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Transient Behavior of Carbon Monoxide Oxidation on Red Lead (Pb_3O_4)

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The transient behavior of carbon monoxide oxidation on red lead (Pb_3O_4) caused by the stepwise change in the concentrations of reaction components was investigated in detail. The experimental results indicated that the reaction between gaseous carbon monoxide and adsorbed oxygen is the slowest step in the overall reaction and that the adsorption of oxygen during the reaction is not in partial equilibrium. Based on these results, a possible reaction mechanism is proposed and the kinetic parameters in each elementary step are determined by means of a computer simulation technique. A characteristic overshoot-type behavior of the response curve of effluent carbon dioxide due to the stepwise change of carbon monoxide in the feed stream can be attributed to the slow adsorption of oxygen on Pb_3O_4. The response curves under different conditions can be also well explained with this interpretation.

1. INTRODUCTION

It has been pointed out by some investigators (*1*, *2*) that some of the heterogeneous catalytic reactions were controlled by more than two elementary steps. However, one cannot easily determine only by using steady state kinetic analyses whether the reaction is controlled by a single elementary step or more than two elementary steps.

As has been described in our previous papers (*3*, *4*), when a reactant concentration jump is imposed at the inlet of catalyst beds, a transient response curve of a reaction product concentration in outlet stream shows a characteristic mode depending on the kinetic structure. Although the oxidation of carbon monoxide proceeds easily on various metal oxides, the kinetic structures of the reaction on different oxides are quite different from each other. For example, the oxidation of carbon monoxide on oxygenated Cr_2O_3 surface is controlled by only one elementary step (*5*), which is the reaction between gaseous carbon monoxide and the surface oxygen species. In this case, the response of the concentration of carbon dioxide in the outlet stream caused by the concentration jump of carbon monoxide in the feed is instantaneous and a new steady state is reached immediately. On the other hand, the oxidation of carbon monoxide on MnO_2 is controlled by two elementary steps (*3*), which are the reaction between gaseous carbon monoxide and the surface oxygen species and the desorption of carbon dioxide produced by the reaction, and the corresponding response in this system is by no means instantaneous but shows a gradual and monotonous approach to a new steady state.

In the present study, the transient behavior of carbon monoxide oxidation on red lead (Pb_3O_4) caused by the concentration jump was investigated in detail, and a possible reaction mechanism is proposed from the analyses of those response curves. The kinetic parameters for each elementary step are also determined by computer simulation.

2. Experimental

Red lead was prepared by thermal decomposition of lead nitrate as follows. After lead nitrate was decomposed to lead monoxide (yellow) at 380°C in an air flow for 5 hr, this oxide was slowly and completely converted into red lead by heating in an oxygen flow at 470°C for 30 h. Examination by X ray diffraction analysis revealed the structure of red lead (Pb_3O_4). The sample used as the catalyst was in 42 ~ 60 mesh granule and found to have BET surface area of 0.4 m^2/g.

Carbon monoxide, carbon dioxide, oxygen, nitrogen and helium from commercial cylinders were purified through a dry ice–methanol trap to remove water vapor. The reactor consists of a Pyrex glass tube of 5 mm i.d. containing 50 g catalyst and the temperature of the catalyst bed was kept uniform within ±0.2°C at desired temperatures.

Experiments were carried out in an ordinary flow system and the total flow rate of gas was always kept constant at 167 ± 2 (NTP) ml/min. For the transient response measurements, the composition of inlet gas mixtures was suddenly changed by using nitrogen or helium as a diluent with special case to keep the total flow rate unchanged. The transient response to the step change in the composition of $He–N_2$ mixture was completed within 15 sec. Reaction conditions were chosen in such a way that the total conversion of carbon monoxide did not exceed 0.05 in all experimental runs.

Gas chromatography was used to analyze the reaction gases while the surface oxygen species were analyzed chemically by using potassium iodide solution (KI method) as follows. The catalyst used under various conditions was carefully displaced into a vessel without exposing to air and the KI solution prepared with various pH was introduced into the vessel allowing to react with the catalyst under vigorous shaking for 6 h. The amount of the surface oxygen species was then determined by titration of produced iodine with a standard sodium thiosulfate solution. A more detailed description of transient response method (*3*) and KI method (*6*) which are used in this study can be found elsewhere.

