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Transient Rate Tracer Studies in Heterogeneous Catalysis: Oxidation of Carbon Monoxide

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Establishment of the mechanism of a catalytic reaction is important from the viewpoints of both catalyst development and construction of suitable rate equations for design purposes. The use of transient tracing employing isotopes is a useful tool for this purpose. In this paper, a new method is described in which the transfer of isotopic species is superposed on a heterogeneous catalytic reaction conducted under steady-state conditions. An efficient method of modeling the system of first-order differential equations describing tracer transfer is presented. The method is applied to the oxidation of carbon monoxide over hopcalite catalyst. A relatively simple model with one type of site for adsorbed carbon oxide species correlates the data well for both $^{13}CO_2$ and ^{13}CO marking. The final step, CO_2 adsorption and desorption, is fast and reversible.

INTRODUCTION

The employment of tracing in which transient transfer of isotopic species is superposed on a heterogeneous catalytic reaction occurring under steady-state conditions is a useful technique for elucidating the mechanism of complex heterogeneous catalytic systems. We have designated this procedure as rate tracing to distinguish it from other isotopic tracing methods (*1*). If a gradientless recirculating reactor is employed, the material balances representing isotopic transfer are a system of first-order differential equations with constant coefficients from which reaction step velocities and surface concentrations of intermediates can be inferred. In a recent experimental study (*2*) we applied this technique to the assessment of step velocities and surface concentrations of surface species for the oxidation of carbon monoxide over commercial hopcalite catalyst. $^{13}CO_2$ Marking was employed and the method of moments was used to interpret the data.

In the present study the theoretical procedure has been amplified to include a nonlinear least-squares regression technique for estimation of the parameters involved, following the procedure described by Spencer *et al.* (*3*). Additional experimental data are also reported here in which ^{13}CO marking is used for carbon monoxide oxidation. The same simplified mechanistic scheme was chosen to interpret the results as previously (*2*):

$$2CO + O_2 = 2CO_2; \qquad (1)$$

$$O_2 + 2l \xrightarrow{v_{+1}} 2Ol,$$

$$CO + Ol \xrightarrow{v_{+2}} CO_2l, \qquad (2)$$

$$CO_2l \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} CO_2 + l.$$

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The three steps in Eq. (2) will add up to the overall reaction Eq. (1), if the first step is taken once and the remaining two steps are each taken twice. $v_{+i}(i = 1, 2, 3)$ represent step velocities; Ol and CO_2l represent intermediates adsorbed on the active sites, l

Bennett (*4*) has recently provided an excellent review of transient method in heterogeneous catalysis studies. Generally a concentration jump of reacting species is employed to perturb the overall reaction rate. As he points out these methods are of great interest in attempts to understand the kinetics of a sequence of steps in heterogeneous catalysis because more information is produced than from steady-state experiments. Thus, explanation of these additional observations must be more nearly correct in order to agree with all the available data.

Conner and Bennett (*5*) have also studied the oxidation of carbon monoxide on nickel oxide catalyst using ^{13}C and ^{18}O. In their studies the tagged gases were pulsed so that not only was tracer transfer transient but the basic reactions themselves were transient as well. The complex response results were interpreted qualitatively. As we also have observed (*2*), Conner and Bennett found that oxide components of the catalyst may exchange with ^{18}O in carbon dioxide, making interpretation of data using ^{18}O more difficult than that with ^{13}C tagging.

Our technique retains a steady-state overall reaction while employing a transient tracer regime. Mathematically our method of interpretation is quite different from that used by Bennett. Since tracer transfer alone is transient there is no need to make any assumption as to the kinetic equations describing the velocities of individual mechanistic steps in terms of rate constants.

THEORY

A considerable simplification in mathematical treatment of transient tracing data is possible, if a rapidly recirculating or stirred tank type of reactor is used to study reaction systems because concentration gradients in space which are present in tabular systems are avoided. In order for the overall reaction in such a system to be at the steady-state condition feed must be continuously introduced and product must be continuously withdrawn. Then, at time $t = 0$, a known concentration of a tagged species is substituted for untagged species in one or more of the feed streams at concentration $\mathbf{z_F}$ and is maintained as a function of time. In our case, we will assume that the initial marking of all species is zero and that a step function change of tagged species is introduced at $t = 0$ and is maintained constant. The fractional marking $\mathbf{z_P}$ of components present over the course of time in the recirculating reaction system may be expressed in terms of material balances, one for each species present in both the gas and chemisorbed phases. These material balances correspond to a system of first-order linear differential equations with constant coefficients. They may be written, for example, as discussed by Amundson (*6*).

$$d\mathbf{z_P}/dt = \mathbf{A}\mathbf{z_P} + \mathbf{b}. \tag{3}$$

The column vector b is determined from the feed input of tracer, which is constant. The **A** matrix consists of coefficients involving the parameters in the material balances, including step velocities and surface concentration of adsorbed species. The solution of Eq. (3) may be expressed as

$$\mathbf{z_P} = \sum_j c_j \mathbf{k}_j e^{\lambda_j t} - \mathbf{A}^{-1}b, \tag{4}$$

where the $\mathbf{k}_j$ are eigenvectors, the λ_j are eigenvalues of **A** and the constants c_j are determined from the initial conditions at $t = 0$. It is of course, possible to determine $\mathbf{z_P}$ if the **A** matrix is specified. The problem here is the inverse, to determine the **A** matrix when all of the solutions corresponding to Eq. (4) are not available. We observe

fractional marking values for reactant and/or product species in the circulating system but generally cannot observe the concentrations of adsorbed species, which will be present in a heterogeneous catalytic system. From these observations, we wish to determine **A**.

