feed mixtures, steady state reactor operation results in a catalyst which is almost completely covered by the more strongly adsorbed carbon monoxide leaving small surface oxygen concentrations. Thus, the observed steady state reaction rate is low, since either of the proposed surface steps leading to product carbon dioxide is proportional to adsorbed atomic oxygen concentration. Since carbon monoxide and oxygen are quite irreversibly adsorbed while product carbon dioxide is not adsorbed, appropriate periodic operation can achieve a platinum catalyst containing both reactant species in such concentrations that the surface reactions as well as the adsorption rates of each reactant can occur so as to maximize the overall time averaged rate. In this periodic mode of operation, the surface rates leading to carbon dioxide serve to relieve the buildup of adsorbed carbon monoxide which otherwise would quench the high reaction rate.

These experimental results indicate that careful attention should be given to periodic processing where the catalytic surface rate processes can be significantly affected. Future work should indicate selectivity changes, as the concentrations of surface species can potentially be controlled by periodic operation. A detailed understand-

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ing of forcing surface processes will require fundamental elementary step models which dynamically describe the entire catalyst system. Once these models become available, there are many interesting aspects of industrial reactor design which will become quite challenging. The engineering of surface rate processes may well have some important implications for new catalyst development, testing, and utilization.

The beneficial effects of periodic processes have been discussed by Douglas (1972) who has shown with a number of examples that periodic operation is sometimes superior to optimal steady state operation. Bailey (1973, 1977) has provided extensive reviews of the periodic operation of chemical reactors, where the numerous simulation studies overwhelm the limited number of experimental studies.

Since the last Bailey (1977) review, experimental studies of forced reactor cycling have been encouraging in that more significant rate and selectivity enhancements have been observed. In studies of sulfur dioxide oxidation over a vanadium oxide catalyst, Unni (1973) has shown rate increases by as much as 30% when the reactor feed composition was periodically altered. Renken (1974) found periodic operation of a tubular reactor for the hydrogenation of ethylene to be superior to steady state operation. In a more recent study, Renken (1976) alternately introduced oxygen and ethylene to a fixed-bed reactor containing a silver catalyst and achieved increased selectivity to product ethylene oxide with a reduction in the bed temperature profiles. Al-Jaie (1978) investigated the hydrogenation of butadiene over a commercial nickel oxide catalyst in a fixed-bed reactor and found that either selectivity or yield could be improved 20% above the values for the optimal steady state conditions. In a similar study of hydrogenation of acetylene in a spinning basket reactor containing nickel catalyst, Bilimoria (1978) obtained improvement in both ethylene and ethane yields. Oh (1978) has demonstrated the use of a single inlet perturbation to achieve more desirable steady operation for carbon monoxide oxidation in an isothermal integral reactor which exhibited multiple steady states attributed to diffusion/reaction processes within catalyst pellets.

It is significant that most of the recent experimental publications discussed above have concluded that the dynamics of fundamental surface rate processes such as adsorption, surface reaction, and desorption can be influenced by the periodic operation of catalytic reactors. In this work, the catalytic oxidation of carbon monoxide over platinum was studied to obtain additional insight into the importance of surface processes during periodic reactor operation. Future papers in this series will attempt to quantitatively account for the effects of periodic reactor operation upon the important surface rate processes.

REACTION SYSTEM

Carbon monoxide oxidation over platinum has received considerable attention in the literature. This interesting reaction system is discussed by Wei (1975) and Carberry (1976). The kinetics are unusual in that the rate is first order with respect to carbon monoxide at low concentrations and negative first order at high concentrations. There is general agreement with the following sequence of elementary steps involved in this reaction:

$$CO + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CO - S \qquad \text{step (1)} \qquad (1)$$

$$O_2 + 2S \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2O - S \qquad \text{step (2)} \qquad (2)$$

$$CO - S + O - S \xrightarrow{k_3} CO_2 + 2S \qquad \text{step (3)} \qquad (3)$$

$$CO + O - S \xrightarrow{k_4} CO_2 + S \qquad \text{step (4)} \qquad (4)$$

where S in step (1) represents two platinum surface atoms for a bridged adsorbed carbon monoxide species and one surface atom for a linear adsorbed carbon monoxide species. It is well known that steps (1) and (2) are very nearly irreversible at low temperatures, as they are the basis for platinum titration procedures which utilize hydrogen and carbon monoxide. Unfortunately, there is little agreement as to the relative importance of carbon dioxide production via the Langmuir-Hinshelwood step (3) and the Eley-Rideal step (4).

