

Application of Transient Response Method to the Study of Heterogeneous Catalysis

III. Simulation of Carbon Monoxide Oxidation Under an Unsteady State

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A likely model for carbon monoxide oxidation over manganese dioxide has been proposed from previous response experiments and the reaction mechanisms were analyzed kinetically by computer simulation of unsteady state reaction data. The rate constants of all elementary steps were successfully determined by the non-linear parameter optimization technique and it was found that the kinetic results were quite consistent with the experimental findings discussed in the previous paper and this substantiates the potential use of the transient response method in the studies of heterogeneous catalysis.

NOMENCLATURE

k_i	rate coefficient for step i , arbitrary unit		catalyst surface = 1.28×10^{-3} and 3.30×10^{-3} moles/g catalyst, respectively
L	total length of the catalyst bed = 83.0 cm	t	time elapsed after the step change of gas composition (min)
P	total pressure = 1 atm	T	temperature ($^{\circ}$ K)
$P_{O_2}, P_{CO}, P_{CO_2}$	partial pressure of oxygen, carbon monoxide and carbon dioxide at the outlet of the catalyst bed, respectively (atm)	U	superficial gas velocity = 620 cm/min
$P_{O_2}^0, P_{CO}^0, P_{CO_2}^0$	partial pressure of oxygen, carbon monoxide and carbon dioxide at the inlet of the catalyst bed, respectively (atm)	U_i	interstitial gas velocity = U/ϵ (cm/min)
$P_{O_2}^{i0}, P_{CO}^{i0}$	partial pressure of oxygen and carbon monoxide at the inlet of the catalyst bed at initial steady state (atm)	x	conversion of carbon monoxide
P_{CO}^{n0}	newly set partial pressure of carbon monoxide at the inlet of the catalyst bed (atm)	Z	distance along reactor length (cm)
q_{O_2}, q_{CO_2}	amount of adsorbate O_2 and CO_2 which may be adsorbed in the saturate values on the	<i>Greek Symbols</i>	
		ϵ	void fraction of packed bed of reactor = 0.5
		$\theta_1, \theta'_1, \theta_2$	coverage for O_2^- , O^- and $CO_2(a)$, respectively
		$\theta_{v_1}, \theta_{v_2}$	fraction of vacant sites for oxygen and carbon dioxide, respectively
		ρ_c	catalyst bed density = 1.94 g catalyst/cm ³ reactor

ρ_m molar density = P/RT
(moles/cm³)

INTRODUCTION

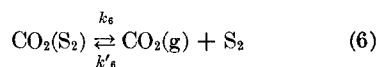
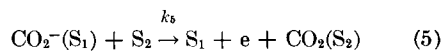
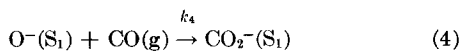
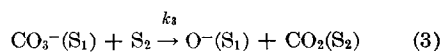
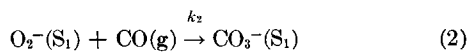
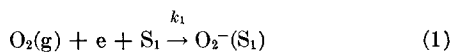
Experimental studies on the transient behavior of heterogeneous systems have been conducted at an increasing pace in recent years, and interesting information has been accumulated through experiments based on this theoretical framework. Stotz (1) showed by analyzing the time variation of the electronic conductivity of FeO films under an unsteady state of the water gas reaction, as the gas phase composition of equilibrium with FeO was suddenly modified, that adsorbed oxygen was the major intermediate for water gas reaction. Hwang and Parravano (2) also showed by studying the unsteady rate of oxidation of CoFe₂O₄ with N₂O and of reduction with CO that both the rate constants and the form of adsorbed oxygen could be determined from the kinetic analysis of transient behavior. In these studies the catalysts were used in the form of a foil or a pressed sample. Lehr, Yurchack and Kable (3) showed by analyzing the behavior of a tubular packed bed reactor with the dehydration of ethyl alcohol under unsteady state that all the experimental observations could be explained qualitatively from the mathematical model proposed. However, the determination of the rate constants of all elementary steps for a complicated heterogeneous catalytic reaction by simulating the behavior of packed bed reactor using parameter optimization has not been done as yet. In our previous study, the transient response to the step change in the concentration of reaction component was followed with an illustrative example of carbon monoxide oxidation on manganese dioxide, and some information was obtained with regard to the mechanisms of the reaction.