For reaction systems in which a marked atomic species passes in a single unbroken path from a reactant through chemisorbed intermediates to a product, the **A** matrix will be tridiagonal. We will be able empirically to determine the values for the constants which appear in Eq. (4) for the marked reactant and/or product. If all reaction steps are reversible, observations of either reactant or product marking will enable us to generate solutions for the unknown intermediates $\mathbf{z_P}$. Known initial values for intermediate marking provide corresponding relationships. Together with the eigenvalues determined from the observed response curve for reactant or product markings, these relationships provide exactly the number of equations required to determine the elements of the **A** matrix (*7*).

For an irreversible reaction, as considered in this paper, one or more of the mechanistic steps will be irreversible. For evaluation of all the elements in the **A** matrix in a single series of experiments, it is necessary to mark the reactant in the *feed* stream and to observe the transient marking in the product stream. Different mechanisms can be assumed and assessed, if they involve different elements in the **A** matrices involved.

In our previous study (*2*), it was established that the adsorption of both CO and O_2 was irreversible. Data were correlated on the basis of material balances for CO_2 and CO_2l for the last step in Eq. (2), involving only v_{+3}. With ^{13}CO marking the same parameters occur but an additional balance for CO is required. Thus the following system of material balances may be written for atomic transfer of ^{13}C which is superposed on a steady overall reaction in which CO is marked in the feed by ^{13}CO following the procedure described in Ref. (2):

$$\frac{F_i^{CO}}{W} z_i^{CO} - \frac{F^{CO}}{W} z^{CO} = \frac{\beta}{W} C^{CO} \frac{dz^{CO}}{dt} + v_{+2} z^{CO}, \quad (5)$$

$$\frac{F_i^{CO_2}}{W} z_i^{CO_2} - \frac{F^{CO_2}}{W} z^{CO_2} = \frac{\beta}{W} C^{CO_2} \frac{dz^{CO_2}}{dt} - v_{+3} z^{CO_2 l} + v_{+3} z^{CO_2}, \quad (6)$$

$$C^{CO_2 l} \frac{dz^{CO_2 l}}{dt} = v_{+2} z^{CO} + v_{-3} z^{CO_2} - v_{+3} z^{CO_2 l}, \quad (7)$$

where C^{CO_2} and C^{CO} = concentrations of gas phase CO_2 and CO in the reaction system, respectively; $C^{CO_2 l}$ = concentration of adsorbed CO_2 on the solid catalyst; F^{CO_2} and F^{CO} = outlet flow rates of CO_2 and CO, respectively; $F_i^{CO_2}$ and F_i^{CO} = inlet flow rates of CO_2 and CO, respectively; t = time following initial injection of isotopic ^{13}CO; $v_{+i} (i = 1, 2, 3)$ = unidirectional step velocities; W = weight of catalyst in system; β = volume of dead space, including that in catalyst pores, voids, and apparatus; z^i = fraction of component i containing tracer (i = CO_2, CO, CO_2l), while those with subscript i indicate inlet fractions. These equations are of the form of Eq. (3) and hence a unique determination of the model parameter groups should be possible.

For convenience in computer programming, (*3*) we will designate as the "state variables" those variables which describe the state of the system at any time, and the differential equations which describe the evolution of the state variables will be called the "system equations." The problem for solution by computer can be formulated

as follows:

$$\begin{aligned} dy_i/dt &= g_i(y_n, b_j, t); \\ y_i(o) &= a_i; \\ i, n &= 1, 2, \ldots, NS; \\ j &= 1, 2, \ldots, NP. \end{aligned} \tag{8}$$

Here t is the independent variable, y_i is the ith state variable, b_j is the jth parameter, and a_i is the initial value of g_i. The functions g_i can be linear or nonlinear. NS represents the number of state variables and NP represents the number of parameters to be determined. We assume that the mth state variable y_m has been measured at times t_k; $k = 1, 2, \ldots, NX$ and denote

$$y_m(t_k) \triangleq Y_k, \quad k = 1, 2, \ldots, NX. \tag{9}$$

Y_k is a function of the unknown parameters b_j,

$$Y_k = Y_k(b_j) \tag{10}$$

and if the measured value of y_m at time t_k is denoted Y_k^*, the problem is to find parameter values b_j such that the NX equations,

$$Y_k(b_j) - Y_k^* = 0, \tag{11}$$

are satisfied. If $NX = NP$, we have NP equations in NP unknowns which could be solved iteratively by the Newton–Raphson method. But generally there are more experimental values than parameters, i.e., $NX > NP$. In this case we cannot demand an exact fit to the data, but must be satisfied with a "best" fit. In this case the "best" fit is taken as a least-square fit which corresponds to minimizing the objective function S,

$$S(b_j) \triangleq \sum_{k=1}^{NX} (Y^*_k - Y_k)^2, \tag{12}$$

which has been quite generally employed in studies of this type. The problem is solved *iteratively*. The curve fitting computer program proceeds by guessing at values for the parameters b_j, using parameter increments to calculate new and improved values, and finally at convergence arrives at a least-squares fit.