Instabilities in the carbon monoxide/oxygen/platinum system have led to oscillatory phenomena which have been reviewed by Sheintuch (1977). These oscillations have been attributed to variations in activation energies of surface steps with surface coverages. However, Cutlip (1978) has observed dramatic oscillations when hydrocarbons were introduced during carbon monoxide oxidation, and perhaps small concentrations of hydrocarbon impurities may have contributed to the observed oscillations in the earlier studies.

EXPERIMENTAL CONSIDERATIONS

Reactor System

The general purpose reactor system shown in Figure 1 was used in this work to study catalytic oxidation reactions over supported platinum catalyst pellets. This equipment allowed up to six precise gas mixtures to be prepared and made available for feed to the reactor. The switching valve directed a desired gas mixture flow to the reactor, while another gas mixture flow was precisely measured by the bubble flowmeter. A switch interchanged the reactor and flowmeter streams so that the reactor could be subjected to periodic step changes in flow and/or composition enabling a wide variety of experiments to be performed.

The reactor was made from a 304 stainless steel cylinder 69.8 mm in diameter and 50.8 mm in length. The catalyst

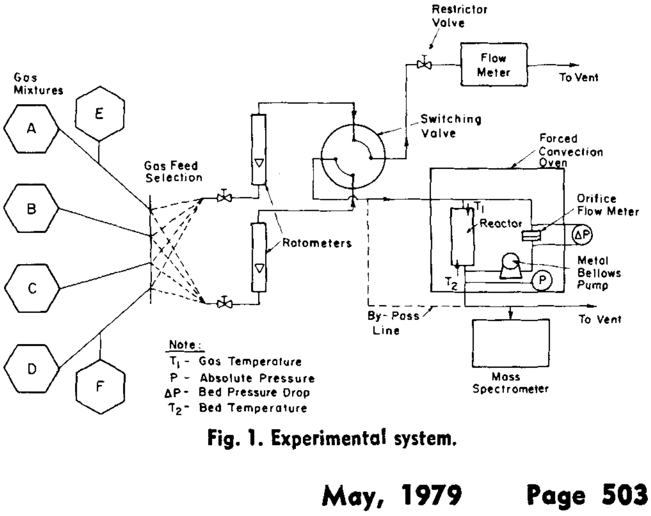

Fig. 1. Experimental system.

Table 1. Catalyst Properties

Platinum percent exposed	
A. H_2 chemisorption	46.7 ± 3.7%
B. H_2 desorption	48.0%
C. CO titration in situ	43%
BET and pore size determinations	
A. Average port radius	20.1Å
B. Total pore volume	0.23 cm^3/g
C. Σ pore areas	212 m^2/g
D. BET area	227 m^2/g
Thickness of impregnated layer	0.03 mm
Pellet density	1.98 g/cm^3

pellets were placed in seven 9.53 mm diameter holes in the cylinder and were retained by screens. The two end closures were sealed by standard copper vacuum gaskets which were gold plated.

A metal bellows recycle pump described by Hanson (1973) was used to maintain a recycle ratio in excess of 30 to 1 so that completely mixed reactor performance was obtained. The reactor, metal bellows pump, and recycle lines were contained in a forced convection oven held at the reaction temperature. An orifice plate in the recycle line enabled the recycle ratio to be measured by a pressure transducer. Reactor/recycle line gas volume was found to be 52 cm^3.

Inlet and outlet analyses were usually obtained by an on-line magnetic-deflection mass spectrometer equipped with a fast response continuous inlet system. An electronic peak select unit allowed up to four mass numbers to be continuously monitored. In some cases, a nondispersive infrared analyzer was used to follow the reaction rate through measurement of the product carbon dioxide concentration.

Catalyst

The catalyst was 10 g of 0.5% platinum by weight, deposited on the surface of ⅛ in. in diameter γ alumina pellets and obtained from Engelhard, Ltd., Cinderford, England. The properties of the catalyst are summarized in Table 1. Catalyst deactivation was not observed during the experimental studies.

EXPERIMENTAL RESULTS

Steady State Multiplicity

Rates were measured for various oxygen rich feed compositions at a fixed feed flow rate of 100 cm^3/min. Regions of multiple steady state reaction rates were determined by maintaining feed composition and flow rate constant and varying the reactor temperature in a programmed manner.