In this paper, the results of kinetic analysis of this heterogeneous catalytic reaction were presented, which was done on the basis of information obtained in the previous study. The rate constants for each elementary step were determined by an electronic computer using the parameter optimization technique and the results

were discussed and compared with the experimental findings in the previous study (4, 5).

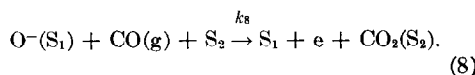
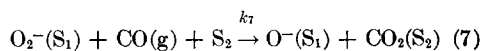
REACTION MECHANISM FOR KINETIC ANALYSIS

The reaction mechanism suggested in the previous study for the catalytic oxidation of carbon monoxide over manganese dioxide can be represented in the sequence of the following steps,



where S₁ and S₂ represent the sites for activated adsorption of oxygen and carbon dioxide, respectively.

As was discussed in the previous paper (5), the steps (3) and (5) are much faster than the steps (2) and (4), respectively, and hence the steps (2) and (3), and (4) and (5) can be reduced to the single steps (7) and (8), respectively, as shown below,



The kinetic analysis of the overall reaction, therefore, will be done by virtue of the steps (1), (7), (8) and (6).

PRESENTATION AND SOLUTION OF EQUATIONS

1. Unsteady State Material Balances

From the presented reaction steps (1), (7), (8) and (6), allowing for accumulation leads to the following material balance equation for gaseous oxygen

$$-\frac{1}{\rho_c RT} \left(P_{O_2} \frac{\partial U}{\partial Z} + U \frac{\partial P_{O_2}}{\partial Z} \right) - k_1 \theta_{v_1} P_{O_2} \\ = \frac{\epsilon \rho_m}{\rho_c P} \cdot \frac{\partial P_{O_2}}{\partial t} \quad (9)$$

Since the conversion of CO is small and the pressure drop and the longitudinal temperature gradient in the reactor are negligible, the value of U can be assumed to be constant along the reactor and the following equation is obtained.

$$\frac{\partial P_{O_2}}{\partial t} = -\frac{U}{\epsilon} \cdot \frac{\partial P_{O_2}}{\partial Z} - \frac{\rho_c RT}{\epsilon} k_1 \theta_{v_1} P_{O_2} \quad (10)$$

Since the amount of oxygen consumed by the reaction is also small, it may be assumed that the longitudinal concentration gradient of oxygen in the gas phase is unvaried along the catalyst bed under both steady and unsteady state conditions. Equation (10) may now be written as

$$\frac{dP_{O_2}}{dt} = \frac{U_i}{L} (P_{O_2}^0 - P_{O_2}) - \frac{\rho_c RT}{\epsilon} k_1 \theta_{v_1} P_{O_2} \quad (11)$$

Similarly, the corresponding equations for carbon monoxide and carbon dioxide are

$$\frac{dP_{CO}}{dt} = \frac{U_i}{L} (P_{CO}^0 - P_{CO}) \\ - \frac{\rho_c RT}{\epsilon} (k_7 \theta_1 + k_8 \theta'_1) \theta_{v_2} P_{CO} \quad (12)$$

$$\frac{dP_{CO_2}}{dt} = \frac{U_i}{L} (P_{CO_2}^0 - P_{CO_2}) \\ + \frac{\rho_c RT}{\epsilon} \left\{ k_6 \theta_2 - \frac{1}{2} k'_6 \theta_{v_2} (P_{CO_2}^0 + P_{CO_2}) \right\} \quad (13)$$

respectively. The material balance for the adsorbed phase becomes

$$\frac{d\theta_1}{dt} = \frac{1}{q_{O_2}} (k_1 \theta_{v_1} P_{O_2} - k_7 \theta_1 \theta_{v_2} P_{CO}) \quad (14)$$

$$\frac{d\theta'_1}{dt} = \frac{1}{q_{O_2}} (k_7 \theta_1 - k_8 \theta'_1) \theta_{v_2} P_{CO} \quad (15)$$

$$\frac{d\theta_2}{dt} = \frac{1}{q_{CO_2}} \left\{ (k_7 \theta_1 + k_8 \theta'_1) \theta_{v_2} P_{CO} \right. \\ \left. + \frac{1}{2} k'_6 \theta_{v_2} (P_{CO_2}^0 + P_{CO_2}) - k_6 \theta_2 \right\} \quad (16)$$

where $\theta_{v_1} = 1 - \theta_1 - \theta'_1$, $\theta_{v_2} = 1 - \theta_2$.