In the present case we have two measured state variables z^{CO} and z^{CO_2}. Moreover, for each experiment β, W, C^{CO}, C^{CO_2}, F^{CO}, F^{CO_2}, $F_i{}^{CO}$, $F_i{}^{CO_2}$, $z_8{}^{CO}$, $z_i{}^{CO_2}$, and V (the overall velocity) are known constants. $C^{CO_2 l}$ and v_{+3} are the unknown parameters to be determined. Thus using the material balance Eqs. (5)–(7) we have the following system equations corresponding to equation (8):

$$\begin{aligned} dy_1/dt &= C_{14} - C_7 y_1, \\ dy_2/dt &= 1/b_1[2C_6 y_1 \\ &\quad + (b_2 - 2C_6)y_3 - b_2 y_2] \\ dy_3/dt &= C_{15} + C_8 b_2 y_2 \\ &\quad - C_8(b_2 + C_9)y_3, \end{aligned} \tag{13}$$

where

$$\begin{aligned} y_1 &= z^{CO} & C_1 &= \beta/W & C_9 &= C_3 - 2C_6 \\ y_2 &= z^{CO_2 l} & C_2 &= F^{CO}/W & C_{10} &= F_i{}^{CO}/W \\ y_3 &= z^{CO_2} & C_3 &= F^{CO_2}/W & C_{11} &= F_i{}^{CO_2}/W \\ & & C_4 &= C^{CO} & C_{12} &= z_i{}^{CO} \\ b_1 &= C^{CO_2 \cdot l} & C_5 &= C^{CO_2} & C_{13} &= z_i{}^{CO_2} \\ & & C_6 &= V & C_{14} &= C_{10}C_{12}/C_1C_4 \\ b_2 &= v_{+3} & C_7 &= \left(\frac{C_2 + 2C_6}{C_1C_4}\right) & C_{15} &= C_{11}C_{13}/C_1C_5. \\ & & C_8 &= \frac{1}{C_1C_5} \end{aligned}$$

The solution of Eq. (13) clearly will provide values for the parameters b_1 and b_2. Since the first equation is uncoupled, it does not contribute to this evaluation, but provides a check for the correctness of the z^{CO} observations.

Though the best parameter values have some value alone, it is also desirable to know how reliable they are. This question can be answered by statistical considerations which are incorporated into the computer program (*3*). The basic method employed involves linear approximations of the model equations around their current values b_i using the so-called variational or sensitivity equations (8) which are derived by partially differentiating each system equation with respect to each parameter. In the course of the iterative procedure for parameter determination both the system and variational equations are solved simultaneously and provide estimates of parameter variances and confidence limits. In this procedure a constant error variance was employed based on the reasonable assumption that the errors are the same for all data points.

EXPERIMENTAL

The experimental procedure employed has been previously described (*2*). An all-glass gradientless recirculating reactor was employed. The gas mixtures used were analyzed by a Finnigan Quadrupole mass spectrometer, Type 1015C, with the electron energy fixed at 70 eV. Hopcalite catalyst (Mines Safety Appliance Co., Lot 21315) was crushed and screened to 30- to 60-mesh size for use in the system. Feed mixtures were injected with a 100-cm^3 injector with a syringe pump (Sage Instruments, Model 351). Flow rate of feed gas was 2.00 cm^3 min^{-1} (STP) and that of helium carrier gas was 100 cm^3 min^{-1}. Time intervals for data observation were taken closer together at the beginning of each run where the marking was varying rapidly, so as to obtain roughly equal spacing of data points along the response curves.

The recirculation rate was approximately 3000 cm^3 min^{-1}. Calculations indicate that with the very low reaction rates and dilute mixtures employed interphase and intraphase concentration and temperature gradients are negligible.

RESULTS

All results reported here are for ^{13}C marking, as this was previously shown to be most reliable (*2*). Our earlier study was based on marking of CO_2 alone and the data reported were for experiments in which $^{13}CO_2$ marking was first brought to a steady state; at time $t = 0$ the traced CO_2 was replaced by untraced CO_2. Present results are based on the reverse procedure. Starting with a steady-state reaction of unmarked species at time $t = 0$ the CO_2 contained in the feed is replaced by marked CO_2 in an abrupt step change. Both methods give essentially the same results but the initial concentrations of $^{13}CO_2$ on the catalyst are not directly observable so that the step-up procedure is slightly preferable. The initial values of ^{13}C fractions are not zero because of the natural abundance of this isotope in ordinary CO and CO_2. The differential Eqs. (5)–(7) for the step-up change in tracer are nonhomogeneous as compared with the homogeneous equations for the step-down change (*2*).