Typical results for a 2% carbon monoxide, 3% oxygen in argon feed composition are shown in Figure 2. This hysteresis curve was generated by starting at a low temperature and obtaining rates at increasing temperatures until the temperature at which the rate jumped to the high rate. The reactor was then slowly cooled for additional rate measurements to the temperature, at which the high rate was extinguished. The effect of feed composition upon the high and low jump temperature is given in Table 2 for a fixed feed flow rate of 100 cm^3/min. These jump temperatures result when the fractional surface coverages of adsorbed carbon monoxide and oxygen undergo dramatic changes. Cutlip et al. (1976) discussed these results in more detail. It is important to note that the regions of steady state multiplicity occur only for feed compositions containing excess oxygen and that the multiplicity region is shifted toward much higher temperatures and finally disappears as the feed approaches stoichiometric.

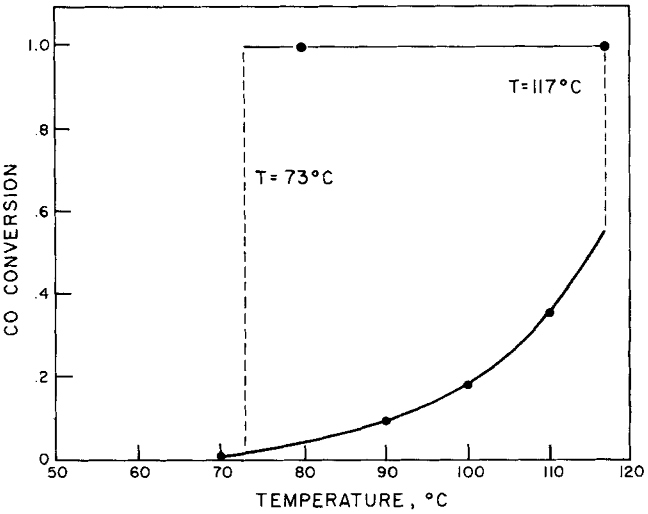

Fig. 2. Multiple steady state region for 2% carbon monoxide, 3% oxygen feed at 100 cm^3/min.

Table 2. Temperature Regions of Multiple Steady States

Feed composition	T_{Low}	T_{High}
1% CO, 3% O_2	57.5°C	99°C
2% CO, 3% O_2	73°C	117°C
4% CO, 3% O_2	101°C	140°C

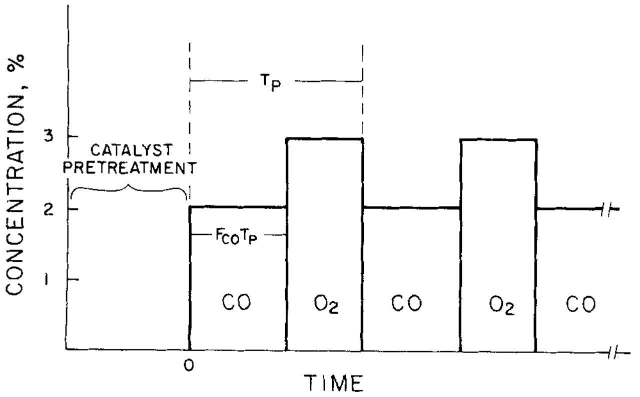

Fig. 3. Feed switching strategy.

At any temperature in the region of the two steady states, the low rate could also be established by switching

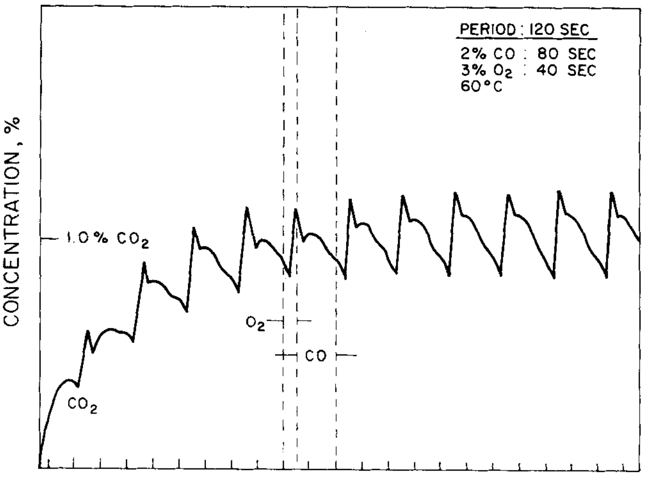

Fig. 4. Start-up to repetitive operation.

