Kinetics of CO Oxidation over Co_3O_4/γ-Al_2O_3

Part II: Reactor Dynamics

The transient responses of a fixed-bed reactor to step increases and decreases in CO, O_2, and/or CO_2 feed concentrations were measured and interpreted. It is shown that dynamic methods yield vastly more phenomenological and mechanistic information than steady state measurements, with significantly less experimental effort.

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SCOPE

Dynamic reactor studies are not new, but they have not been widely used. The unsteady state is inherently more complex than the steady state in the same reaction device. However, the very complexity that is so intimidating is also the source of exceptional insight when exploited. This is especially true in catalytic kinetics. Here we are concerned with metal oxide catalysis, a poorly understood field compared with catalysis by supported metals. From the previous paper (Part I), the extent of and limits on understanding available from steady state experimentation on Co_3O_4/γ-Al_2O_3 catalyzed CO oxidation is clear. It was established that catalyst dynamics needed to be explored. In this research, 39 dynamic experiments were performed. They involved step changes in the feed concentrations of one, two, or three components (CO, O_2, and/or CO_2) to the fixed-bed reactor. Interpretations of the observed transient responses led to many deductions on the phenomena involved in this reaction in particular and metal oxide catalysis in general. The results demonstrate the potential for dynamic discernment of catalytic kinetics. The following paper (Part III) will combine these results with information from the literature and from the previous paper (Part I) to postulate and evaluate a reaction mechanism.

CONCLUSIONS AND SIGNIFICANCE

The reactor dynamics studies confirmed and made more definitive many conclusions from the steady state studies. Among them were: 1) the dynamic involvement of the catalyst, 2) the lack of major impact of CO_2 on the rate of reaction, and 3) the rate-determining character of the reoxidation of a reaction site. Further, it was demonstrated that CO_2 was reversibly adsorbed in substantial amounts, but that there was no reversible adsorption of CO and O_2. There was substantial evidence for the existence and involvement of two kinds of adsorbed oxygen besides the lattice oxygen. Similarly, there appear to be three kinds of sites involved in reaction on an oxidized catalyst. Also there appear to be parallel mechanisms active in reaction on a reduced catalyst. All of these conclusions and more will play a role in the postulation of a catalytic mechanism in Part III. Finally, it is shown that dynamic methods yield vastly more information than conventional steady state measurements with significantly less experimental effort.

INTRODUCTION

Dynamic reactor studies are not new, but they have not been widely used in spite of the fact that they can provide a wealth of information regarding reaction mechanisms. Dynamic behavior of a reactor can be brought about in various ways. Most of them involve a disturbance from steady state operation by the imposition of a change in one or more of the operating variables, namely, the concentrations of the reactants, the reactor temperature, the

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pressure, or the total flow rate. The change can be a pulse, a step, or periodic in nature.

One of the earliest works done in this area was by Wagner and Hauffe (1939), who applied a perturbation technique to study the oxidation of adsorbed hydrogen on palladium. To elucidate the reaction mechanism, they measured the response of electrical conductivity to a change in oxygen flow rate. More recently, Stotz used the same technique to study the mechanism of the water-gas shift reaction over FeO (1966a) and oxygen uptake by Cu_2O and NiO foils (1966b).

The most extensive use of the dynamic response technique to elucidate reaction mechanisms was made by Kobayashi and Kobayashi (1972a,b,c; 1975; 1976a,b) and Kobayashi et al. (1976). They studied CO oxidation over MnO_2, Pb_3O_4, and Co_2O_3. Mechanisms were deduced by performing various dynamic experiments involving step changes in the concentrations of the feed to the reactor.

Comprehensive reviews on the use of dynamic kinetic studies in heterogeneous catalysis have been written by Hulbert and Kim (1966), Kobayashi and Kobayashi (1974), and Bennett (1976). The theoretical aspects of periodic operation of reactors are provided by Bailey (1974), while a good review of experimental findings for periodic reactor operation can be found in Abdul-Kareem's doctoral work (1978).

In this research, oxidation of carbon monoxide over supported cobalt oxide (Co_3O_4/Al_2O_3) was studied by both dynamic and conventional steady state methods (see Part I for the latter). The limited results reported in Part I required a year of experimentation to obtain. The emphasis in the present paper is on the description and interpretation of a variety of dynamic experiments. The power of dynamic experiments, as compared to the more familiar steady state investigations, is analyzed. The reader is urged to study also the following paper (Part III), where the results presented here are combined with other information to arrive at a rather coherent, mechanistic picture of oxidation-reduction catalysis by a metal oxide.

EXPERIMENT

Equipment and Materials

The same reaction apparatus and catalyst were used in both steady state and dynamic experiments and were discussed more fully in the previous paper (Part I). Complete details on the equipment, methods of calibration, data analysis, etc., can be found in Perti (1980). For the dynamic experiments 18.69 g of catalyst was packed between two layers of inert glass beads.