In the present study the catalyst was usually pretreated before use by passing a mixture through the system of $CO/O_2 = 2/1$ at room temperature for 24 hr, followed by the passage of helium carrier gas alone. Following this, the desired feed mixture ratio was introduced and the rate of reaction was observed. The rate became constant after a short time, but was periodically monitored every 4 min during the course of an experiment to assure that it remained constant.

Table 1 gives a summary of results for

TABLE 1

$^{13}CO_2$ Step Function Tracing: Oxidized Catalyst[a]

	Run No.		
	030675	031375	100975
Catalyst weight (g)	0.25	0.25	0.25
F^{CO_2} (cm^3 min^{-1}, 24°C)	0.275	0.274	0.38
β (cm^3)	90	90	90
$z_F{}^{CO_2}$ (fractional marking in feed)	0.10 ($\pm 0.5 \times 10^{-2}$)	0.097 ($\pm 0.5 \times 10^{-2}$)	0.06 ($\pm 0.3 \times 10^{-2}$)
C^{CO_2} (outlet volume fraction)	2.7×10^{-3}	2.7×10^{-3}	3.8×10^{-3}
Feed mixture ratio ($CO/O_2/CO_2$)	6/3/1	3/6/1	8/1/1
P (atm)	1.0	1.0	1.0
T (°C)	24.0	24.0	24.0
V (cm^3 of O_2 min^{-1} g^{-1})	0.15 (± 0.03)	0.148 (± 0.03)	0.36 (± 0.2)
v_{+1} (cm^3 of O_2 min^{-1} g^{-1})	0.15 (± 0.03)	0.148 (± 0.03)	0.36 (± 0.2)
v_{+2} (cm^3 of CO min^{-1} g^{-1})	0.30 (± 0.06)	0.296 (± 0.06)	0.72 (± 0.4)
v_{+3} (cm^3 of CO_2 min^{-1} g^{-1})	3.30 (± 0.18)	1.53 (± 0.13)	4.20 (± 0.43)
v_{-3} (cm^3 of CO_2 min^{-1} g^{-1})	3.00 (± 0.18)	1.24 (± 0.13)	3.50 (± 0.43)
$C^{CO_2 \cdot l}$ (cm^3 g^{-1})	2.87 (± 0.10)	2.10 (± 0.15)	2.08 (± 0.20)

[a] Values reported in parentheses are observed standard deviations for V, v_{+1}, v_{+2}, and z_F and computed estimates of standard errors for v_{+3} and $C^{CO_2 \cdot l}$.

$^{13}CO_2$ tracing including new data for $CO/O_2/CO_2$ feed ratios equal to 8/1/1. All results were recomputed using the present technique.

These results were all calculated by the regression procedure described above rather than by using the method of moments as done previously. Evaluation of moments becomes increasingly inaccurate with higher moments because of the occurrence

TABLE 2

^{13}CO Step Function Tracing: Oxidized Catalyst[a]

	Run No.		
	091175	121175	121375
Catalyst weight (g)	0.25	0.25	0.25
F^{CO_2} (cm^3 min^{-1}, 24°C)	0.29	0.27	0.25
β (cm^3)	90	90	90
$z_F{}^{CO_2}$ (fractional marking in feed)	0.15 ($\pm 0.8 \times 10^{-2}$)	0.13 ($\pm 0.7 \times 10^{-2}$)	0.097 ($\pm 0.5 \times 10^{-2}$)
C^{CO_2} (outlet volume fraction)	2.8×10^{-3}	2.6×10^{-3}	2.45×10^{-3}
Feed mixture ratio ($CO/O_2/CO_2$)	6/3/1	3/6/1	8/1/1
P (atm)	1.0	1.0	1.0
T (°C)	24.0	24.0	24.0
V (cm^3 of O_2 min^{-1} g^{-1})	0.18 (± 0.03)	0.14 (± 0.03)	0.10 (± 0.05)
v_{+1} (cm^3 of O_2 min^{-1} g^{-1})	0.18 (± 0.03)	0.14 (± 0.03)	0.10 (± 0.05)
v_{+2} (cm^3 of CO min^{-1} g^{-1})	0.36 (± 0.06)	0.28 (± 0.06)	0.20 (± 0.10)
v_{+3} (cm^3 of CO_2 min^{-1} g^{-1})	2.41 (± 0.26)	2.80 (± 0.32)	2.76 (± 0.27)
v_{-3} (cm^3 of CO_2 min^{-1} g^{-1})	2.05 (± 0.26)	2.52 (± 0.32)	2.56 (± 0.27)
$C^{CO_2 \cdot l}$ (cm^3 g^{-1})	2.40 (± 0.21)	2.33 (± 0.17)	1.71 (± 0.06)

[a] Values reported in parentheses are observed standard deviations for V, v_{+1}, v_{+2}, and z_F and computed estimates of standard errors for v_{+3} and $C^{CO_2 \cdot l}$.