The initial conditions for Equations (11)–(16) are

$$P_{O_2}^0 = f(O), P_{CO}^0 = f(O), P_{CO_2}^0 = f(O), \\ \text{at } t = 0 \quad (17)$$

$$P_{O_2} = \left(1 - \frac{1}{2} x \right) P_{O_2}^0, P_{CO} = (1 - x) P_{CO}^0, \\ P_{CO_2} = P_{CO_2}^0 + x P_{CO}^0 \quad \text{at } t = 0 \quad (18)$$

$$\theta_1 = g(O), \theta'_1 = g(O), \theta_2 = g(O) \\ \text{at } t = 0. \quad (19)$$

Conditions (17) are for the inlet partial pressures of oxygen, carbon monoxide and carbon dioxide at $t = 0$. Conditions (18) are for the outlet partial pressures of oxygen, carbon monoxide and carbon dioxide at the initial steady state. Conditions (19) are for the fractional surface coverage of O_2^- , O^- and $CO_2(\alpha)$ at the initial steady state. The fractional surface coverage of carbon dioxide at the initial steady state given in Eq. (19) can be obtained from the graphical integration of the transient response curve as described in the earlier paper (5). The fractional surface coverages of O_2^- and O^- can not be determined experimentally but are estimated by the steady state approximation as follows. At the steady state $d\theta_1/dt = d\theta'_1/dt = 0$, and hence solving the Eqs. (14) and (15) we obtain the steady state coverages, $\theta_1(ss)$ and $\theta'_1(ss)$, as given by the following equations, respectively.

$$\theta_1(ss) = \frac{k_1 P_{O_2}}{k_7 \theta_{v_2} P_{CO} + k_1 P_{O_2} [1 + (k_7/k_8)]} \quad (20)$$

$$\theta'_1(ss) = \frac{k_1 P_{O_2}}{k_7 \theta_{v_2} P_{CO} + k_1 P_{O_2} [1 + (k_8/k_7)]} \quad (21)$$

Since the partial pressure of oxygen is very large compared with the carbon monoxide under the reaction conditions and also k_1 is very large compared with k_7 as revealed with the experimental data (4), we obtain

$$k_7 \theta_{v_2} P_{CO} \ll k_1 P_{O_2} \left(1 + \frac{k_7}{k_8} \right) \quad (22)$$

$$k_7 \theta_{v_2} P_{CO} \ll k_1 P_{O_2} \left(1 + \frac{k_8}{k_7} \right) \quad (23)$$

Hence, Eqs. (20) and (21) can be reduced to

$$\theta_1(\text{ss}) = \frac{k_8}{k_7 + k_8} \quad (24)$$

$$\theta'_1(\text{ss}) = \frac{k_7}{k_7 + k_8} \quad (25)$$

Equations (24) and (25) indicate that the fractional surface coverages $\theta_1(\text{ss})$ and $\theta'_1(\text{ss})$ are dependent only on the values of k_7 and k_8 .

2. Solution of Equations and Determination of Constants

All six equations (11)–(16) must be solved simultaneously with the initial conditions given by Eqs. (17), (18) and (19). For example, when the partial pressure of only one component P_{CO} is changed to a different value at -26°C , the initial conditions may now be written as

$$\begin{aligned} P_{\text{O}_2}^0 &= P_{\text{CO}}^{i0}, & P_{\text{CO}}^0 &= P_{\text{CO}}^{n0}, & P_{\text{CO}_2}^0 &= 0, \\ P_{\text{O}_2} &= \left(1 - \frac{1}{2}x\right)P_{\text{O}_2}^{i0}, & P_{\text{CO}} &= (1-x)P_{\text{CO}}^{i0}, \\ & & P_{\text{CO}_2} &= xP_{\text{CO}}^{i0}, \\ \theta_1 &= \frac{k_8}{k_7 + k_8}, & \theta'_1 &= \frac{k_7}{k_7 + k_8}, \\ & & \theta_2 &= 0.904P_{\text{CO}} \text{ at } t = 0. \end{aligned} \quad (26)$$

