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Theoretical Analysis of Transient Homomolecular Exchange Reaction of Carbon Monoxide on Supported Catalysts

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The transient response of the homomolecular exchange reaction of carbon monoxide over supported catalysts in a batch reactor has been analyzed using an adsorption–desorption–surface reaction model. Results have revealed that the existing method of data analysis developed by E. R. S. Winter (*J. Chem. Soc.*, 5781, 1964) based on a lumped homogeneous model is inadequate for determining the intrinsic exchange rate under most general experimental conditions, even though it has been widely used in the catalysis literature. In this study we have developed a more sound and general method of transient data analysis for the exchange reaction of carbon monoxide over supported catalysts with particular emphasis on Rh/Al_2O_3. In addition to identifying the intrinsic shortcomings of Winter's method, we have also discussed the important sources of kinetic disguises which must be eliminated or taken into proper consideration in the design and/or analysis of transient experiments. © 1990 Academic Press, Inc.

INTRODUCTION

The homomolecular exchange reaction of CO, defined as the reaction involving exchange of oxygen (or carbon) atoms among CO molecules, has been known to occur on transition metals such as Fe, Ni, Co, Ru, and Rh, and has been used as a measure of CO dissociation and recombination (*1, 2*). This exchange reaction has recently been studied rather extensively owing primarily to its relevance to the kinetic mechanism of CO hydrogenation over these metal catalysts: it helps elucidate whether the catalytic CO hydrogenation involves dissociation of CO (*3–6*). This reaction is also important in elucidating the catalytic mechanism of CO oxidation over Rh/Al_2O_3 occurring in automobile catalytic converters, in view of recent observations of significant CO dissociation and/or disproportionation activity over supported Rh catalysts (*7–12*).

In many ways the dissociation of CO on Rh surfaces has been controversial in the literature for the past decade or so. On single-crystal or polycrystalline Rh surfaces under ultrahigh vacuum conditions, for example, Thiel *et al.* (*16*), Yates *et al.* (*17*), Campbell and White (*18*), and Gorodetskii and Nieuwenhuys (*19*) observed no appreciable CO dissociation activity, whereas Sexton and Somorjai (*13*), Castner and Somorjai (*14*), and Castner *et al.* (*15*) reported significant CO dissociation activity on surface irregularities such as steps, kinks, and defects. The latter observations were subsequently disputed by Yates *et al.* (*20*) who demonstrated that the electron impact during AES measurements can induce an appreciable amount of CO dissociation activity in agreement with later results reported by DeLouise and Winograd (*21*). Interestingly, however, DeLouise and Winograd's results also indicated that CO dissociation activity of Rh is on the same order of magnitude as that of Ni which is known for its good activity for CO dissociation. Thus, they did not exclude a strong possibility of CO dissociation at high temperature and high pressure. Yamada and Tamaru (*2*) observed appreciable CO disproportionation activity on Rh producing CO_2, even though they could not directly detect the accumu-

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lation of carbon from the reaction. On supported Rh, on the other hand, the dissociation of CO appears less controversial compared with that on single-crystal or polycrystalline Rh; on Rh/Al_2O_3, for example, CO dissociation has been reported to occur at an appreciable rate above 200°C at atmospheric pressure (*7, 8, 11, 12, 22*). However, in a recent study of isotopic exchange reaction of CO on Rh/Al_2O_3, Panayotov *et al.* (*23*) reported extremely low efficiency of the exchange reaction at temperatures below 195°C.

In analyzing transient experimental data obtained from batch reactor experiments of the homomolecular exchange reaction of CO, the brief analysis by Winter (*24*) has been widely used in the literature [e.g., (*3, 23*)]. It is important to note, however, that the analysis carried out by Winter is based on a lumped homogeneous model which does not explicitly account for the process occurring on the catalyst surface, and thus is inadequate for determining the intrinsic kinetics of a surface reaction. Failure to recognize those limitations inherent in Winter's analysis can lead to a serious misinterpretation of the transient experimental data as will be shown in this paper.

In an attempt to establish a sound theoretical basis on which we can develop a logical experimental scheme, we present in this paper a formal transient analysis of the CO exchange reaction occurring in a batch reactor over supported catalysts, with special emphasis on Rh/Al_2O_3. In contrast to Winter's analysis, we adopt a heterogeneous model which includes adsorption, desorption, and surface reaction occurring on the catalyst surface. Results will help us identify the experimental conditions which permit the measurement of the intrinsic rate constant of the exchange reaction. Naturally this analysis will show that the rate constant determined based on Winter's analysis is not the intrinsic one in general. It is hoped that this paper will help reconcile the discrepancies surrounding the CO dissociation activity of Rh/Al_2O_3 catalysts.