The reaction gases, O_2, CO, and CO_2, and the diluent, He, were metered through rotameters and mixed prior to their entry to the reactor. The mixing junction was designed such that any of the reaction gases could be introduced or removed from the stream to simulate a step increase or decrease of the component in question.

Procedures

In this work, the dynamic response of the reactor to a step change in concentration of one or more components in the reactor feed was studied. Such step changes were made either from or to the zero value of the component concentration in question. This was achieved by either removing or introducing the desired component from or to the reactor feed by use of a three-way valve. Since the partial pressures were kept low, such a scheme did not significantly affect either the total flow rate or the partial pressures of the remaining gases. Care was taken to introduce the component gas at the same pressure as that prevailing in the mixing junction to avoid any flow rate change caused by such introduction.

The concentrations of all components were monitored before and after the step change. Since the chromatographic separation took finite time (4 min), only a limited number of data points could be taken for the response to each dynamic experiment. In the event of a rapid transient, the experiment was repeated until sufficient data were obtained. All runs were performed at a temperature of 488.6 ± 1 K and a total pressure of 108.3 kPa. Experiments in which the reactor was bypassed were conducted at room temperature.

RESULTS AND DISCUSSION

Table 1 summarizes all of the experiments that are referred to in this paper. For any one experiment, it indicates the volumetric flow rates and the concentrations of each of the components in the feed both before and after the step is imposed.

Nature of the Steps Imposed

As mentioned earlier, the steps were imposed on the concentration of one or more of the feed components by either introducing or removing the component(s) in question from the feed stream. Due to equipment characteristics and the procedure used, the input perturbations deviated from perfect step functions. Figure 1 shows the CO concentration profiles for a step increase and decrease of CO in a helium/gas stream (experiments I and II). This particular experiment was performed by routing the gas stream via a reactor bypass. The zero time was the instant at which the three-way valve was manipulated to initiate the step.

The initial time lags, approximately 33 s, are the same for both the step increase and the step decrease experiments. This lag is caused by the tubing volume, etc., between the mixing junction where the step is imposed and the gas sampling valve for the gas chromatographs. Calculations bear out this fact quantitatively (Perti, 1980). In the rest of the results presented in this paper, this lag time has been subtracted from the time scale of the concentration responses.

The CO concentration profiles also show distinct S-shapes. Such a deviation from perfect step behavior can be accounted for by a small dead space (1 mL) in the three-way valve used. The details of this deduction can be found in Perti (1980). In this work, no attempt has been made to separate the impact on the response of this equipment-related input imperfection from the actual response due to interaction of the feed components with the catalytic reactor. In the cases where the actual reactor responses are long (minutes), the equipment-related nonideality does not affect the qualitative deductions. For short-term (seconds) responses, care had to be taken while interpreting the results. Truly quantitative information, however, cannnot be obtained from the responses unless the shapes of the imposed input functions are quantified.

Limitations and Quantification

The potential of the dynamic experiments was not fully realized until long after they had been completed. Looking back, it would have been well to obtain more complete data in better defined experiments. That, however, awaits a new generation of apparatus with greatly reduced analysis time, more accurate flow measurements, and a mixing junction capable of producing true step changes. These alterations would allow full quantitative modeling of the fixed-bed reactor dynamics along the lines of Denis and Kabel (1970). Nevertheless, the phenomenological and mechanistic insight presented in this paper requires only qualitative interpretation. At the same time, Perti (1980) provides quantitative support for many of the observations and conclusions presented here.

It was explained in Part I that the absence of physical complications, which was demonstrated for the steady state experiments, could not be guaranteed in the transient experiments. Nowhere in this research were there any indications of mass transfer influences. Likewise, the steady state and most of the transient experiments manifested no heat transfer effects. The only exception is when flow of a reacting mixture (CO and O_2) was initiated or