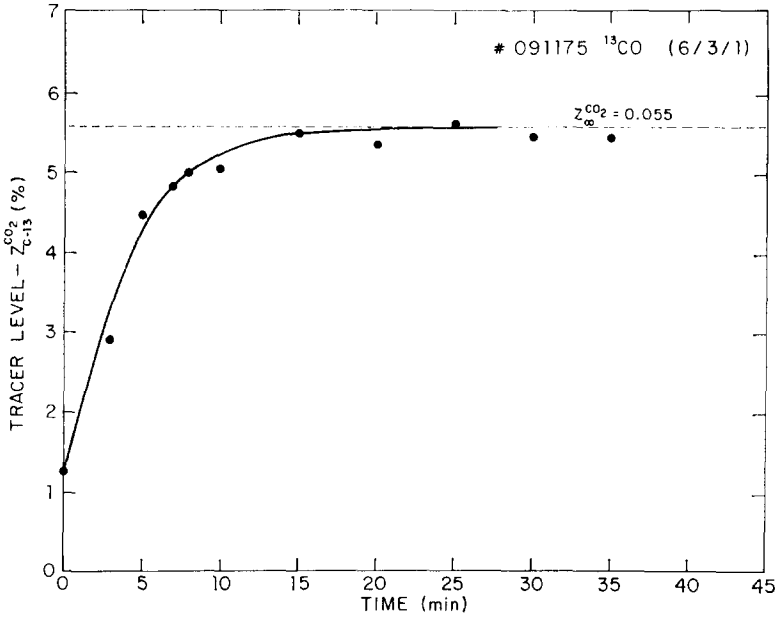

FIG. 1. ^{13}CO Tracing: oxidized catalyst. Solid line represents correlation curve. Points represent data. The steady-state concentration $z_\infty^{CO_2} = 0.055$. Run No. 091175. Feed molal ratio, $CO/O_2/CO_2 = 6/3/1$.

of multiplication by powers of t in the integrand which place increasing significance on the data collected at higher times. While the method of moments is useful in enabling a simple explicit solution of desired parameters, it also becomes unwieldly

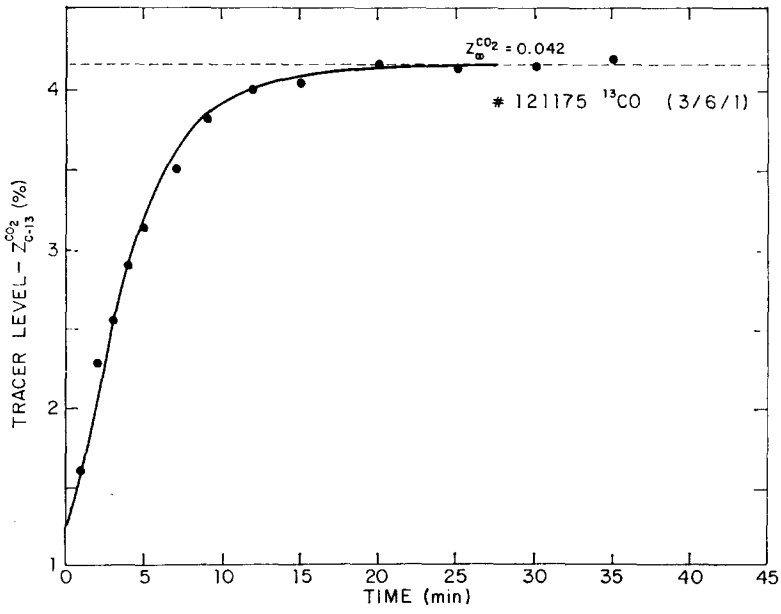

FIG. 2. ^{13}CO Tracing: oxidized catalyst. Solid line represents correlation curve. Points represent data. The steady-state concentration $z_\infty^{CO_2} = 0.042$. Run No. 121175. Feed molal ratio, $CO/O_2/CO_2 = 3/6/1$.

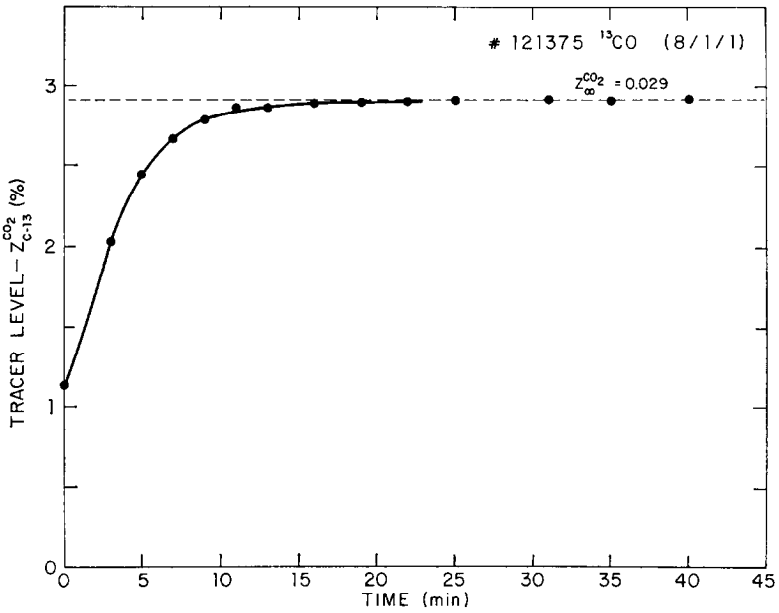

FIG. 3. ^{13}CO Tracing: oxidized catalyst. Solid line represents correlation curve. Points represent data. The steady-state concentration $z_{\infty}^{CO_2} = 0.029$. Run No. 121375. Feed molal ratio, $CO/O_2/CO_2 = 8/1/1$.

when higher moments than the first are required. Present results for $^{13}CO_2$ tracing lead to the previously reported conclusion. The rate of step 3 in Eq. (2) is about 10 times as fast as steps 1 and 2 which are irreversible. The amount of chemisorbed species on the catalyst is about 2 cm^3 g^{-1} in agreement also with separate desorption experiments.