where the value of θ_2 was estimated by the straight line 2 in Fig. 6, in the previous report (5). The unknown parameters are the rate constants in the Eqs. (11)–(16), i.e., k_1 , k_6 , k'_6 , k_7 and k_8 . However, the adsorption equilibrium constant for carbon dioxide was obtained from transient adsorption experiments as $K_{\text{CO}_2} = 46 \text{ atm}^{-1}$ at -26°C . Hence $k'_6 = 46k_6$, the unknown parameters are reduced to the following four constants, k_1 , k_6 , k_7 and k_8 . The unsteady state material balance Eqs. (11)–(16) must be solved with the initial conditions given by Eq. (26) with simultaneous determination of the optimum values of unknown parameters so as to fit the experimental transient response data. In the present case, the experimental data of the CO–CO₂ response to the step change in P_{CO} between 0.034 and 0.07 atm were used for this purpose, because the surface state of the catalyst does not change in this carbon monoxide partial pressure range (6). Among many of the tools for deter-

ministic nonlinear optimization, Marquardt's method (7, 8) was employed in the present study. The Runge-Kutta-Gill's method (9) was used for the numerical integration of Eqs. (11)–(16). A digital computer, FACOM 230-60, was used for this calculation.

RESULTS AND DISCUSSION

The optimum values of the five rate constants were determined as follows.

$$\begin{aligned} k_1 &= 5.46 \times 10^{-3} \text{ moles/g min atm} \\ k_6 &= 9.8 \times 10^{-5} \text{ moles/g min} \\ k'_6 &= 4.51 \times 10^{-3} \text{ moles/g min atm} \\ k_7 &= 4.0 \times 10^{-6} \text{ moles/g min atm} \\ k_8 &= 2.0 \times 10^{-4} \text{ moles/g min atm.} \end{aligned}$$

In Fig. 1, the predicted response curve with these rate constants (broken line) is compared with the experimental response data (open circle), which were used for the determination of optimum parameters. Other response data under different conditions (solid circle) were also compared with the predicted curve (solid line) showing a satisfactory agreement. The CO–CO response curves calculated with the rate constants given above show that the response is instantaneous and is in good agreement with the experimental results as shown in Fig. 2. Although the CO– θ_2 response curve can not be obtained experimentally, the predicted amounts of CO₂ at the steady states can be compared with that obtained in the experiments. Figure 2 shows the satisfactory agreement of both amounts. The predicted CO– θ_1 , CO– θ'_1 response curves showed that θ_1 and θ'_1 are unvaried regardless of the change in the partial pressure of carbon monoxide in the reaction mixture which is consistent with the experimental result in that the amount of catalytically active oxygen O_s^h was independent of the partial pressure of carbon monoxide. Moreover, the predicted fractional surface coverage θ_1 is very large compared with θ'_1 . This result is also consistent with the conclusion of many investigators in that the adsorbed oxygen at low temperature is mainly O_2^- (10–12).

At the steady state, where $\theta_2 \ll 1$, the

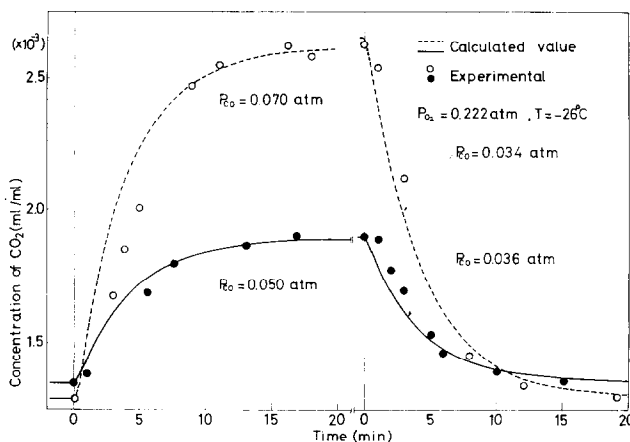


FIG. 1. The experimental and calculated CO-CO₂ response curves during the reaction.