3. Results and Discussion

The response of a component Y in the outlet gas mixture to a step change in the concentration of X in the inlet gas stream is designated as X–Y response. When X is increased, X(inc.)–Y and when decreased, X(dec.)–Y, and when X is increased from nil, X(inc.,0)–Y, and when decreased down to nil, X(dec.,0)–Y.

3.1. Transient Behavior of Carbon Monoxide

It is our primary concern in the kinetic study of the reaction to know whether carbon monoxide is adsorbed on the surface or not. One can easily obtain the information for the adsorption of carbon monoxide by examining the CO–CO response. If carbon monoxide is adsorbed on the surface during the reaction, the response of carbon monoxide at the outlet of the reactor due to the step change in the inlet concentration of carbon monoxide will be slow. The CO–CO response observed at 250°C was instantaneous as shown in Fig. 1, indicating no appreciable adsorption of carbon monoxide. This result was also supported by the following separate experiments.

After a catalyst was kept under a steady state of the reaction, the inlet carbon monoxide concentration was decreased down to nil by switching over to a stream of either pure helium or helium containing oxygen (21%). The carbon dioxide response in each case was separately fol-

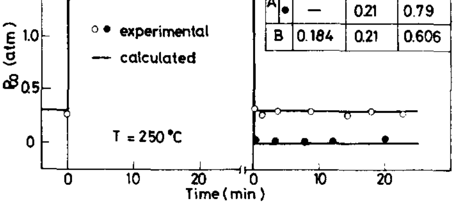


FIG. 1. CO–CO response.

lowed and compared. If carbon monoxide were adsorbed on the surface, the CO(dec.,0)-CO_2 response obtained in the stream of helium containing a large amount of oxygen should be higher than that obtained in the stream of pure helium due to the reaction between gaseous oxygen and adsorbed carbon monoxide. However, the CO(dec.,0)-CO_2 response in both cases were exactly the same. Moreover, even when the catalyst, which had been pretreated with helium-carbon monoxide mixture for 5 h, was heated up to 320°C in a helium stream, the desorption of neither carbon monoxide nor carbon dioxide was detected.

From these results, it may be concluded that the gaseous carbon monoxide reacts directly with active surface oxygen species according to the Rideal-Eley mechanism.

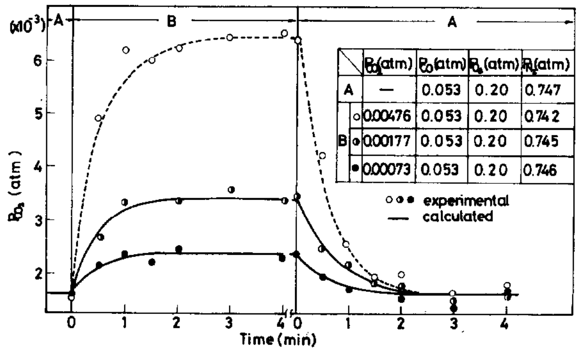
3.2. *Transient Behavior of Carbon Dioxide*

After the catalyst had established a steady state in a feed stream of $P_{CO} = 0.035$, $P_{O_2} = 0.21$ and $P_{N_2} = 0.755$ atm at 250°C, carbon dioxide of various partial pressure ($P^{no}_{CO_2}$) was introduced into the inlet gas stream without changing the concentration of carbon monoxide and oxygen and the CO_2(inc.,0)-CO_2 response was followed. Subsequently the carbon dioxide in the inlet gas stream was cut off again and the CO_2(dec.,0)-CO_2 response was followed. Both response curves obtained are shown in Fig. 2. The transient state of the response was observed for about 3 min indicating that carbon dioxide was adsorbed on the surface during the reaction. At the newly established steady state, the partial pressure of carbon dioxide in the exit gas stream was exactly equal to the sum of initial partial pressure of carbon dioxide and $P^{no}_{CO_2}$. It means that the rate of carbon dioxide formation is not affected by the adsorption of carbon dioxide and this will further suggest that the adsorption site of carbon dioxide is different from that of oxygen, because unless otherwise the adsorption of carbon dioxide will retard the adsorption of oxygen and eventually suppress the rate of the reaction.