^{13}CO Tracing data are desirable to confirm these results and the fact that no chemisorbed species containing carbon exist other than the chemisorbed CO_2. Table 2 presents such results. The results are very similar to those given in Table 1 with high exchange rate of CO_2 and about 2 cm^3 g^{-1} of CO_2 chemisorbed. Figures 1–3 give a comparison of the predicted and observed levels of ^{13}C marking. The curves are a good representation of the data. Ninety-five percent confidence limits which will be two to three times the standard errors of the parameters v_{+3} and $C^{CO_2 l}$ are also reasonable. Thus there does not appear to be any substantial formation of additional carbon-containing intermediates.

Separate experiments were conducted in which catalyst was reduced by pretreatment. Instead of passing a stoichiometric composition mixture corresponding to $CO/O_2 = 2/1$ over the catalyst, a reducing mixture of $CO/O_2 = 8/1$ was passed over it for 24 hr. After the pretreatment, the system was fed as usual with a predetermined $CO/O_2/CO_2$ mixture which was maintained constant during the course of an experiment. Reaction rates were measured periodically and did not change appreciably over the course of an experiment. Results of these tests are reported in Table 3. Rates of conversion were substantially lower in all cases than those given in Table 2. In these experiments the amount of chemisorbed CO_2 was also somewhat smaller after prolonged exposure of the catalyst to a reducing atmosphere. Figures 4–6 give comparisons of the correlation with observed values of ^{13}C marking. Agreement is generally good with no evidence of unusual systematic deviations.

Calculations were made to determine the 95% confidence limits on parameter values

TABLE 3

^{13}CO Step Function Tracing: Reduced Catalyst[a]

	Run No.		
	080676	081376	012376
Catalyst weight (g)	0.25	0.25	0.25
F^{CO_2} (cm³ min⁻¹, 24°C)	0.23	0.23	0.22
β (cm³)	90	90	90
$z_F{}^{CO_2}$ (fractional marking in feed)	0.114 ($\pm 0.6 \times 10^{-2}$)	0.091 ($\pm 0.5 \times 10^{-2}$)	0.11 ($\pm 5 \times 10^{-2}$)
C^{CO_2} (outlet volume fraction)	2.2×10^{-3}	2.3×10^{-3}	2.2×10^{-3}
Feed mixture ratio ($CO/O_2/CO_2$)	6/3/1	3/6/1	8/1/1
P (atm)	1	1	1
T (°C)	24.0	24.0	24.0
V (cm³ of O_2 min⁻¹ g⁻¹)	0.057 ($\pm$0.01)	0.066 ($\pm$0.01)	0.066 ($\pm$0.01)
v_{+1} (cm³ of O_2 min⁻¹ g⁻¹)	0.057 ($\pm$0.01)	0.066 ($\pm$0.01)	0.066 ($\pm$0.01)
v_{+2} (cm³ of CO min⁻¹ g⁻¹)	0.114 ($\pm$0.02)	0.132 ($\pm$0.02)	0.132 ($\pm$0.02)
v_{+3} (cm³ of CO_2 min⁻¹ g⁻¹)	0.70 ($\pm$0.06)	1.50 ($\pm$0.17)	1.95 ($\pm$0.19)
v_{-3} (cm³ of CO_2 min⁻¹ g⁻¹)	0.59 ($\pm$0.06)	1.37 ($\pm$0.17)	1.82 ($\pm$0.19)
$C^{CO_2 l}$ (cm³ g⁻¹)	1.40 ($\pm$0.10)	1.50 ($\pm$0.10)	1.70 ($\pm$0.10)

[a] Values in parentheses are observed standard deviations for V, V_{+1}, v_{+2}, and z_F and computed estimates of standard errors for v_{+3} and $C^{CO_2 \cdot l}$.

v_{+3}, $C^{CO_2 l}$. As before these generally are about two to three times as great as the standard error values for these parameters in the tables and indicate that there is no significant parameter correlation.