MATHEMATICAL DESCRIPTION OF THE SYSTEM

We consider a closed system of a batch reactor containing gaseous reactants and supported catalyst particles, the mathematical description of which is based on the following assumptions. The bulk gas phase is in a well-mixed condition, and mass-transfer resistance from the bulk gas phase to the catalyst particles is negligible. Catalytically active metal is impregnated in a narrow band near the external surface of the support, so that diffusional resistance within the catalyst particles is also negligible. The support does not participate in the adsorption–desorption–exchange reaction of CO. The adsorption–desorption of CO on the catalytic surface follows Langmuir kinetics (*25, 26*), while the exchange reaction between adsorbed CO molecules follows bimolecular Langmuir–Hinshelwood mechanism (*2, 3, 23*). Transient reactor experiments are performed under isothermal conditions. All the above conditions can be justified or easily realized in typical batch reactor experiments.

The isotopic exchange reaction between adsorbed CO molecules on the catalytic surface can be written as

$$A + B \overset{k_x}{\rightleftarrows} C + D, \tag{1}$$

where $A = {}^{12}C^{18}O$, $B = {}^{13}C^{16}O$, $C = {}^{12}C^{16}O$, $D = {}^{13}C^{18}O$, and k_x is the rate constant of the exchange reaction. The rate constant of the forward and backward reactions in Eq. (1) can be taken to be equal neglecting the kinetic effects of the isotopic molecules (*24*). For the same reason, the rate constants of adsorption and desorption can be assumed to be the same for different isotopic carbon monoxide species.

The transient mass balances for the individual carbon monoxide species in the reactor yield the following. For the gas phase,

$$V\frac{dc_i}{dt} = -\sigma\{k_a c_i(1-\theta) - k_d\theta_i\}, \tag{2}$$

where the subscript *i* refers to the species of interest, that is, i = A, B, C, or D. The total surface coverage of carbon monoxide, θ, is defined as

$$\theta = \theta_A + \theta_B + \theta_C + \theta_D. \tag{3}$$

For the catalytic surface,

$$\frac{d\theta_i}{dt} = k_a c_i(1 - \theta) - k_d\theta_i + \nu_i k_x(\theta_A\theta_B - \theta_C\theta_D), \tag{4}$$

where $\nu_i = -1$ for i = A or B, and $\nu_i = 1$ for i = C or D. The overall mass balance for the whole reactor (i.e., including both the gas phase and the catalytic surface) can be obtained by combining Eqs. (2) and (4):

$$\frac{d}{dt}(Vc_i + \sigma\theta_i) = \nu_i\sigma k_x(\theta_A\theta_B - \theta_C\theta_D). \tag{5}$$

When the adsorption–desorption rate is much faster than the exchange reaction on the surface (*24*), the adsorption–desorption process can be assumed to be in equilibrium. In this case it can be shown [e.g., (*27*)] that

$$\theta_i = Kc_i/(1 + Kc), \tag{6}$$

where K is the adsorption equilibrium constant and c is the total concentration of carbon monoxide species in the gas phase defined as

$$c = c_A + c_B + c_C + c_D. \tag{7}$$

Since c is constant at a given temperature and pressure, summation of Eq. (6) from i = A to i = D results in the Langmuir isotherm

$$\theta = Kc/(1 + Kc). \tag{8}$$

Noting that θ is constant at a given temperature and pressure, we obtain from Eqs. (6) and (8) that

$$\theta_i = \theta x_i, \tag{9}$$

where x_i is the mole fraction of carbon monoxide species i in the gas phase. Note in Eq. (9) that the surface coverage of each carbon monoxide species follows a linear isotherm if the total surface coverage is kept constant. Equation (8) indicates that the value of Kc must be kept constant to keep the total surface coverage constant. As will become apparent later, this information is useful in the design of experiments and/or in the analysis of transient experimental data.

Summation of Eq. (5) from i = A through D yields

$$\frac{d}{dt}(Vc + \sigma\theta) = 0, \tag{10}$$

indicating that

$$Vc + \sigma\theta = \text{constant with respect to time}, \tag{11}$$

where Vc and $\sigma\theta$ represent the amounts of carbon monoxide in the gas phase and on the catalytic surface, respectively. Equation (11) thus states that the total amount of carbon monoxide in the closed system (i.e., batch reactor) is conserved during the course of exchange reaction experiments.