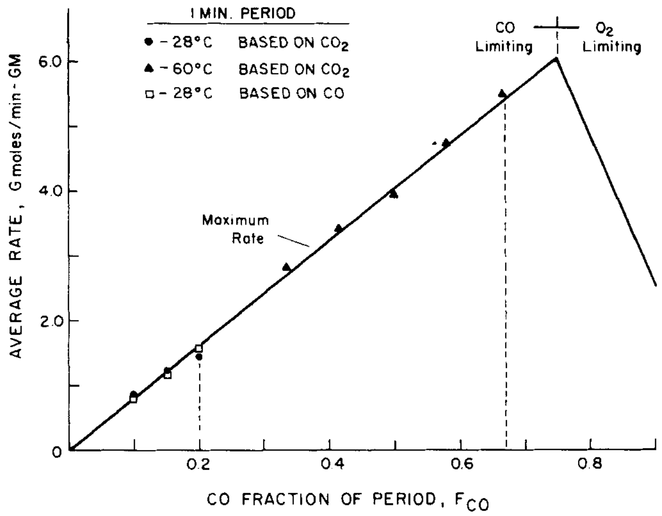

Fig. 5. Average rates for a 1 min period.

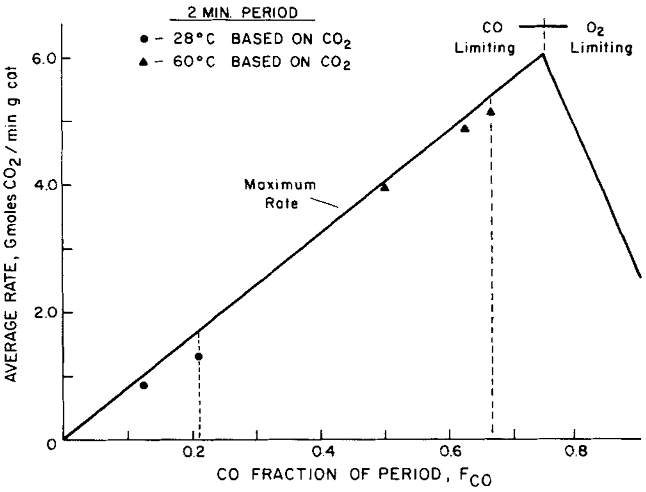

Fig. 6. Average rates for a 2 min period.

to the reactor a mixture of 10% carbon monoxide in argon until the catalyst was saturated with the carbon monoxide, then switching to the feed mixture. Pretreatment with 5% oxygen in argon until carbon dioxide was no longer produced gave the high rate steady state. These results indicate that the initial coverages of the platinum surface dictate the final rate in the multiple steady state region, with the low rate occurring at high coverages of carbon monoxide and the high rate occurring at high coverages of oxygen.

External gradients were experimentally eliminated by increasing the recycle ratio to 30/1, where the characteristics jump temperatures were no longer affected. Extensive calculations of interphase and intraphase heat and mass transfer also indicate the absence of gradients.

Periodic Feed Switching

The feed switching strategy utilized in this work was based on the 2% carbon monoxide, 3% oxygen feed mixture at a total flow rate of 100 cm^3/min. The reactor feed was always alternated between a stream of 2% carbon monoxide in argon at 100 cm^3/min and a stream of 3% oxygen in argon at 100 cm^3/min. After an initial catalyst pretreatment, both the total period of switching T_P and the fraction of the period for carbon monoxide flow F_{CO} were held constant, as indicated in Figure 3, until the reactor effluent reached repetitive concentration profiles.

Results at 60°C

An initial set of experiments were conducted at a temperature of 60°C, where the catalyst pretreatment consisted of 5% oxygen in argon. The fraction of the period for carbon monoxide flow, F_{CO}, was varied for total periods of 1, 2, and 3 min. A typical product carbon dioxide concentration profile in the reactor effluent is given in Figure 4. This represents the typical buildup to a repetitive concentration pattern, where the time averaged reaction rate is obtained by integrating the carbon dioxide concentration profile over a repetitive period.

For T_P's of 1, 2, and 3 min, the F_{CO} was varied. The results are presented in Figures 5, 6, and 7. In these figures, the solid line with a maximum at an F_{CO} of 0.75 indicates the maximum rate which would be obtained if all of the incoming carbon monoxide or oxygen were reacted. All three T_P's had the common characteristic of essentially following the maximum rate curve to a particular F_{CO} indicated by the dashed line where the rate became abruptly negligible. In other words, almost complete conversion of the carbon monoxide was accomplished until a critical F_{CO} was reached which reduced the rate to zero.