DISCUSSION

Recent studies conducted at temperatures higher than those employed in this investigation (24°C) have suggested more complicated mechanisms than we have

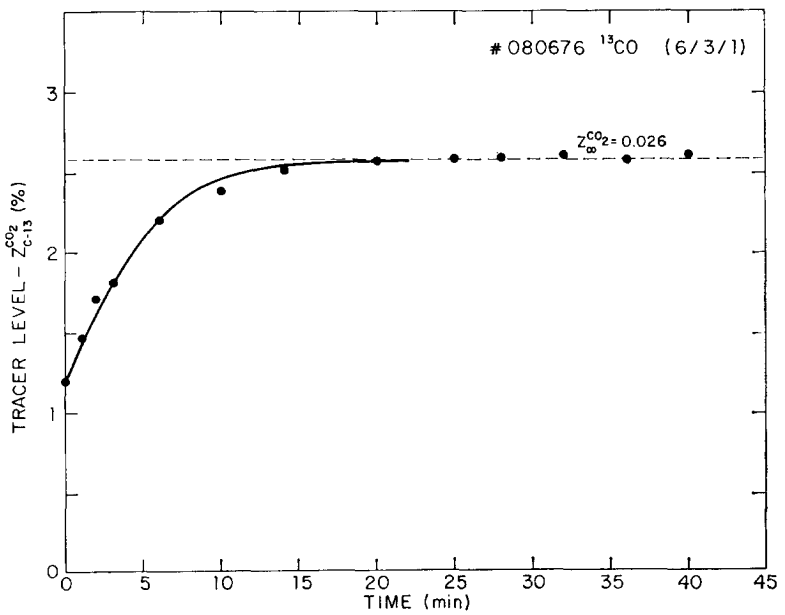

FIG. 4. ^{13}CO Tracing: reduced catalyst. Solid line represents correlation curve. Points represent data. The steady-state concentration $z_\infty{}^{CO_2} = 0.026$. Run No. 080676. Feed molal ratio, $CO/O_2/CO_2 = 6/3/1$.

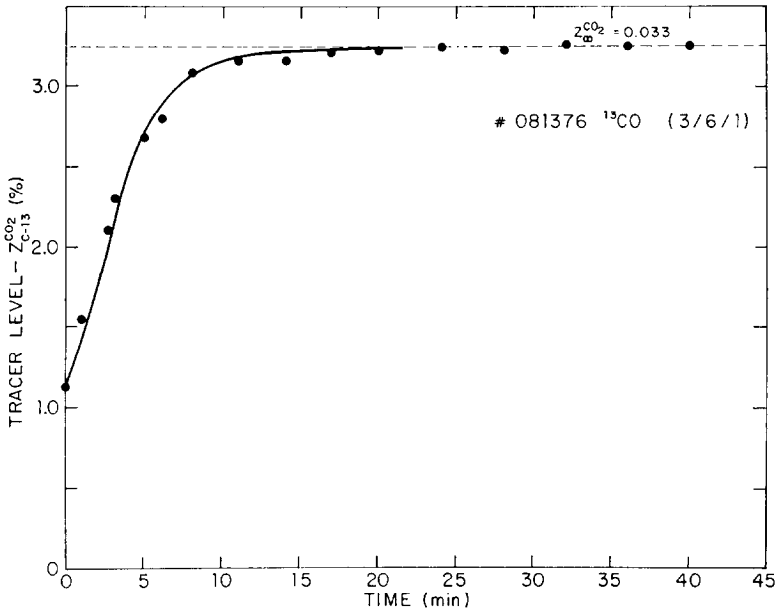

FIG. 5. ^{13}CO Tracing: reduced catalyst. Solid line represents correlation curve. Points represent data. The steady-state concentration $z_{\infty}^{CO_2} = 0.033$. Run No. 081376. Feed molal ratio, $CO/O_2/CO_2 = 3/6/1$.

found necessary to correlate the data we have obtained with hopcalite catalyst. Thus, in the tracer studies of Conner and Bennett (*5*) it was concluded that carbon monoxide oxidation proceeds on nickel oxide (at 160–180°C) by simultaneous

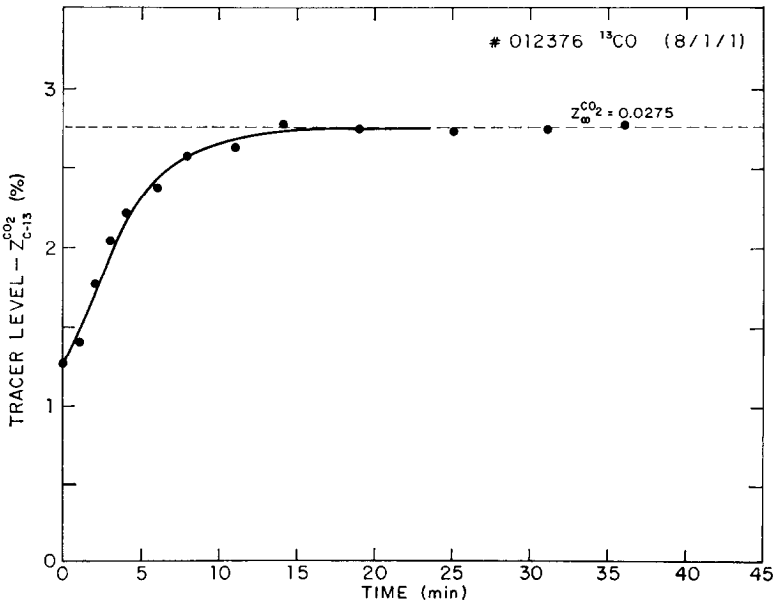

FIG. 6. ^{13}CO Tracing: reduced catalyst. Solid line represents correlation curve. Points represent data. The steady-state concentration $z_{\infty}^{CO_2} = 0.0275$. Run No. 012376. Feed molal ratio, $CO/O_2/CO_2 = 8/1/1$.