TABLE 1. INPUT CONDITIONS FOR TRANSIENT EXPERIMENTS

Exp. No.	$10^7 \times$ Vol. Feed Rate, m^3/s*	Inlet Concentrations, mol/m^3					
		At Initial Steady State			After Step Change		
		O_2	CO	CO_2	O_2	CO	CO_2
I	He: 66.7 CO: 0 → 1.57	0.00	0.00	0.00	0.00	0.94	0.00
II	He: 66.7 CO: 1.57 → 0	0.00	0.94	0.00	0.00	0.00	0.00
1	He: 66.7 O_2: 0 → 1.32	0.00	0.00	0.00	0.49	0.00	0.00
2	He: 66.7 O_2: 1.32 → 0	0.49	0.00	0.00	0.00	0.00	0.00
3, 4, 5	He: 66.7 CO: 0 → 1.57	0.00	0.00	0.00	0.00	0.62	0.00
6	He: 66.7 CO: 1.57 → 0	0.00	0.60	0.00	0.00	0.00	0.00
7	He: 156.67 CO_2: 0 → 0.183	0.00	0.00	0.00	0.00	0.00	0.031
8	He: 156.67 CO_2: 0.183 → 0	0.00	0.00	0.031	0.00	0.00	0.00
9	He: 156.67 CO_2: 0 → 0.423	0.00	0.00	0.00	0.00	0.00	0.067
10	He: 156.67 CO_2: 0.423 → 0	0.00	0.00	0.067	0.00	0.00	0.00
11	He: 156.67 CO_2: 0 → 1.58	0.00	0.00	0.00	0.00	0.00	0.27
12	He: 156.67 CO_2: 1.58 → 0	0.00	0.00	0.27	0.00	0.00	0.00
13	He: 156.67 O_2: 1.32 CO_2: 0 → 1.58	0.21	0.00	0.00	0.21	0.00	0.28
14	He: 156.67 O_2: 1.32 CO_2: 1.58 → 0	0.21	0.00	0.28	0.21	0.00	0.00
15	He: 156.67 O_2: 1.32 CO_2: 0 → 1.10	0.20	0.00	0.00	0.20	0.00	0.19
16	He: 156.67 O_2: 1.32 CO_2: 1.10 → 0	0.20	0.00	0.19	0.20	0.00	0.00
17	He: 156.67 CO: 1.57 CO_2: 0 → 1.10	0.00	0.26	0.00	0.00	0.26	0.19
18	He: 156.67 CO: 1.57 CO_2: 1.10 → 0	0.00	0.26	0.19	0.00	0.26	0.00
19	He: 156.67 O_2: 1.32 CO: 0 → 1.57	0.22	0.00	0.00	0.22	0.25	0.00
20	He: 156.67 O_2: 1.32 CO: 1.57 → 0	0.21	0.25	0.00	0.22	0.00	0.00
21	He: 156.67 O_2: 1.32 → 0 CO: 1.57 → 0	0.21	0.25	0.00	0.00	0.00	0.00
22	He: 156.67 O_2: 0 → 1.32 CO: 1.57	0.00	0.25	0.00	0.21	0.25	0.00
23	He: 156.67 O_2: 1.32 → 0 CO: 1.57	0.21	0.25	0.00	0.00	0.25	0.00
24	He: 156.67 O_2: 1.32 CO: 1.57 CO_2: 0 → 1.31	0.21	0.25	0.00	0.21	0.25	0.21
25	He: 156.67 O_2: 1.32 CO: 1.57 CO_2: 1.31 → 0	0.21	0.25	0.21	0.21	0.25	0.00

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* → indicates the component and direction of step change.

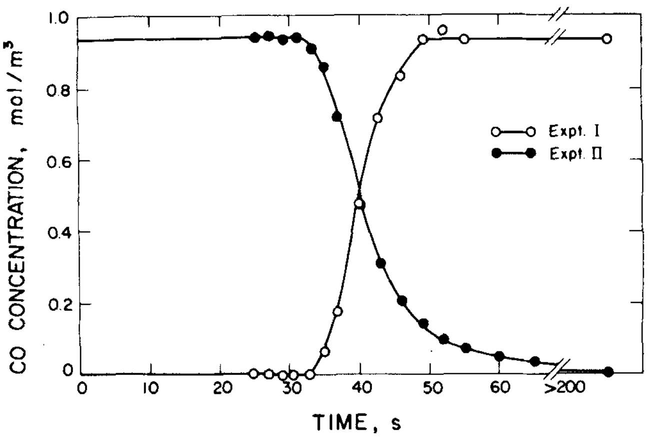

Figure. 1. Shapes of imposed step changes (obtained via the reactor bypass).

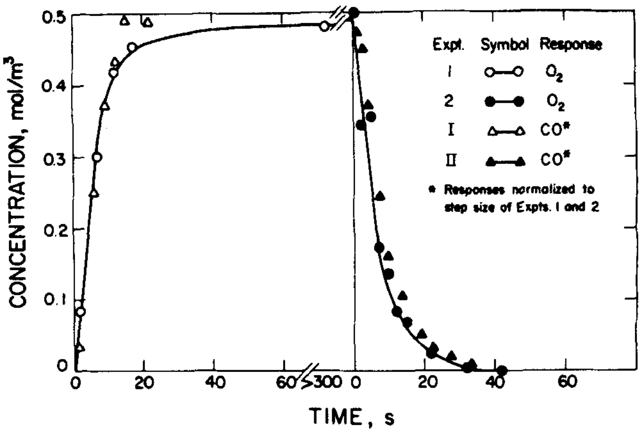

Figure 2. O_2 responses to step changes in O_2 feed concentration.

terminated and a shift in bed temperature was observed. This shift resulted from the heat release of the reaction at a 50% conversion level, never exceeded 4 K, and quickly followed the imposition of the step change. The temperature was controlled throughout the transient period within ±1 K. The matter will be addressed again briefly in the discussion of experiments 19–23. The impact is thought to be minor, however, and all interpretations here and in Part III are based in reaction and adsorption phenomena.

Results of One-Component Experiments

As the title implies, these experiments involved only one feed component besides the diluent helium. One-component transient experiments were performed using each of the three components of interest: O_2, CO, and CO_2. These are described separately in this section.