With the help of Eqs. (9) and (11), we can reduce Eq. (5) to

$$\frac{dx_i}{dt} = \nu_i k_0(x_A x_B - x_C x_D), \tag{12}$$

where k_0 is the overall exchange rate constant which is related to the intrinsic rate constant k_x by

$$k_0 = \sigma\theta^2 k_x/(Vc + \sigma\theta). \tag{13}$$

It is useful to note the interesting similarities and differences between Eq. (12) and the model equation presented by Winter (*24*); Winter's equation based on a lumped homogeneous model can be reduced to the same form as that of Eq. (12) but his overall rate constant defined as $\sigma k_x/Vc$ cannot be reduced to Eq. (13). Note, however, that our heterogeneous model becomes equivalent to Winter's lumped model for the special case of $\theta = 1$ and $Vc \gg \sigma\theta$. In other words, Winter's analysis is valid only when the catalytic surface is completely covered with carbon monoxide and the amount of carbon monoxide on the surface is negligibly small compared with that in the gas phase. These crucial limitations in Winter's analysis originate from the fact that the important mechanistic information associated with the adsorption–desorption–surface reaction process is absent in Winter's formulation, whereas it is included in our analysis resulting in Eq.(13). In the following we describe how to determine k_0 and k_x from transient experimental data.

DETERMINATION OF THE OVERALL RATE CONSTANT FOR EXCHANGE REACTION (k_0)

The overall rate constant can be determined by measuring transient responses of either the absolute mole fraction of individual carbon monoxide species in the gas phase or its relative mole fraction with respect to an arbitrary reference species. Note that the absolute mole fraction is in fact a normalized concentration with respect to the total concentration, whereas the relative mole fraction is a normalized concentration with respect to the concentration of a reference species.

Use of Absolute Mole Fraction

It is useful to note from Eq. (12) that

$$\frac{d}{dt}(x_A + \nu_i x_i) = 0, \quad i \neq A. \tag{14}$$

This means that $(x_A + \nu_i x_i)$ is constant and thus can be written as

$$x_A + \nu_i x_i = x_A^o + \nu_i x_i^o, \tag{15}$$

where the superscript ^{o} denotes the initial condition at $t = 0$. Equation (12) can now be linearized with the help of Eq. (15) to yield

$$\frac{dx_i}{dt} = -k_0(x_i - x_i^\infty), \tag{16}$$

where x_i^∞ is the steady-state mole fraction of species i which is given by

$$x_A^\infty = (x_A^o + x_C^o)(x_A^o + x_D^o), \tag{17}$$

$$x_i^\infty = x_i^o + \nu_i(x_A^o - x_A^\infty), \quad i = \mathrm{B, C, D}. \tag{18}$$

Note that the initial mole fraction of each species in the gas phase of the reactor is identical to that in the feed gas. Solution of Eq. (16) gives the transient response of the absolute mole fraction of each species:

$$\ln|x_i - x_i^\infty| - \ln|x_i^o - x_i^\infty| = -k_0 t. \tag{19}$$

Thus a plot of $\ln|x_i - x_i^\infty|$ versus t should yield a straight line with a slope of $-k_0$ and its intercept of $\ln|x_i^o - x_i^\infty|$ at $t = 0$. Note that the absolute values are indicated in Eq. (19) for both $x_i - x_i^\infty$ and $x_i^o - x_i^\infty$ to include such species that satisfy $x_i^o < x_i^\infty$. Equation (19) is a general relation that can be used to determine the apparent exchange rate constant k_0 from the measurements of mole fractions of any CO species as a function of time.

Use of Relative Mole Fraction

The transient response of the relative mole fraction in the gas phase can be obtained from Eq. (19) as shown in Appendix B,

$$\ln\left|\frac{R_{ij} - R_{ij}^\infty}{R_{ij} - \nu_{ij}}\right| - \ln\left|\frac{R_{ij}^o - R_{ij}^\infty}{R_{ij}^o - \nu_{ij}}\right| = -k_0 t \tag{20}$$

where $i \neq j$ and

$$R_{ij} = x_i/x_j, \quad R_{ij}^o = x_i^o/x_j^o, \quad R_{ij}^\infty = x_i^\infty/x_j^\infty, \tag{21}$$

$$\nu_{ij} = \nu_i/\nu_j, \tag{22}$$

and the superscript ∞ denotes the steady-state condition. Equation (20) indicates that a plot of $\ln|(R_{ij} - R_{ij}^\infty)/(R_{ij} - \nu_{ij})|$ versus t should yield a straight line with a slope of $-k_0$ and its intercept of $\ln|(R_{ij}^o - R_{ij}^\infty)/(R_{ij}^o - \nu_{ij})|$ at $t = 0$. It is remarkable that any combination in the concentration ratio of two different species can be used in Eq. (20). It is thus a complete generalization of the results obtained by Winter (*24*). In particular, when $i = \mathrm{A}$ and $j = \mathrm{D}$, it is straightforward to show from Eq. (20) that

$$\ln\left|\frac{R_{AD} - \alpha}{R_{AD} + 1}\right| - \ln\left|\frac{R_{AD}^o - \alpha}{R_{AD}^o + 1}\right| = -k_0 t, \tag{23}$$

where α is the ratio of C-12 to C-13 in the reactor. That is,

$$\alpha = (x_A^o + x_C^o)/(x_B^o + x_D^o), \quad (24)$$

which can be shown to be identical to R_{AD}^{∞} by the use of Eqs. (17) and (18). Note that Eq. (23) is equivalent to the relationship obtained by Winter (*24*). The relative merits of using Eq. (19) or (20) will be discussed later.