The maximum attainable rates at 60°C are plotted against the total period in Figure 8. Since both the maxima at the 1 and 2 min T_P's were at an average input concentration of 1.33% carbon monoxide, 1%

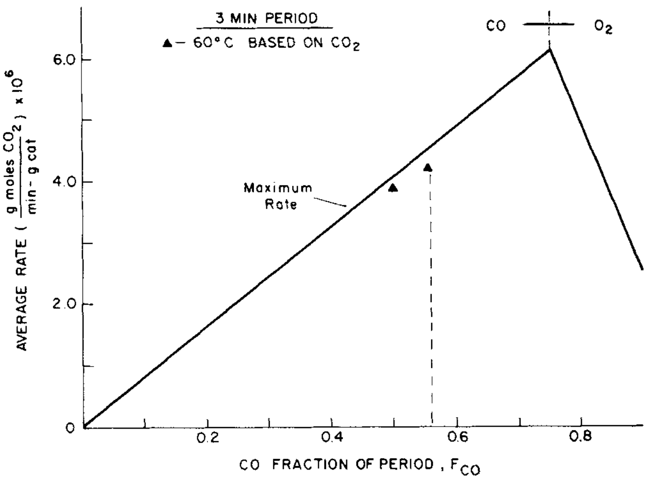

Fig. 7. Average rates for a 3 min period.

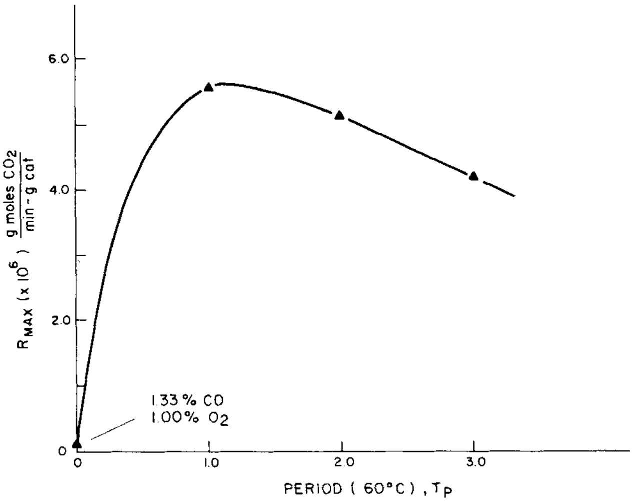

Fig. 8. Maximum rate vs. the period.

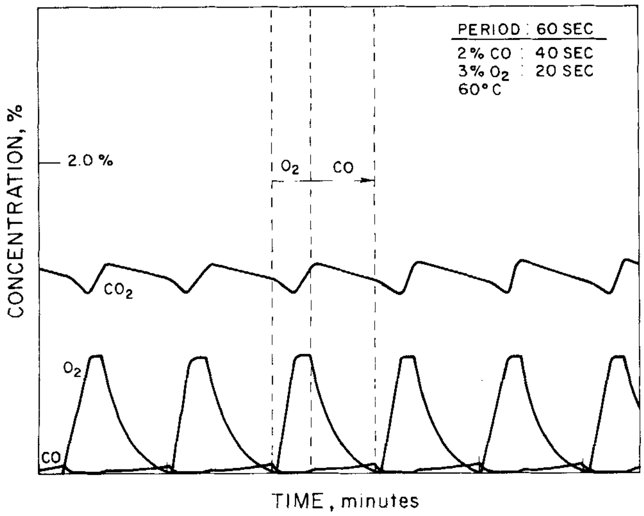

Fig. 9. Reactor outlet concentrations during a 1 min period at 60°C.

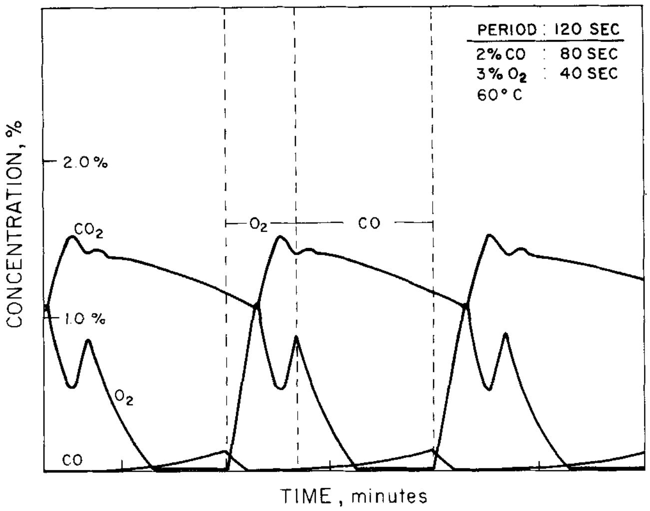

Fig. 10. Reactor outlet concentration during a 2 min period at 60°C.