Experiments with O_2. Experiments 1 and 2 were performed to obtain O_2 concentration responses when a step increase or decrease in O_2 concentration was imposed. The results are shown in Figure 2. Also plotted in Figure 2 are normalized results of experiments I and II. The normalization is done by calculating the ratio of the CO concentration at any time to the magnitude of the CO step (experiments I and II) and multiplying it by the magnitude of the O_2 step in experiments 1 and 2.

Comparing the results of experiments 1 and I, one finds that CO has reached the steady state value of 0.49 within 20 s, while the O_2 response takes a longer time to achieve steady state, reaching only 0.46 in 17 s and 0.48 in 72 s. This implies that there is a slight uptake of O_2 by the catalyst. If the uptake were very slow, it could have been totally disguised by the scatter in the data. In a separate experiment, not listed in Table 1, the catalyst bed was reduced in CO and He for 24 h before an O_2 step increase was imposed. Only O_2 was observed in the reactor effluent and the O_2 response was similar to that of experiment 1. Thus one can conclude that the O_2 uptake by the catalyst is small but discernible.

Comparison of the results of experiments 2 and II indicates that there are no significant differences in the responses. Thus, whatever O_2 might be adsorbed on the catalyst is not eluted when a step decrease of O_2 concentration is imposed. Even if O_2 desorption were slow, it would have been detected by the gas chromatographs. However, no lingering tail was found in the O_2 response of experiment 2.

Experiments with CO. The responses to step changes in CO concentration over a catalyst that had been reduced in CO for periods of up to 24 h were identical to those for normalized results from experiments I and II. It can be concluded that minimal reversible CO adsorption occurs over the reduced catalyst.

The picture is different, however, for oxidized catalysts. Experiments 3, 4, and 5 were conducted to obtain responses to step increases of CO concentration for the cases where catalyst was pretreated for periods of 1, 16, and 66 h, respectively, in a stream of helium containing 0.49 mol O_2/m^3 at 488 K. After each pretreatment, pure helium was passed through the catalyst bed to purge any unadsorbed oxygen from the reactor and accessory tubing. The O_2 and CO_2 responses are shown in Figure 3. Solid curves are drawn to roughly represent the sparse and scattered data for CO_2. In all three cases, CO_2 was observed in the reactor effluent. Oxygen, however, appeared only in experiments 4 and 5. A single dashed curve passes through all O_2 data points for both 16 and 66 h pretreatment cases. The data are too few and scattered to confirm or refute the implied, but unlikely, identical responses.

The amount of CO_2 formed, as is evident from the areas under the CO_2 curves, shows an increase as the pretreatment time in O_2 was increased. In separate experiments not reported in this paper, increasing the oxygen pretreatment time above 66 h did not change the amount of CO_2 formed beyond that found in experiment 5. The shape of the CO_2 response of experiment 3 (1 h O_2 pretreatment) shows an initial maximum followed by a steady decline, while those in experiments 4 and 5 (higher O_2 pretreatment times) show distinct rises, with delayed maxima occurring around 6 min, followed by slowing declines.

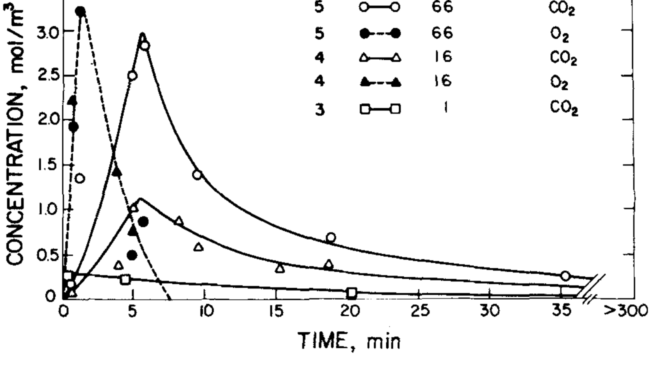

Figure 3. CO_2 and O_2 responses to step increases of CO over preoxidized catalyst.

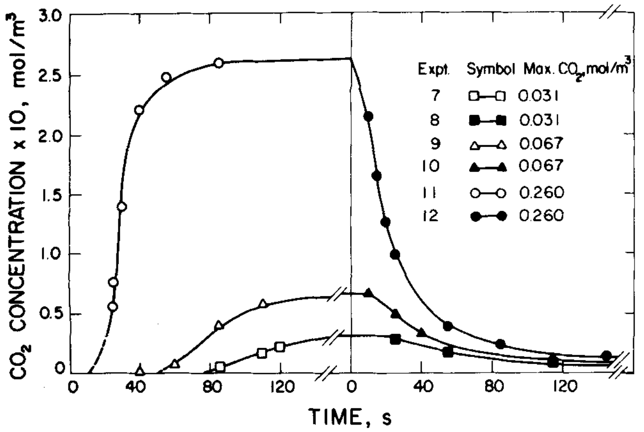

Figure 4. CO_2 responses to step changes in CO_2 feed concentration.