production rate of CO₂ can be expressed by using Eqs. (7) and (8) as follows:

$$\gamma_{\text{cal}} = \frac{2k_7k_8}{k_7 + k_8} \cdot P_{\text{CO}}^0$$

Introducing $k_7 = 4.0 \times 10^{-6}$ and $k_8 = 2.0 \times 10^{-4}$, one may obtain

$$\gamma_{\text{cal}} = 7.68 \times 10^{-6} P_{\text{CO}}^0, \quad (27)$$

Similarly, from Eq. (6),

$$\begin{aligned} \gamma_{\text{cal}} &= k_6\theta_2 - 23k_6P_{\text{CO}_2} \\ &= (0.951 - 23x)k_6P_{\text{CO}}^0. \end{aligned}$$

With $x = 0.038$ and $k_6 = 9.8 \times 10^{-5}$,

$$\gamma_{\text{cal}} = 7.55 \times 10^{-6} P_{\text{CO}}^0. \quad (28)$$

Both production rates of CO₂ calculated from the different elementary steps are quite the same. This result shows that the production rates of CO₂ calculated from each elementary steps are also the same at the steady state. On the other hand, the experimental reaction rate can be obtained from the straight line 3 in Fig. 6 in the earlier paper (5), as follows:

$$\gamma_{\text{exp}} = 6.91 \times 10^{-6} P_{\text{CO}}^0. \quad (29)$$

The agreement between both calculated and experimental values is satisfactory. The results and the discussion presented so far would show that the reaction mechanism proposed is sound and the kinetic analysis performed thereby in this paper reflects the true details of this reaction.

From the comparison of the k_i values presented earlier, one may easily recognize that the reaction between the surface oxygen species O₂⁻ and gaseous CO is the slowest step in the overall reaction. The desorption step of carbon dioxide is the second slowest step and it is consistent with the discussion in the previous work in that the amount of carbon dioxide adsorbed on the catalyst during the reaction is in excess to that expected when the desorption of carbon dioxide is fast and the adsorbed carbon dioxide is in equilibrium with gaseous carbon dioxide. If the value of k_6 is doubled in the simulation with computer, the mode of the CO-CO₂ response

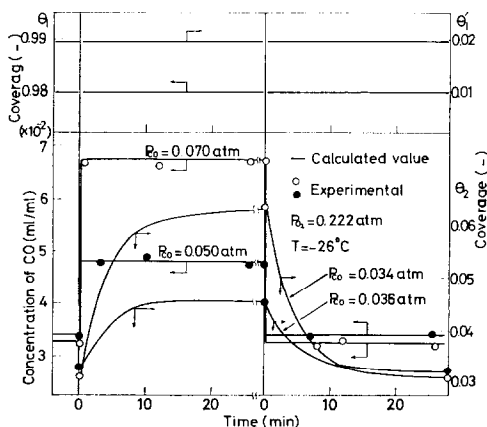


FIG. 2. The experimental and calculated CO-CO and CO- θ_1 , θ_1 , and θ_2 response curves during the reaction.

curve and the amount of CO₂ adsorbed are appreciably changed. This fact also supports this conclusion.

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REFERENCES

1. STOTZ, S., *Ber. Bunsenges. Phys. Chem.* **70**, 37 (1966).
2. HWANG, T., AND PARRAVANO, G., *J. Electrochem. Soc.* **114**, 478 (1967).
3. LEHR, C. G., YURCHACK, S., AND KABEL, R. L., *AIChE J.* **14**, 627 (1968).
4. KOBAYASHI, M., AND KOBAYASHI, H., *J. Catal.* **27**, 100-107 (1972).
5. KOBAYASHI, M., AND KOBAYASHI, H., *J. Catal.* **27**, 108-113 (1972).
6. KOBAYASHI, M., MATSUMOTO, H., AND KOBAYASHI, H., *J. Catal.* **21**, 48 (1971).
7. BALL, W. E., AND GROENWEGHE, L. C. D., *Ind. Eng. Chem. Fundam.* **5**, 181 (1966).
8. MARQUARDT, D. W., *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).
9. MILNE, W. E., "Numerical Solution of Differential Equations." Wiley, New York, 1953.
10. DOI, Y., *Kogyo Kagaku Zasshi* **74**, 803 (1971).
11. TARAMA, K., YOSHIDA, S., ISHIDA, S., AND DOI, Y., *Bull. Chem. Soc. Jap.* **42**, 1161 (1969).
12. CORNAZ, P. F., VAN HOOFF, J. H. C., PLUUM, F. J., AND SCHUIT, G. C. A., *Discuss. Faraday Soc.* **41**, 290 (1966).