DETERMINATION OF THE INTRINSIC RATE CONSTANT FOR EXCHANGE REACTION (k_x)

Once the overall rate constant (k_0) is known, the intrinsic rate constant (k_x) can be obtained from Eq. (13). In fact, Eq. (13) itself reveals two important points. One is that the overall rate constant is always smaller than the intrinsic rate constant, since $\sigma\theta/(Vc + \sigma\theta) < 1$ and $\theta \leq 1$. This means that the intrinsic rate constant can be only underestimated, but never overestimated, if the overall rate constant is mistaken for the intrinsic one. The other is that k_0 depends not only on k_x but also on θ. This suggests that the energetic parameters determined from k_0 will be different from those of k_x, unless θ is kept constant during the entire experiment or proper adjustments are made to correct for varying θ. Since θ depends on the adsorption equilibrium constant (K) which in turn depends on temperature, the energetic parameters determined from k_0 should depend on the temperature of experiments.

For further discussion, we express both rate constants in the form

$$k_0 = A_0 \exp(-E_o/RT), \quad (25)$$

$$k_x = A_x \exp(-E_x/RT). \quad (26)$$

From Eqs. (8) and (13) we note that, at low temperature and/or high pressure conditions where $Kc \gg 1$ and thus $\theta \simeq 1$,

$$k_0 \simeq \sigma k_x/(Vc + \sigma\theta). \quad (27)$$

At high temperature and/or low pressure conditions where $Kc \ll 1$ and thus $\theta \simeq Kc$,

$$k_0 \simeq \sigma c^2 K^2 k_x/(Vc + \sigma\theta). \quad (28)$$

Equation (27) thus indicates that

$$E_o = E_x \quad \text{at low temperatures and/or high pressures}, \quad (29)$$

while Eq. (28) indicates that

$$E_o = E_x - 2E_a \quad \text{at high temperatures and/or low pressures}, \quad (30)$$

where E_a is the heat of CO adsorption on the catalytic surface. Note that E_a is always positive for nonactivated adsorption such as CO adsorption on Rh surfaces, since E_a is the activation energy of desorption subtracted by the activation energy of adsorption. Figure 1 illustrates the nature of temperature dependence of the energetic parameters determined from k_0 at a fixed total pressure. The solid line represents the overall exchange rate constant determined by either Eq. (19) or (20) when E_x is smaller than $2E_a$. The overall activation energy (E_o) varies with temperature; in the low-temperature regime it is identical to the intrinsic activation energy (E_x), whereas in the high-temperature regime it is equal to $E_x - 2E_a$ as shown in Eqs. (29) and (30). It should be noted that, if $E_x < 2E_a$, the overall rate constant decreases with an increase in temperature in the high-temperature regime. Phys-

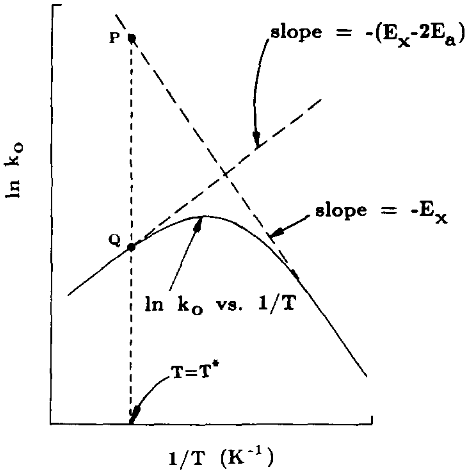

FIG. 1. Overall exchange rate constant as a function of catalyst temperature.

ically, this is due to the faster decrease in K^2 than the corresponding increase in k_x with temperature in the high-temperature regime, as can be seen in Eq. (28). At temperature T^* in Fig. 1, point Q represents the overall rate constant observed under conditions of varying surface coverage, while point P represents the exchange rate constant with its true activation energy. The large difference between P and Q suggests that, under certain experimental conditions, the true rate can be considerably faster than the observed rate. A similar conclusion can be drawn for the case of $E_x > 2E_a$.

To avoid this kinetic disguise associated with the varying total surface coverage, it is necessary either to measure θ over the entire temperature range or to keep it constant. Note that the importance of the total surface coverage in the kinetic measurement of the CO exchange reaction in a batch reactor has not been recognized in the literature. Instead, the condition of $Vc \gg \sigma\theta$ has often been cited as a necessary experimental condition (*3, 23*). It is clear in this paper, however, that this latter condition is really unnecessary because $Vc + \sigma\theta$ remains constant anyway in a closed system as shown earlier. Furthermore, imposing the unnecessary condition of $Vc \gg \sigma\theta$ may make it difficult to eliminate mass-transfer resistance in the gas phase, as will be shown later.