There was no oxygen observed in the reactor effluent of experiment 3. However, in experiments 4 and 5, distinct oxygen responses with sharp rises and slightly less sharp declines were observed. After about 8 min no further oxygen response was observed.

The following conclusions can be drawn from these results:

- CO must be reacting with either adsorbed or lattice oxygen in each of these experiments.
- Since the amount of CO_2 formed increases with increases in O_2 pretreatment time, the catalyst surface must be capable of adsorbing oxygen in increasing quantities over a long period of time (between 16 and 66 h).
- The appearance of O_2 responses in experiments 4 and 5 indicates the presence of some weakly adsorbed oxygen that is released by interaction of CO with the catalyst.
- The maxima in the CO_2 responses of experiments 4 and 5 occur at about the same time at which the O_2 responses vanish. This suggests that the weakly bonded oxygen may be blocking the sites on which CO reacts with oxygen to form CO_2.
- The monotonous decline of the CO_2 response in experiment 3 indicates that CO, upon reacting with surface oxygen, forms an adsorbed species on the catalyst and that the subsequent desorption of the CO_2 is a much faster step in the overall process. Otherwise, the CO_2 response would have displayed a delayed maximum (Kobayashi, 1982). The decline in CO_2 formation occurs because the surface oxygen concentration continually declines as CO_2 is formed.

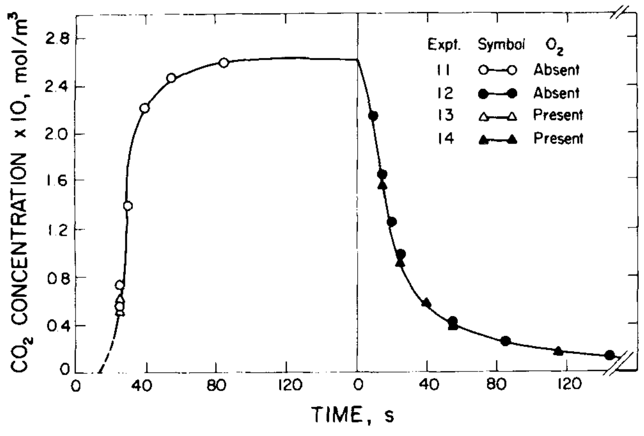

Figure 5. CO_2 responses to step changes of CO_2 in presence and absence of O_2.

The responses of CO to the CO step increases for the catalyst with its three initial levels of oxygen content are not shown here. The responses were, however, seen to be increasingly slow (compared to the normalized response of experiment I) as the pretreatment time in oxygen increased. This observation is consistent with the conclusions given immediately above.

Experiment 6 was a sister experiment to experiments 3, 4, and 5. A CO step decrease was imposed on the reactor after a long exposure to CO in the absence of oxygen. The data are not presented in this paper, but they showed a response similar to the normalized response of experiment II. This implies that no CO comes off the catalyst after the down step and thus CO is not reversibly adsorbed on the catalyst.

Experiments with CO_2. Experiments 7, 9, and 11 were conducted to obtain the reactor responses to step increases in CO_2 concentration of three different magnitudes. The corresponding step decrease responses were obtained in experiments 8, 10, and 12. The results are plotted in Figure 4.

These responses are distinctly slower and different than the normalized results of experiments I and II (Figure 2). Thus it can be concluded that CO_2 adsorbs in significant quantities over the catalyst. The early delays in CO_2 responses in experiments 7, 9, and 11 are not the result of lag time in tubing, etc., but are caused by adsorption of CO_2 in the catalyst bed. Prior to imposing the CO_2 step increase, the bed is void of any adsorbed CO_2. As CO_2 enters the bed, it must be adsorbing rapidly, first at the entrance and in time throughout the length of the bed. Thus a finite amount of time elapses before CO_2 is detected in the effluent. This time of delay should increase with decreasing CO_2 concentration. Adsorption isotherms are normally concave downward. Thus at lower concentrations, the adsorbent takes up a larger proportion of the adsorbate in the gas than at higher concentrations.

Similar delays for corresponding reasons are found in the down step experiments (8, 10, and 12). It should be noted that for a step decrease experiment the time until the CO_2 response starts decreasing is shorter than the delay at the start of the CO_2 response for the corresponding step increase experiment. This can be explained by a slower rate of CO_2 desorption, even near saturation, than the rate of adsorption under nonequilibrium conditions.

One may be interested in extrapolating the trend of the upstep curves for CO_2 in Figure 4 to the level of concentration for O_2 in Figure 2. It may be that the upstep CO_2 response would appear similar to that of oxygen. To see that CO_2 is adsorbed vastly more than O_2, which is negligible, merely compare any of the CO_2 downstep curves to that for experiments 2 and II (Figure 2).