TABLE 4

Results from Incorporation of Five-Step Mechanism into Same Nonlinear Least-Squares Regression Program[a]

	v_{+3} (cm³ of CO_2 min^{-1} g^{-1})	C^{CO_2} (cm³ g^{-1})	α (fraction)
Run No. 091175 (6/3/1 feed; oxide catalyst)			
3-Step mechanism	2.41 (±0.26)[a]	2.40 (±0.21)	—
3 + 2-Step mechanism	2.44 (±0.58)	1.53 (±0.90)	0.02 (±0.03)
Run No. 121175 (3/6/1 feed; oxide catalyst)			
3-Step mechanism	2.80 (±0.32)	2.33 (±0.17)	—
3 + 2-Step mechanism	2.14 (±1.22)	1.40 (±1.34)	0.13 (±0.23)
Run No. 121375 (8/1/1 feed; oxide catalyst)			
3-Step mechanism	2.76 (±0.27)	1.71 (±0.06)	—
3 + 2-Step mechanism	1.24 (±0.48)	1.26 (±0.25)	0.058 (±0.03)
Run No. 080676 (6/3/1 feed; reduced catalyst)			
3-Step mechanism	0.70 (±0.06)	1.40 (±0.10)	—
3 + 2-Step mechanism	0.63 (±0.43)	1.17 (±0.60)	0.049 (±0.52)
Run No. 081376 (3/6/1 feed; reduced catalyst)			
3-Step mechanism	1.50 (±0.17)	1.50 (±0.10)	—
3 + 2-Step mechanism	1.17 (±0.19)	1.20 (±0.15)	0.05 (±0.03)
Run No. 012376 (8/1/1 feed; reduced catalyst)			
3-Step mechanism	1.95 (±0.19)	1.70 (±0.10)	—
3 + 2-Step mechanism	1.84 (±0.80)	1.52 (±0.90)	0.049 (±0.28)

[a] Values reported in parentheses are computed estimates of standard errors.

mechanisms involving two different rates for adsorption of carbon oxide species. A similar conclusion was reached in the recent comprehensive study of Kobayashi and Kobayashi (*8*) who used a transient method but without isotopes for the oxidation of carbon monoxide over chromium sesquioxide (at 131–140°C). It was therefore thought desirable to test a model involving a second chemisorbed species as outlined by Kobayashi and Kobayashi (*9*). The following mechanistic sequence was assumed:

$$\begin{aligned} O_2 + 2l &\xrightarrow{v_{+1}} 2Ol, \\ CO + Ol &\xrightarrow{v_{+2}} CO_2 \cdot l, \\ CO_2 \cdot l &\underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} CO_2 + l, \\ O_2 + 2m &\xrightarrow{v_{+4}} 2Om, \\ CO + Om &\xrightarrow{v_{+5}} CO_2 + m. \end{aligned} \qquad (14)$$

It is seen that CO_2 can be formed on two different types of sites, l and m. That produced on the m sites is not chemisorbed. The mechanism differs from that which we have used, Eq. (2), in the incorporation of the two additional steps (4) and (5). If we define the overall reaction rates as previously V = cubic centimeters of O_2 per (minute) (gram-catalyst) and introduce an additional parameter, α = the fraction of the overall reaction which occurs on the m sites:

$$\alpha V = v_{+4} = v_{+5}/2; \qquad (15)$$

$$(1 - \alpha)V = v_{+1} = v_{+2}/2 = (v_{+3} - v_{-3})/2. \qquad (16)$$

v_{+5} must be unidirectional if it exists, because otherwise $^{13}CO_2$ tracing would result in ^{13}CO production and this was not observed. We developed the system and

variational equations for this model, which include the additional parameter α. Table 4 shows the results of computations for this model. The optimum value of $\alpha \cong 0.05$ is quite small and correlation is poor. Furthermore to accommodate such behavior the population of surface species $C^{CO_2 l}$ is considerably reduced so that it no longer checks that obtained by independent CO_2 desorption experiments.

It is not possible by means of the present experiments to determine the nature of the adsorbed carbon oxide species. If more than one such species is present, it appears that they must equilibrate very rapidly with each other since the amount of CO_2 desorbed by separate experiments agrees with that determined independently by isotopic transfer. The fact that $^{13}CO_2$ marking does not result in the production of ^{13}CO and that the same amount of carbon oxides is produced both by ^{13}CO and $^{13}CO_2$ marking further serves to restrict possible mechanistic models for the reaction.

CONCLUSIONS

The main conclusion of this study is the demonstration that transient tracing superposed on a steady-state complex catalytic reaction is a relatively simple and viable method for assessing the intermediate mechanistic step velocities and surface concentrations for a chosen model and for discriminating between models. The method involves a minimum of simplifying assumptions about the kinetics of individual steps and the nature of the active sites.

As applied to the oxidation of carbon monoxide over a typical oxide catalyst, a very simple mechanism correlates the data satisfactorily and is consistent with other information available such as desorption of the adsorbed materials. It appears that catalytic activity is related to the surface population of adsorbed CO_2, which is less when the catalyst has been subjected to reducing conditions for a long period of time.

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