From the graphical integration of CO_2(inc.,0)-CO_2 and CO_2(dec.,0)-CO_2 response curve in Fig. 2, respectively, one can easily calculate the amounts of adsorbed and desorbed carbon dioxide. Both quantities are in good agreement and this result indicates that carbon dioxide is reversibly adsorbed on the surface. Furthermore, it is shown that a plot of the amounts of adsorbed carbon dioxide against its partial pressure follows a Langmuir adsorption isotherm and the saturated amount of adsorbed carbon dioxide is estimated to be 3×10^{-6} mole/g at 225°C.

3.3. *Determination of Catalytically Active Oxygen Species*

As has been pointed out in our previous paper (*6*), the nature of oxygen species adsorbed on oxide surface is not the same but widely distributed in oxidation power and only a particular part of them is



		P_{CO_2}(atm)	P_{CO}(atm)	P_{O_2}(atm)	P_{N_2}(atm)
A		—	0.053	0.20	0.747
B	○	0.00476	0.053	0.20	0.742
	◐	0.00177	0.053	0.20	0.745
	●	0.00073	0.053	0.20	0.746

FIG. 2. CO_2-CO_2 response.

catalytically active. To determine the amount of surface oxygen species which are active for the oxidation of carbon monoxide on Pb_3O_4, both the transient response method and the KI method were used.

Namely, after the fresh catalyst had been placed in an oxygen (20%)-helium stream for a sufficient time, the stream was switched over to a carbon monoxide (1.5%)-helium stream. The change of the concentrations of carbon dioxide in the outlet gas stream (CO(inc.,0)-CO_2 response) was followed for 5 h and the results are shown in Fig. 3. The rate of carbon dioxide formation reached rapidly to a maximum value and then decreased slowly. The graphical integration of the CO(inc.,0)-CO_2 response curve in Fig. 3 gives the amount of carbon dioxide produced by the reaction between gaseous carbon monoxide and surface oxygen species which are catalytically active, and the amount of oxygen reduced by carbon monoxide within 5 h was estimated to be 4.2×10^{-5} mole/g. This value was found to be unchanged even when the oxygenated surface was pretreated with pure helium stream for about 30 minutes prior to the above runs, but it was appreciably decreased by the same pretreatment for about 10 h. This indicates that the desorption rate of oxygen is extremely slow.

On the other hand, the results obtained by the KI method are presented in Fig. 4. As can be seen from Fig. 4, the surface oxygen species on the catalysts can be classified into two parts, one which has a higher oxidation power than 9 and the other which has a lower oxidation power than 9, and they are designated as O_s^h and O_s^l, respectively. The distribution curves of oxygen obtained with catalysts which had been reduced by carbon monoxide for various periods of time showed the decrease in the amount of O_s^h as compared with that of the fresh catalyst, while the amounts of O_s^l remained almost unchanged. This result clearly indicates that the O_s^h is responsible for the carbon monoxide oxidation. The amount of O_s^h initially existed on the fresh catalyst surface was 6.2×10^{-5} mole/g and that on the catalyst which had been reduced for 5 hr was 3.1×10^{-5} mole/g. The difference between both amounts, 3.1×10^{-5} mole/g, gives the amount of O_s^h which was picked up by carbon monoxide. This value is fairly close to that estimated by the response method.

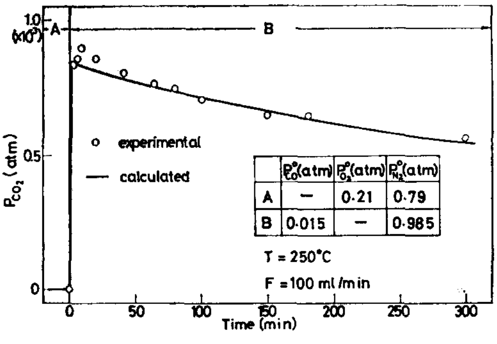


FIG. 3. CO(inc.,0)-CO_2 response.