To interpret properly the CO_2 adsorption on the supported catalyst ($Co_3O_4/\gamma\text{-}Al_2O_3$), any effects of the support alone should be considered. It was found from steady state experiments that $\gamma\text{-}Al_2O_3$ did not catalyze CO oxidation at the reaction conditions of this work. In dynamic experiments, similar to experiments 7–12 except that a bed of pure support material ($\gamma\text{-}Al_2O_3$) replaced the bed of supported catalyst, CO_2 was found to be adsorbed on the $\gamma\text{-}Al_2O_3$. Quantitative comparisons between the supported catalyst and pure support experiments showed that about two-thirds of the CO_2 adsorption took place on the Co_3O_4 and only one-third on the $\gamma\text{-}Al_2O_3$, despite the fact that the Co_3O_4 comprises only 6.5% by weight of the catalyst. Thus, while CO_2 adsorption on the catalyst support may have a minor influence on the responses shown in Figure 4, adsorption on the Co_3O_4 phase is the dominant factor. This is even more true when the adsorbed CO_2 is produced on the catalytically active sites. In this case all the support phase could do is to retard the appearance of CO_2 following an upstep in CO. And yet initial maxima were observed in experiment 3 and, more impressively, in experiment 19 to be presented later. Thus the qualitative observations discussed in this paper and the mechanistic

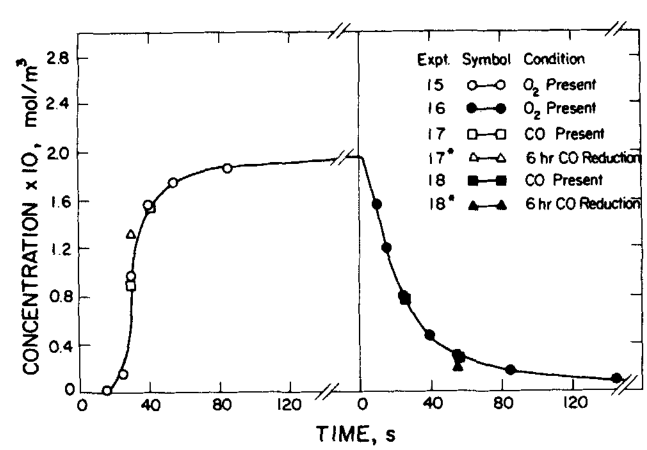

Figure 6. CO_2 responses to step changes of CO_2 in presence of O_2 or CO.

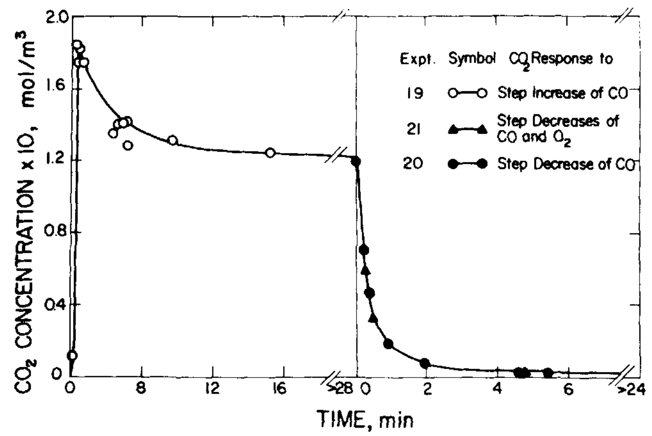

Figure 7. CO_2 responses to step changes of CO in presence of O_2.

ideas presented in Part III are not influenced significantly by CO_2 adsorption on the γ-Al_2O_3.

Results of Two-Component Experiments

Such experiments can be divided into two groups. One involves nonreactive pairs O_2-CO_2 and CO-CO_2; the other involves the reactive pair CO-O_2.

Nonreactive Pairs: O_2-CO_2 and CO-CO_2. Figure 5 includes the results of experiments 13 and 14 in which CO_2 step responses were obtained in the presence of O_2. Also included in Figure 5 are the one-component CO_2 responses of experiments 11 and 12 in which no O_2 was present. All data available suggest that the responses are identical; i.e., the presence of O_2 does not affect CO_2 adsorption. In a separate (unreported) experiment, 16 h of O_2 pretreatment (the same as in experiment 4) was followed by shutting off the oxygen flow and purging the reactor with pure helium. Then a step increase in CO_2 was imposed. No oxygen was found in the reactor effluent. This suggests that interaction of CO_2 with extensively oxidized catalyst does not release weakly adsorbed oxygen as did CO in experiments 4 and 5.

Experiments 15 and 16 were similar to 13 and 14 but at a lower magnitude of the CO_2 step. These also were done in the presence of O_2. The results are shown in Figure 6. Also included in Figure 6 are the results of experiments 17 and 18 in which CO_2 steps were performed in the presence of CO. Prior to CO introduction, the bed was pretreated in O_2 to minimize catalyst reduction. Experiments 17 and 18 were completed within a 2 h period, thus the reduction of the catalytic surface was not extensive. There is no difference to be seen between the CO_2 responses in the presence of CO and those in the presence of O_2.

However, after about 6 h of reduction in CO, the CO_2 adsorption was found to be significantly lower. This can be seen from the solitary triangles in Figure 6 where CO_2 breakthroughs come earlier in each experiment. The solitary data points were verified twice and should be considered valid.