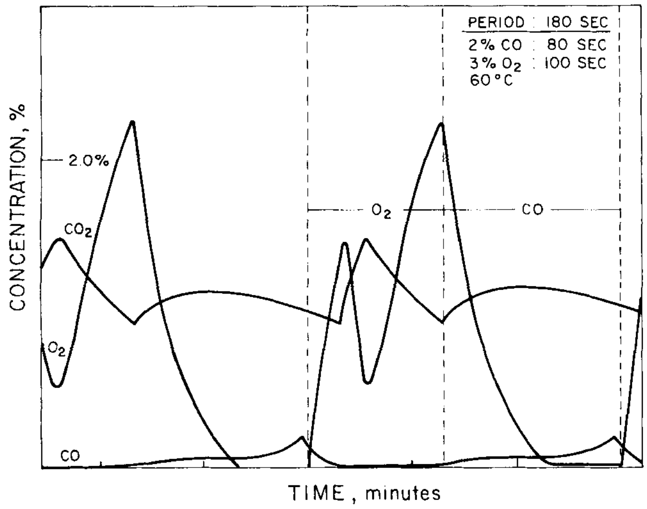

Fig. 11. Reactor outlet concentrations during a 3 min period at 60°C.

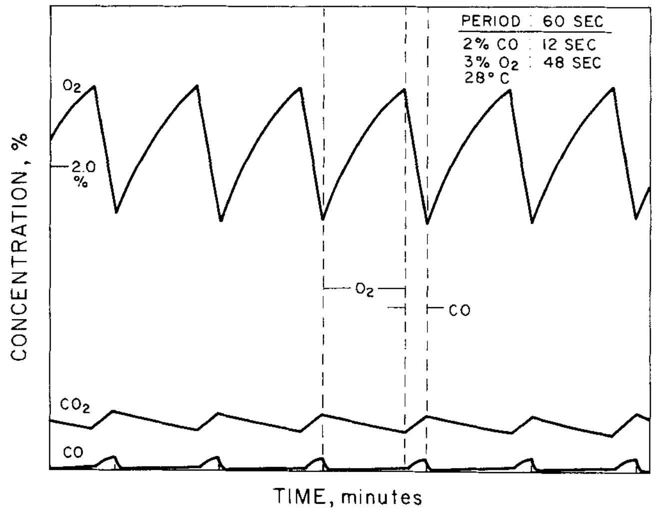

Fig. 12. Reactor outlet concentrations during a 1 min period at 28°C.

oxygen, the steady state for this feed composition is plotted for the zero period length. Clearly, the maximum rate attainable corresponds to a total period of approximately 1 min which represents almost complete conversion of the entering carbon monoxide and is quite significantly higher than conventional steady state operation with the feed composition corresponding to the average of that of the optimal periodic operation.

The mass spectrometer analysis also allowed the reactant concentrations to be measured simultaneously with the product carbon dioxide. These repetitive profiles are shown in Figures 9, 10, and 11 for those conditions, where the rate was at its maximum for the particular period. The dashed lines indicate the introduction of the oxygen and the carbon monoxide feed streams. These figures do confirm the highest conversion for carbon monoxide at a T_P of 1 min. In addition, the relevant surface rate processes yield extremely interesting profiles of oxygen and carbon dioxide for periods of 2 and 3 min which reflect the surface rate processes very dramatically. The carbon dioxide profile of Figure 11 clearly indicates two relative maxima in the oxidation rate per period during both oxygen and carbon monoxide feed introduction to the reactor.

Results at 28°C

Similar experiments were conducted at room temperature, where the catalyst was again pretreated with 5% oxygen in argon. Total periods of 1 and 2 min were used, and the results are also presented in Figures 5 and 6. As before, close to complete conversion was obtained as F_{CO} was increased to a critical value where the rate fell abruptly away to zero. Figures 12 and 13 show the repetitive profiles yielding these maximum rates. The period of 1 min yielded a slightly higher maximum rate.