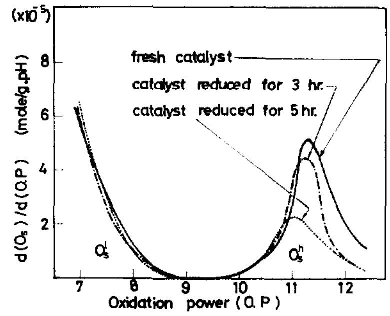


FIG. 4. Variation of the distribution curves of oxidation power of the surface oxygen caused by the reduction with CO.

The amounts of O_s^h under steady states of the reaction were measured at various concentrations of carbon monoxide and the results were shown in Fig. 5 together with the reaction rates which were measured simultaneously. One can see from Fig. 5 that there is a slight decreasing tendency of the amount of O_s^h with increasing partial pressure of carbon monoxide with which the reaction rates increase linearly. As has been mentioned in the earlier section, carbon monoxide is not adsorbed on the surface and the adsorption site of carbon dioxide is different from that of oxygen, hence the decrease in the amount of O_s^h cannot be attributed to the competitive adsorption of oxygen and either carbon

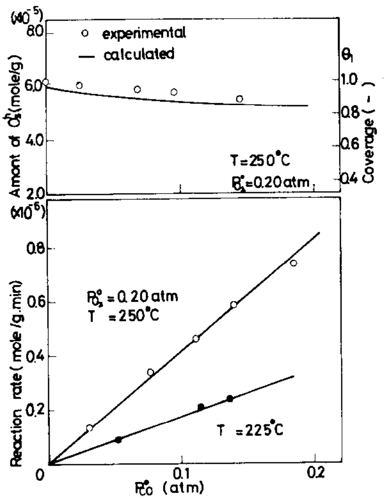


FIG. 5. The reaction rate and θ_1 as a function of $P_{CO}{}^0$.

monoxide or carbon dioxide. It may, therefore, be attributed to the slow rate of oxygen adsorption on vacant active sites which are generated by the reduction with carbon monoxide, i.e., the adsorption of oxygen during the reaction will not be fast enough to attain substantial adsorption equilibrium.

3.4. Simulation of Transient Behavior of Carbon Monoxide Oxidation

(1) Presentation of reaction mechanism. According to the discussion presented in the earlier sections, gaseous carbon monoxide reacts directly with the surface oxygen species and produces the adsorbed carbon dioxide, and the carbon dioxide is reversibly adsorbed on the active sites which is different from that of oxygen. One can represent this sequence as follows:

$$O_2(g) + 2S_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2O \cdot S_1, \qquad (1)$$

$$CO(g) + O \cdot S_1 + S_2 \xrightarrow{k_3} CO_2 \cdot S_2 + S_1, \qquad (2)$$

$$CO_2 \cdot S_2 \underset{k_5}{\overset{k_4}{\rightleftharpoons}} CO_2(g) + S_2, \qquad (3)$$

where S_1 and S_2, respectively, represent the sites for activated adsorption of oxygen and carbon dioxide.

(2) Simulation of transient response curves. The procedures of making the unsteady state material balance for each reaction component, the solution of differential equations and the determination of rate constants are exactly the same as described in the previous papers (*3*, *4*).