Measuring θ over the entire range of reaction temperature and then making appropriate adjustments to the overall rate constant based on Eq. (13) seems straightforward. However, determination of θ is not that easy, and therefore keeping θ constant is more practical solution. A convenient way of keeping θ constant in a closed system over a wide range of temperature is to keep it close to unity at the highest reaction temperature. Assuming ideal gas behavior of the gas phase, the following condition can be used as a practical guide:

$$KP/RT > 20. \qquad (31)$$

This ensures that the value of θ is within 5% of unity. Obviously it is necessary to get the kinetic information on adsorption–desorption on the catalytic surface to find out the right experimental condition which satisfies Eq. (31). Figure 2 shows the relation between reaction temperature and pressure that can satisfy the condition in Eq. (31) for carbon monoxide on Rh/Al_2O_3, where the kinetic data in Oh *et al.* (*26*) were used for adsorption–desorption of carbon monoxide on Rh/Al_2O_3. The shaded area in Fig. 2 represents the feasible experimental conditions satisfying Eq. (31), and the boundary line is the line on which θ is 0.95. Note in Fig. 2 that, at a given total pressure, there is a certain temperature level above which constant θ (i.e., $\theta \simeq 1$) cannot be safely assumed.

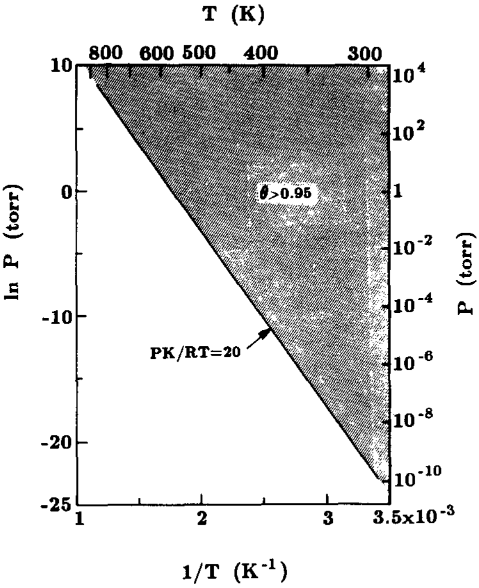

FIG. 2. Temperature–pressure relationship in the reactor to maintain $\theta > 0.95$ on Rh/Al_2O_3.

OTHER CONSIDERATIONS

In addition to the above-mentioned kinetic disguise caused by varying total surface coverage, there are other sources of disguises that are important in the transient kinetic study of the carbon monoxide exchange reaction over supported catalysts. We want to briefly examine the two sources most commonly overlooked in the literature: external (i.e., gas-to-solid) mass-transfer resistance and adsorption on the support. It is interesting to note in the literature that the absence of external mass-transfer limitation is often taken for granted, while careful attention is customarily taken to eliminate internal diffusional resistance within catalyst particles.

Rate of External Mass Transfer

It is a rather common practice to conduct the carbon monoxide exchange reaction in a constant-volume reactor under vacuum conditions without deliberate stirring of the gas phase, with a notable exception of Bossi *et al.* (*3*). When the pressure level in the reactor is low enough to ensure that molecular flow is the predominant transport mechanism in the gas phase, the external mass-transfer resistance can be safely ignored. In the viscous flow regime, however, there is always a strong possibility that the external transport process is an important part of the entire exchange process even when a stirred reactor is used. In particular, when the reactor operates in the viscous flow regime without gas-phase mixing, mass transport in the gas phase is dominated by a diffusional process which can easily disguise the intrinsic kinetics under transient experimental conditions.

Molecular flow in the gas phase is assured when Knudsen number (N_k), defined as the ratio of the characteristic dimension of the reactor (i.e., the reactor diameter) to the mean free path of the gas molecules, is less than unit (*28*). It is sufficient, therefore, to satisfy

$$N_k < 1 \tag{32}$$

in an unstirred reactor for the absence of external mass-transfer resistance. Obviously, the intrinsic rate constant can be determined when experimental conditions satisfy both Eqs. (31) and (32). If the sufficient condition [Eq. (32)] is not satisfied, there may exist external mass-transfer resistance whose significance in disguising the overall reaction kinetics must be evaluated by checking the necessary condition which can be derived as follows.