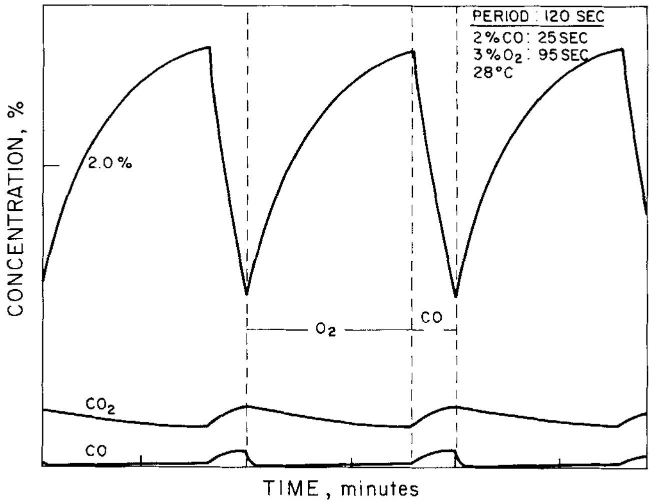

Fig. 13. Reactor outlet concentrations during a 2 min period at 28°C.

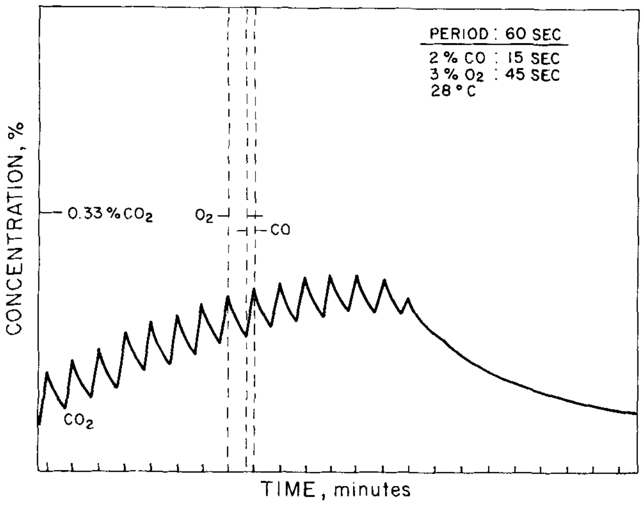

Fig. 14. Start-up to a quenched reaction rate.

As with the 60°C data, a periodic startup of the reactor using the oxygen pretreatment when the F_{CO} was too large resulted in carbon dioxide production as illustrated in Figure 14. The production of carbon dioxide went through a maximum and then tailed off to a negligible value. The excessively long transient of carbon dioxide in Figure 14 results from the desorption from the alumina support at this low reaction temperature.

Carbon monoxide pretreatment of the catalyst followed by periodic feed simply gave negligible reaction for all of the conditions which gave appreciable rates for the oxygen pretreatment.

EFFECT OF TEMPERATURE

Production of carbon dioxide was measured by continuous NDIR at various reactor temperatures for periodic switching between the 2% carbon monoxide and 3% oxygen streams at a total period of 1 min. The maximum average rate due to this periodic operation is plotted in Figure 15 at each temperature. Note that the horizontal dashed line corresponds to a F_{CO} of 0.75 which represents stoichiometric carbon monoxide and oxygen and denotes the maximum possible reaction rate. Thus complete conversion of both carbon monoxide and oxygen are obtained at temperatures greater than 70°C under periodic operation.

The steady state reaction rate corresponding to an F_{CO} of 0.75, 1.5% carbon monoxide and 0.75% oxygen, is also shown on Figure 15. It should be noted that this steady state feed composition does not exhibit rate multiplicity. This allows a direct comparison between periodic operation leading to complete conversion of both reactants and a stoichiometric feed stream at steady state. A conservative estimate at 70°C is that the periodic switching yields complete conversion and achieves a rate which is twenty times the steady state rate when the time average feed stream compositions are identical and stoichiometric.

DISCUSSION OF RESULTS

A qualitative interpretation of these results is best made by reference to the elementary steps for this reaction system. For simplicity, the last step, the Eley-Rideal step, will not be considered further, so that the only step leading directly to carbon dioxide production is the surface interaction between adsorbed carbon monoxide and adsorbed atomic oxygen. The rate of this step would be a maximum where the surface coverages of both CO-S and O-S would be equal. If the periodic operation is such that these surface coverages are kept near to these desirable surface coverages, then the rate would be at its highest value. These ideas are qualitatively presented in Figure 16.

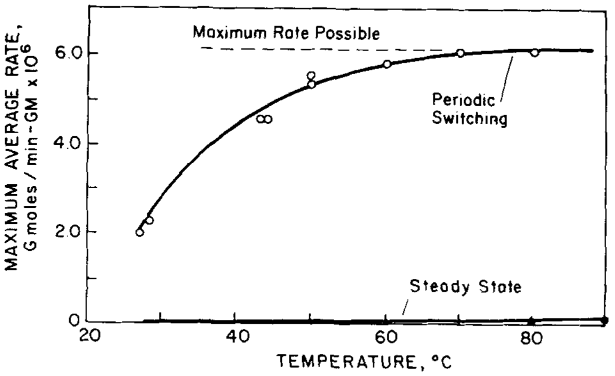

Fig. 15. Rate comparison of periodic to steady state operation for stoichiometric feed.