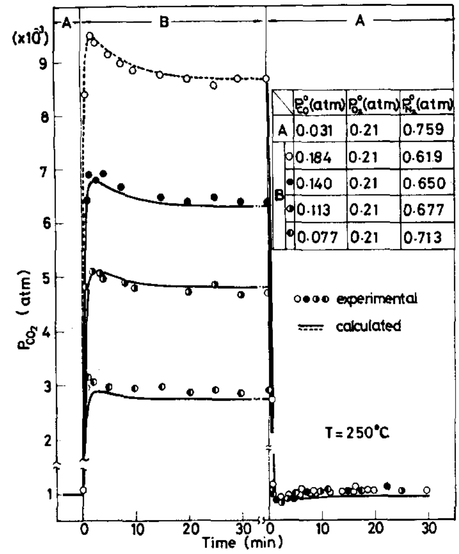
In determining the unknown parameters which appear in unsteady state material balance equations by means of a parameter optimization technique, it is preferable to minimize the number of unknown parameters such as θ_i and k_j. The surface coverage of adsorbed oxygen during the reaction, θ_1, can be estimated as the ratio of adsorbed oxygen during the reaction and the total amount of $O_s{}^h$ determined by the KI method, 6.2×10^{-5} mole/g. Also the surface coverage of carbon dioxide during the reaction, θ_2, can be estimated in the same way with the saturated amount of carbon dioxide calculated from the Langmuir adsorption isotherm, 3×10^{-6} mole/g, which has already been mentioned in the preceding section. Therefore, the remaining unknown parameters are $k_1 \sim k_5$ in Eqs. (1)–(3).

Since the simultaneous determination of all five unknown parameters is rather difficult, the two parameters k_4 and k_5 in Eq. (3) are to be determined first by using the CO_2–CO_2 response data in Fig. 2. The CO_2(inc.,0)–CO_2 response obtained by the step change in the inlet partial pressure of carbon dioxide between nil and 4.76×10^{-3} atm (open circle in Fig. 2) were used for this purpose. Marquardt's method (*7*) for deterministic nonlinear optimization was employed and Runge–Kutta–Gill's method (*8*) was used for the numerical integration. These calculations were performed by a digital computer, FACOM 230-60.

The optimum values of the two rate constants determined are

$$k_4 = 2.0 \times 10^{-5} \text{ mole/g} \cdot \text{min},$$
$$k_5 = 4.5 \times 10^{-4} \text{ mole/g} \cdot \text{min} \cdot \text{atm},$$

and the response curve calculated by using these rate constants is shown with dotted line in Fig. 2. Another response data under different conditions are also compared with the calculated curves (solid lines) showing



		P°_{CO} (atm)	$P^\circ_{O_2}$ (atm)	$P^\circ_{N_2}$ (atm)
A		0.031	0.21	0.759
B	○	0.184	0.21	0.619
	●	0.140	0.21	0.650
	◑	0.113	0.21	0.677
	◐	0.077	0.21	0.713

FIG. 6. CO–CO_2 response.

a satisfactory agreement as can be seen in the same figure.

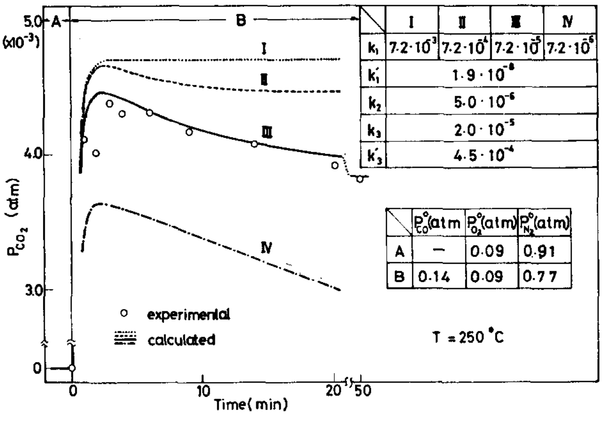
Subsequently, by using the values of k_4 and k_5 determined above, another three parameters $k_1 \sim k_3$ in Eqs. (1) and (2) can be easily determined in the same way by utilizing the CO–CO_2 response data shown in Fig. 6. As can be seen from Fig. 6, a characteristic overshoot behavior was observed in all experimental runs and this characteristic behavior is more pronounced in the runs of higher carbon monoxide concentrations. The CO(inc.)–CO_2 response curves in the run of highest carbon monoxide concentration, which was shown with open circle in Fig. 6, was used to estimate the values of $k_1 \sim k_3$ and the determined values are

$$k_1 = 7.2 \times 10^{-5} \text{ mole/g} \cdot \text{min} \cdot \text{atm},$$
$$k_2 = 1.9 \times 10^{-8} \text{ mole/g} \cdot \text{min},$$
$$k_3 = 5.0 \times 10^{-6} \text{ mole/g} \cdot \text{min} \cdot \text{atm}.$$