The coupled reaction–diffusion process at the interface between a catalyst pellet and the external gas phase can be described by mass balance equations for the *i*th species of CO at the interface,

$$aD_g \left(\frac{\partial c_i}{\partial z}\right)_{\text{interface}} = -\nu_i \sigma \theta^2 k_x (x_A x_B - x_C x_D), \tag{33}$$

which can be reduced to a dimensionless form to yield

$$\left(\frac{\partial x_i}{\partial \xi}\right)_{\text{interface}} = -\nu_i \phi (x_A x_B - x_C x_D), \tag{34}$$

where ξ is the dimensionless distance from the catalyst to the detector and ϕ is a reaction–diffusion modulus defined by

$$\xi = z/L, \tag{35}$$

$$\phi = \sigma \theta^2 k_x RTL/aPD_g. \tag{36}$$

Equation (34) indicates that the concentration gradient at the interface can be safely ignored if ϕ is much smaller than unity. That is,

$$\phi \ll 1 \tag{37}$$

is the necessary condition for negligible external diffusional resistance. Note that the necessary condition requires a priori knowledge of both reaction kinetics and surface coverage, whereas the sufficient condition does not. Frequently it may be more practical, therefore, to satisfy the sufficient condition than to satisfy the necessary condition if both the reaction rate constant and the surface coverage are unknown.

Effect of Product Retention by Support

Alumina support is known to have a significant capacity for carbon monoxide below 100°C through physical adsorption (*29–*

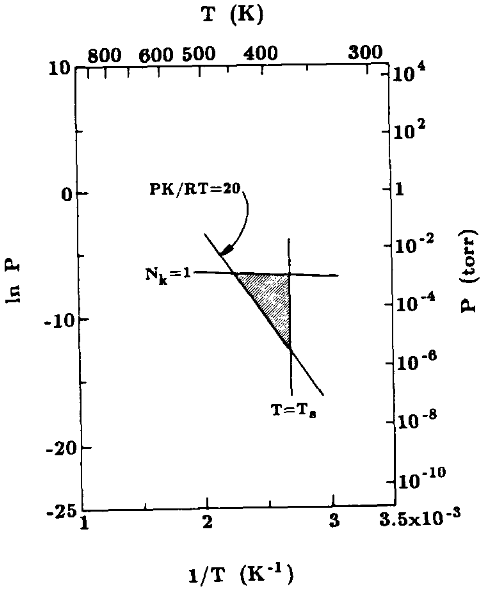

FIG. 3. Feasible experimental conditions that satisfy $\theta > 0.95$, $N_k < 1$, and $T > T_s$ on Rh/Al_2O_3.

31). Therefore, in the low-temperature regime (i.e., below 100°C), the retention of carbon monoxide on the support can significantly delay the transport of the product species from catalytic surface to the monitoring device, thereby effectively reducing the observed exchange rate. Obviously, this support effect can be virtually eliminated by raising the reaction temperature to above 100°C. For typical experimental conditions listed in Table 1, Fig. 3 illustrates the area of feasible experimental conditions which satisfy Eqs. (31), (32), and the condition of negligible adsorption on the support. In Fig. 3, T_s denotes the minimum catalyst temperature above which the adsorption effect on the support can be ignored. Comparing Fig. 3 with Fig. 2 we note that the size of the feasible experimental conditions can be sharply reduced to avoid both mass-transfer limitations and the interference from the product retention on the support.

DISCUSSION

We have formally analyzed the transient response of the homomolecular exchange reaction of carbon monoxide over supported catalysts using a heterogeneous model which accounts for adsorption, desorption, and surface reaction on the catalyst surface. It has been shown that the existing method of analysis developed by Winter (*24*) is a special case of our general analysis presented in this paper. Our results have revealed the intrinsic shortcomings of Winter's analysis; it can be used only when $\theta = 1$ and $VC \gg \sigma\theta$. Furthermore, we will illustrate shortly that the latter condition (i.e., $Vc \gg \sigma\theta$) may not be compatible with the model assumption of negligible external mass-transfer resistance.

The new recipe developed in this paper has the following two distinct features that are not available in the literature.

1. It can be used to measure the true exchange rate on the catalytic surface under most general experimental conditions by including all the relevant mechanistic information.
2. It is versatile to use. That is, either the mole fraction of a species or the ratio of mole fractions of any two species can be used as the only observed variable.

Equation (19) or (20) can be used to determine the overall exchange rate constant from transient batch experiments. Which of the two equations to use should be a matter of experimenter's preference, even though the following features may be taken into consideration. The use of the absolute mole fraction in Eq. (19) is expected to yield less

TABLE 1

Experimental Conditions Considered in Figs. 3 and 4

Reactor geometry	Spherical
Reactor diameter	8 cm
Catalyst	Rh/Al_2O_3
Amount of catalyst	30 mg
Rh loading	2 wt%
Rh dispersion	100%
Total adsorption capacity of Rh surface	5.8×10^{-6} mol

scattered data than the use of the relative mole fraction in Eq. (20), because the absolute mole fraction is a normalized concentration with respect to the total concentration, whereas the relative mole fraction is a normalized concentration with respect to an individual species concentration. (Note that the total concentration is more stable than an individual species concentration.) On the other hand, the use of the relative mole fraction in Eq. (20) can enhance the sensitivity of the transient response if the species i and j are chosen from the opposite side of the reaction equation (1). That is, if i is one of the reactants and j is one of the products, the variation in the relative mole fraction of i to j as a function of time should be more pronounced than the case where both i and j are either from the reactant side or from the product side of Eq. (1).