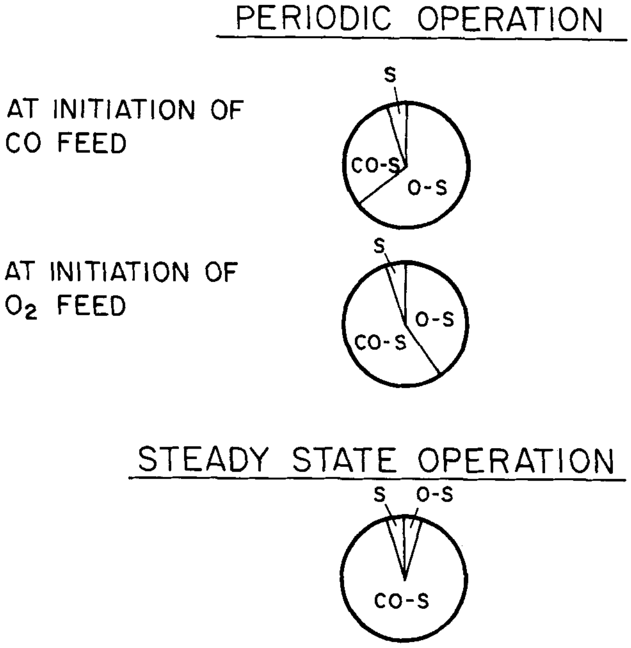

Fig. 16. Relative surface coverages during periodic and steady state operation for stoichiometric feed.

Steady state operation for stoichiometric feed, however, leads to a very large surface coverage of CO-S and very low coverage of O-S. These steady state coverages lead to very low rates as shown in Figure 16 when compared to the coverages under periodic operation. The strong irreversible adsorption of carbon monoxide postulated here is consistent with the periodic concentration profiles, where carbon monoxide concentrations are always quite low. Significant carbon monoxide in the reactor indicates that the platinum surface is almost completely covered with carbon monoxide, and this quenches the reaction rate because oxygen can no longer adsorb to undergo reaction. Good evidence for this is the extinguishing of the high rate during periodic switching as the F_{CO} is increased beyond a critical valve. Here if the surface rate cannot remove the CO-S, then the rate of reaction is very effectively quenched.

ACKNOWLEDGMENT

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Mixing with Helical Ribbon Agitators

Of necessity, the mixing process is sometimes restricted to the laminar regime, although turbulent mixing is generally more desirable. Common examples of laminar mixing are found when the fluid has a very high viscosity, or when one of the mixture components is shear sensitive. It has been pointed out that the helical ribbon agitator (HRA) is admirably suited to the low Reynolds number mixing process. This work derives a model to predict the power consumption of the HRA. The model has been developed with the aid of experimental data and tested extensively using literature data. For a wide range of mixer geometries and sizes, it predicts power consumption with an average deviation of 13%.

The concept of relative efficiency of mixers is also described as an aid to comparing different HRA mixer geometries. Finally, the problem of scale-up of different HRA configurations is discussed.

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Part II. Newtonian Fluids

SCOPE

The mixing of very viscous fluids is qualitatively and quantitatively quite different from the process of blending low viscosity fluids. Parker (1964) noted that the helical ribbon agitator (HRA) is particularly well suited for mixing viscous liquids where the mixer flow is laminar. This observation is supported by the data of Gray (1963) and Johnson (1967). The choice of a mixer configuration is governed by three characteristic parameters: mixing time, power consumption, and mixer efficiency. The efficiency of a mixer is related to the total energy required to achieve a given degree of homogeneity. Mixing efficiency has been virtually ignored by previous workers, undoubtedly due to the impossibility of finding a usable definition of the (thermodynamically) perfect mixing process. This difficulty can be avoided by defining an efficiency relative to an arbitrary, standard mixer. This work proposes a standard mixer. This work proposes a standard mixer, and the relative efficiency $(\mathrm{eff})_{\mathrm{rel}}$ has been used to evaluate five HRA's of different geometries.

Correspondence concerning this paper should be addressed to Pierre Carreau. C. Y. Yap is with the University of Malaysia.

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