By using the values of $k_1 \sim k_5$ determined, another CO–CO_2 response data under different reaction conditions are simulated and shown with solid line in Fig. 6. All calculated response curves are in fair agreement with the experimental response data. Furthermore, the CO(inc.,0)–CO_2 response in Fig. 3 and the CO–CO response in Fig. 1 can be also simulated with satisfactory agreement by the same calculation. From the good agreement between experimental and calculated values, it may be concluded that the values of k_j determined in the present study are reasonable.

From the comparison among the values of k_j, one may easily recognize that the slowest step in the forward reactions is the reaction between gaseous carbon monoxide and the surface oxygen species and this result is consistent with the apparent first order dependence of the reaction rate with respect to the concentration of carbon monoxide.

Since k_4 is four times larger than k_3, k_3 can be roughly estimated from the initial



	I	II	III	IV
k_1	$7.2 \cdot 10^{-3}$	$7.2 \cdot 10^{-4}$	$7.2 \cdot 10^{-5}$	$7.2 \cdot 10^{-6}$
k'_1	$1.9 \cdot 10^{-8}$			
k_2	$5.0 \cdot 10^{-6}$			
k_3	$2.0 \cdot 10^{-5}$			
k'_3	$4.5 \cdot 10^{-4}$			

	P°_{CO} (atm	$P^\circ_{O_2}$ (atm)	$P^\circ_{N_2}$ (atm)
A	—	0.09	0.91
B	0.14	0.09	0.77

FIG. 7. CO(inc.,0)–CO_2 response.

reaction rate obtained by the extrapolation of the CO(inc.,0)–CO_2 response curve to the intercept at $t = 0$ in Fig. 3. The production rate of carbon dioxide from Eq. (2) is

$$\gamma = k_3 P_{CO} \theta_1 \theta_{v_2}, \tag{4}$$

where θ_1 is the surface coverage of oxygen and θ_{v_2} the fraction of vacant sites for carbon dioxide adsorption. With the experimental data, $\gamma = 7.5 \times 10^{-8}$ mole/g·min, $P_{CO} = 0.015$ atm, and $\theta_1 = \theta_{v_2} = 1.0$ in Eq. (4), the value of k_3 is determined to be

$$k_3 = 5 \times 10^{-6} \text{ mole/g} \cdot \text{min} \cdot \text{atm}.$$

This value is exactly the same with that obtained by the simulation.

The value of k_2 is about two orders of magnitude smaller than that of other k_j, and this result is also consistent with the experimental findings that the surface oxygen was desorbed extremely slowly from the oxygenated surface in the helium stream as mentioned in the earlier section.

It was suggested in the earlier section that the rate of oxygen adsorption was not fast enough to attain the adsorption equilibrium during the reaction, whereas the value of k_1 determined above is one order of magnitude larger than k_3. Let us examine the effect of the value of k_1 upon the mode of CO–CO_2 response by the simulation with various values of k_1. The results are shown in Fig. 7. From the comparison of the simulated response curves with different values of k_1, one can recognize that the higher the value of k_1, the less significant becomes the overshoot-type behavior and it disappears at higher values of k_1 than 7.2×10^{-3}. It clearly indicates that the overshoot-type behavior can be attributed to the rate of adsorption of oxygen, which is not fast enough to attain adsorption equilibrium.

Since larger amount of adsorbed oxygen is present on the surface under lower partial pressure of inlet carbon monoxide as shown in Fig. 5, the stepwise increase in the partial pressure of carbon monoxide will result in the sudden increase of effluent carbon dioxide due to the initial higher concentration of surface oxygen, followed by a gradual decrease of carbon dioxide due to the decrease of the surface oxygen species as a result of insufficient rate of oxygen adsorption.

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