Results have indicated that the true (i.e., intrinsic) exchange rate on the catalytic surface is always greater than the overall exchange rate observed in the transient experiments. The overall exchange rate depends on the total surface coverage of carbon monoxide; more specifically, it is proportional to the square of the total surface coverage. Therefore, it is necessary to know the total surface coverage to extract the intrinsic exchange rate from the overall one. Since the existing Winter formula (*24*) does not properly account for this surface-coverage dependence, the exchange rate constant obtained using Winter's formula can be quite different from the true value.

The condition

$$VC/\sigma\theta \gg 1 \qquad (38)$$

has been frequently imposed in a batch reactor system in the literature [e.g., (*3, 23*)] in an attempt to use the Winter formula without modifications. However, it is important to recognize the possible incompatibility between Eqs. (32) and (38) under low-vacuum conditions (i.e., near atmospheric pressure). For the experimental conditions listed in Table 1, for example, we cannot find a combination of system pressure and temperature that satisfy both Eq. (32) (shaded area A) and Eq. (38) (shaded area B) as illustrated in Fig. 4. In other words, there is a strong possibility that the observed exchange rate constant may have been disguised by the external mass-transfer resistance, if it were obtained under the experimental conditions listed in Table 1 at 10 Torr pressure for example. The severity of this disguise can be of several orders of magnitude depending on the intrinsic rate of the exchange reaction. Under such experimental conditions, it is therefore necessary to check whether the necessary condition [Eq. (37)] can be satisfied.

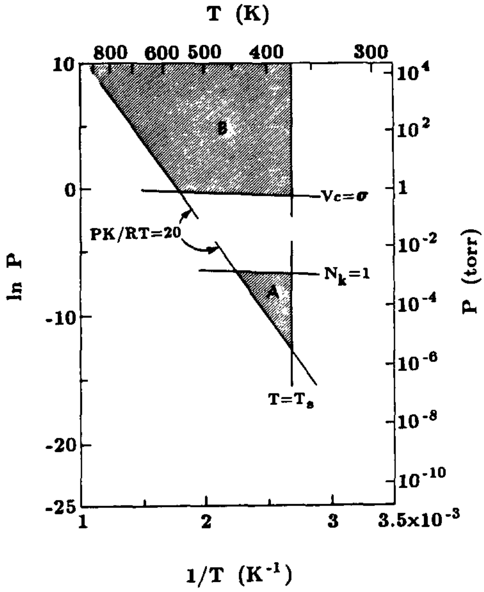

FIG. 4. Possible incompatibility in the experimental conditions on Rh/Al_2O_3. (Area A satisfies $\theta > 0.95$, $T > T_s$, and $N_K < 1$; area B satisfies $\theta > 0.95$, $T > T_s$, and $Vc > \sigma$.)

It is apparent that using an unstirred reactor for supported catalysts may not be a good idea, because it offers only very limited operational flexibility as shown earlier in Fig. 3. Thus a well-stirred reactor may be required under most experimental conditions to avoid kinetic disguises associated with mass-transfer resistances. Note that this work has identified necessary conditions and/or precautions to be taken, so that the intrinsic exchange rate constant can be obtained from the transient batch reactor experiments. Since the homomolecular exchange reaction has been used as a measure of carbon monoxide dissociation, it is hoped that the general treatment presented in this paper will help resolve the existing controversies surrounding the interpretation of the exchange rate and/or dissociation rate of carbon monoxide on Rh/Al_2O_3. Certainly the methodology developed here is not limited to the carbon monoxide system; it can be applied with minor modifications to other homomolecular exchange systems such as H_2–D_2 exchange reaction.