It can be concluded that neither O_2 nor CO directly influences the adsorption of CO_2 except insofar as they influence the oxidation state of the catalyst.

Reactive Pair: CO-O_2. Experiments 19 and 20 were conducted to obtain the responses of the reactor to step changes in CO concentration in the presence of O_2. The oxygen pretreatment never exceeded 1 h. Experiment 19 is similar to experiment 3 except that in 3 the oxygen flow was shut off prior to the introduction of CO while in 19 it was not.

Figure 7 shows the CO_2 responses to a CO step increase and decrease. For the CO step increase the response is a typical "overshoot" type (Kobayashi, 1977). Such a response indicates that CO_2 is formed and desorbed much faster than the regeneration of adsorbed oxygen on the surface can take place. Early in the transient, when the concentration of surface oxygen is at a maximum, the largest amount of CO_2 is formed. The quantity of CO_2 formed then declines because adsorbed oxygen is consumed faster than it can be replenished from the gas phase. At the apparent steady state the rate of consumption of surface oxygen must equal the rate of its adsorption from the gas phase. Experiment 3 also showed a similar CO_2 response, except that there was no gas phase oxygen available to regenerate the surface oxygen.

The response of CO_2 to a CO step decrease (experiment 20, Figure 7) is substantially slower than the normalized result of bypass experiment II (Figure 2). This demonstrates that the CO_2 formed on the catalyst by reaction at the previous steady state requires finite time to desorb. Figure 7 also includes the results of experiment 21 in which step decreases in CO and O_2 were imposed simultaneously. The responses in experiments 20 and 21 are identical. This shows that the presence of CO_2 in the reactor effluent results from desorption of CO_2 previously formed on the catalytic surface. The possibility of a reaction between adsorbed CO (if it exists) and gaseous oxygen can be ruled out, because then the CO_2 responses in the presence and absence of O_2 would have been different.

Experiments 22 and 23 were the opposite of 19 and 20, in the sense that CO_2 responses to a step increase and decrease of O_2 in the presence of CO were obtained. Prior to the imposition of the O_2 step, CO was passed over the catalyst for about 0.5 h. Figure 8 shows the results.

The CO_2 response to the step increase in O_2 concentration rises almost instantaneously and then declines slowly. The decline is too rapid to be explained by the catalyst deactivation discussed in Part I. If CO_2 were forming by the interaction of gaseous CO with oxygen adsorbed after the step change, one would expect CO_2 formaton to rise slowly because O_2 adsorption has been shown to be a slow step. The observed behavior could mean that the 0.5 h of pretreatment in CO is not sufficient to remove all of the adsorbed oxygen from the catalyst. However, the achievement of a steady state within 0.5 h in experiment 19 (see Figure 7) contradicts this idea. Alternatively, there may be a parallel mechanism for CO_2 formation over a reduced catalyst. One such mechanism can be ruled out, as it was shown earlier that adsorbed CO (if it exists) does not react with gaseous oxygen. In another unreported experiment, after the 0.5 h hour reduction in CO, the CO was shut off and the reactor was purged with helium. Upon initiation of the step increase in oxygen, no CO_2 was observed in the reactor effluent. This further substantiates the lack of reaction between O_2 and adsorbed CO.

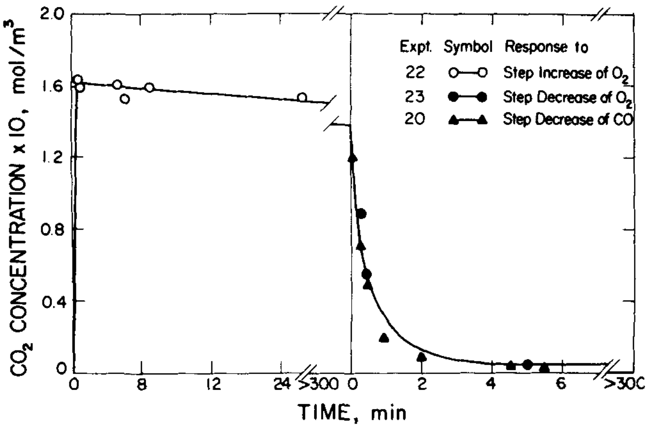

Figure 8. CO_2 responses to step changes of O_2 in presence of CO.

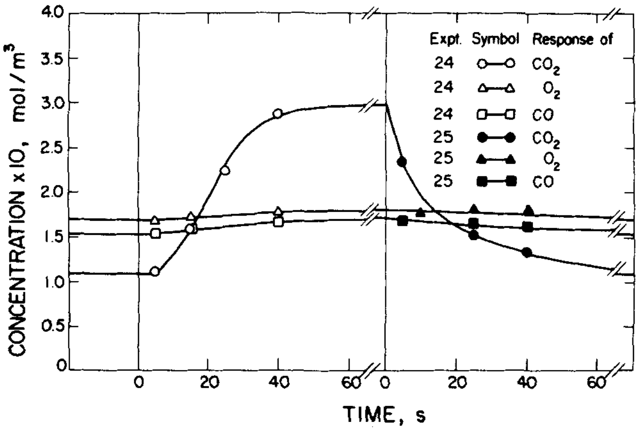

Figure 9. O_2, CO, and CO_2 responses to step changes in CO_2 feed concentration.