APPENDIX A: NOMENCLATURE

a	External surface area of catalyst pellet, cm^2
A_0	Preexponential factor for overall exchange rate constant, s^{-1}
A_x	Preexponential factor for intrinsic exchange rate constant, s^{-1}
c	Total gas-phase concentration of carbon monoxide, mol/cm^3
c_i	Gas-phase concentration of carbon monoxide species i, mol/cm^3
D_g	Diffusion coefficient of CO, cm^2/s
E_a	Heat of adsorption for carbon monoxide, cal/mol
E_o	Activation energy for overall exchange rate constant, cal/mol
E_x	Activation energy for intrinsic exchange rate constant, cal/mol
k_a	Adsorption rate constant, $(mol/cm^3)^{-1}$ s^{-1}
k_d	Desorption rate constant, s^{-1}
k_0	Overall exchange rate constant, s^{-1}
k_x	Intrinsic exchange rate constant, s^{-1}
K	Adsorption equilibrium constant, $(mol/cm^3)^{-1}$
L	Distance from the catalyst pellet to the detector, cm
N_k	Knudsen number
P	Total pressure in the reactor, Torr
R	Ideal gas constant
R_{ij}	Relative mole fraction, x_i/x_j
t	Time, s
T	Absolute temperature, K
T_s	Minimum temperature to avoid adsorption on support, K
V	Total reactor volume, cm^3
x_i	Mole fraction of carbon monoxide species i in the gas phase
z	Coordinate along the distance between the catalyst pellet and the detector, cm

Subscripts

A	Carbon monoxide species, $^{12}C^{18}O$
B	Carbon monoxide species, $^{13}C^{16}O$
C	Carbon monoxide species, $^{12}C^{16}O$
D	Carbon monoxide species, $^{13}C^{18}O$
i	Carbon monoxide species i

Superscripts

o	Initial condition
∞	Steady-state condition

Greek Letters

α	Ratio of C-12 to C-13 in the reactor
θ	Total surface coverage of carbon monoxide
θ_i	Surface coverage of carbon monoxide species i
ν_i	Stoichiometric coefficient in the exchange reaction, -1 for reactants, $+1$ for products
ν_{ij}	Ratio of stoichiometric coefficient, ν_i/ν_j
ξ	Dimensionless distance from the catalyst to the detector, z/L
σ	Total adsorption capacity of catalytic surface, mol CO
ϕ	Reaction–diffusion modulus defined in Eq. (36)

APPENDIX B: DERIVATION OF EQ. (20)

For the species i and j, Eq. (19) can be written as

$$x_i = x_i^\infty + (x_i^\circ - x_i^\infty)\exp(-k_0 t), \quad \text{(B1)}$$

$$x_j = x_j^\infty + (x_j^\circ - x_j^\infty)\exp(-k_0 t). \quad \text{(B2)}$$

Dividing Eq. (B1) by (B2) we get

$$\frac{x_i}{x_j} = \frac{x_i^\infty + (x_i^\circ - x_i^\infty)\exp(-k_0 t)}{x_j^\infty + (x_j^\circ - x_j^\infty)\exp(-k_0 t)}. \quad \text{(B3)}$$

But from Eq. (18) we have the relation

$$x_i^0 - x_i^\infty = \nu_{ij}(x_j^0 - x_j^\infty) \qquad \text{(B4)}$$

which can be used to reduce Eq. (B3) to

$$R_{ij} - \nu_{ij} = \frac{x_i^0 - \nu_{ij}x_j^0}{x_j^\infty + (x_j^0 - x_j^\infty)\exp(-k_0 t)}, \qquad \text{(B5)}$$

or equivalently

$$\frac{1}{R_{ij} - \nu_{ij}} = \frac{x_j^\infty/x_i^0 + (R_{ji}^0 - x_j^\infty/x_i^0)\exp(-k_0 t)}{1 - \nu_{ij}R_{ji}^0}. \qquad \text{(B6)}$$

But

$$\begin{aligned} x_j^\infty/x_i^0 &= (x_i^\infty/x_i^0)R_{ji}^\infty \\ &= (1 - \nu_{ij}R_{ji}^0 + \nu_{ij}x_j^\infty/x_i^0)R_{ji}^\infty, \end{aligned} \qquad \text{(B7)}$$

due to Eq. (B4). Solving Eq. (B7) for x_j^∞/x_i^0 yields

$$x_j^\infty/x_i^0 = R_{ji}^\infty(1 - \nu_{ij}R_{ji}^0)/(1 - \nu_{ij}R_{ji}^\infty), \qquad \text{(B8)}$$

which can be used to reduce Eq. (B6) to

$$\begin{aligned} &\frac{1}{R_{ij} - \nu_{ij}} - \frac{1}{R_{ij}^\infty - \nu_{ij}} \\ &= \left(\frac{1}{R_{ij}^0 - \nu_{ij}} - \frac{1}{R_{ij}^\infty - \nu_{ij}}\right)\exp(-k_0 t). \end{aligned} \qquad \text{(B9)}$$

Equation (B9) can then be easily transformed to

$$\frac{R_{ij}^\infty - R_{ij}}{R_{ij} - \nu_{ij}} = \left(\frac{R_{ij}^\infty - R_{ij}^0}{R_{ij}^0 - \nu_{ij}}\right)\exp(-k_0 t), \qquad \text{(B10)}$$

which is equivalent to Eq. (20).

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