A possible explanation of the behavior shown in Figure 8 could be that anionic vacancies exist on the reduced surface. Such a vacancy could react with a gaseous oxygen molecule to fill the vacancy and form a highly reactive dissociated oxygen atom. Such an oxygen species could react with CO in the gas phase to produce CO_2. Such CO_2 formation would be rapid and should decline quickly as the vacancies become filled. Meanwhile, though, oxygen would be adsorbing on the surface and CO_2 formation via CO interaction with adsorbed oxygen would increase. The cumulative response for CO_2 formation could be that shown in Figure 8. Thus two methods are postulated for the production of CO_2 on a reduced catalyst: (1) reaction of CO with lattice oxygen producing a lattice vacancy, and (2) reaction of CO with dissociated oxygen atoms produced when lattice oxygen is restored. This is, however, speculation as there is no direct evidence of such a dual mechanism for the unsteady state reaction over the reduced catalyst.

The CO_2 response to a step decrease in O_2 concentration while CO feeding continues shows slightly more formation of CO_2 than in experiments 20 and 21, where CO flow was stopped along with O_2. This is to be expected because CO can react continually with surface oxygen to form small quantities of CO_2 for a long period of time. The O_2 and CO responses in experiments 19, 20, 22, and 23 are conceptually interesting but are not shown here because they merely reinforce conclusions that have already been reached. Complete details on these and all other experiments are available from Perti (1980).

The foregoing interpretations on reactive pair (CO-O_2) experiments have ignored the thermal transients that were known to be momentarily present in experiments 19–23. Although the thermal transients may have had some quantitative impact on the data of experiments 19, 20, 21, and 23, it is believed that the qualitative features of these experiments, and hence their interpretation, remain unchanged. Only in experiment 22 (Figure 8) is there the prospect of qualitative change. This curve was explained somewhat speculatively by a combination of phenomena. The addition of another phenomenon, the thermal transient, does not invalidate the explanation. More definitive measurements and quantitative modeling are required to reconcile the situation.

Results of Three-Component Experiments

In this category of experiments only the effect of adding CO_2 into the reactor already undergoing reaction at steady state was studied. Figure 9 shows the results.

Prior to CO_2 addition, CO_2 is being formed as a reaction product. The CO_2 response, as the CO_2 step increase is imposed on the reactor, increases slowly. This shows that considerable adsorption occurs on the catalyst. The rate of reaction is depressed as is evident by slight increases in CO and O_2 levels. However, this decrease in conversion (about 10%) resulted from a near-tripling of CO_2 concentration in the reactor. This shows that most of the CO_2 adsorption occurs on sites other than where reaction takes place;

TABLE 2. COLLECTED EXPERIMENTAL OBSERVATIONS AND DEDUCED CONCLUSIONS

• Catalyst state changes • Catalyst deactivation is reversible • CO_2 has little effect on rate of reaction	• No reversible O_2 adsorption • No reversible CO adsorption • Substantial reversible CO_2 adsorption
• No effect of O_2 and CO on CO_2 adsorption • CO_2 adsorption is less on extensively reduced catalyst • CO_2 adsorption occurs on sites other than reaction sites • 3 kinds of oxygen Lattice Adsorbed (reactive) Adsorbed (weakly bound) • Weakly bound oxygen inhibits CO_2 formation	• CO_2 desorption is more rapid than formation • CO_2 formation and desorption is more rapid than regeneration of oxygen site • No reaction occurs between adsorbed CO and gaseous O_2 • 3 kinds of sites on oxidized catalyst Lattice oxygen Where reactive oxygen is adsorbed Where CO_2 and weakly bound oxygen are adsorbed • Parallel mechanisms exist to produce CO_2 on reduced catalyst

otherwise the supression of conversion would have been more pronounced.

Upon a step decrease in CO_2 concentration, the CO_2 response decreases and achieves its original value. This indicates that CO_2 adsorption is totally reversible. Likewise, the CO and O_2 concentrations return to their previous levels.

CONCLUSIONS

Some 39 dynamic experiments were performed and most of them have been presented here. The conclusions deduced from these experiments are collected in Table 2. The power of relatively simple to perform, dynamic experiments in a conventional fixed-bed catalytic reactor is evident. Such experiments provide considerably more information on reaction mechanism than familiar steady state methods. Further, the steady state experiments, described in Part I, took more than a year to conduct. In contrast, the dynamic experiments were completed in less than four months. Thus the dynamic methods yielded vastly more phenomenological and mechanistic information with significantly less experimental effort than did the steady state measurements. In Part III the results described here are combined with the results of other experimenters to provide a coherent mechanistic picture of CO oxidation over $Co_3O_4/\gamma\text{-}Al_2O_3$.

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