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# Kinetic Partitioning in Competitive Reaction Systems

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The efficient reduction of NO by CO in the presence of a stoichiometric excess of $O_2$ requires a catalyst which selectively promotes the CO–NO reaction over the CO–$O_2$ reaction. In such a system CO may be said to be kinetically partitioned between the two oxidants, and this can lead to unusual relationships between the amount of catalytically active component and the conversion of NO. A general treatment of kinetic partitioning will be given with emphasis on the transition from an activity-controlled regime to a selectivity-controlled regime. The manner in which the selectivity parameter of a catalyst can effect performance in the selectivity-controlled regime will be illustrated in general and for the particular example of the NO–CO–$O_2$ system.

## INTRODUCTION

In employing supported-metal catalysts, one is accustomed to a pronounced dependence of catalytic performance upon metal concentration. Generally this relationship will be fairly linear unless interrupted by factors such as approach to equilibrium or decrease in dispersion at higher metal levels. In the case of noble metals in particular, optimal concentrations must be arrived at by striking a balance between catalytic performance and catalyst cost.

We have recently reported a system in which the relationship between catalyst performance and metal concentration contrasts sharply with the normal pattern (*1*). This occurs in the case of the selective reduction of NO by CO in the presence of a stoichiometric excess of $O_2$. Unless a selective catalyst is employed, NO conversion will be minimal in this system because of consumption of CO by the CO–$O_2$ reaction. Iridium/alumina was found to be selective indeed, achieving more than 90% reduction in NO with 70% stoichiometric excess of $O_2$. It was particularly noteworthy that this conversion could be attained with iridium concentrations of either 0.1 or 0.001% (10 ppm). In a discussion of these findings, we pointed out that such metal-concentration-invariant behavior should not be specific to iridium but rather was applicable to a class of competitive reactions, of which CO–NO–$O_2$ was an example.

The finding that catalytic performance can survive a large reduction in metal concentration is of obvious significance to any deployment of noble metal catalysts for the selective reduction of NO in automotive exhaust. Recently Schlatter and Taylor have confirmed metal-concentration-invariant behavior for the selective reduction of NO over rhodium/alumina catalysts (*2*). The latter are considered prime candidates as components for the so-called three-way-catalyst system which incorporates selective NO reduction.

In view of the relevance of metal-concen-

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tration-invariance to interesting and perhaps commercially important systems, it appears worthwhile to present the derivation more explicitly in the context of *kinetic partitioning* in competitive reaction systems. In addition, this treatment will be used to relate NO conversion numerically to gas composition and catalyst selectivity in the NO-CO-$O_2$ system. Finally, a more general treatment will deal with the conditions required for metal-concentration-invariant behavior to occur.

## KINETIC PARTITIONING IN THE NO-CO-$O_2$ SYSTEM

Let us consider an NO-CO-$O_2$-inert gas mixture in the presence of a catalyst and stipulate a stoichiometric excess of $O_2$. Assume that the reaction of CO with either oxidant is first order with respect to each species, i.e.,

$$\frac{d(\mathrm{NO})}{dt} = -k_1(\mathrm{NO})(\mathrm{CO}) \tag{1}$$

$$\frac{d(\mathrm{O_2})}{dt} = -k_2(\mathrm{O_2})(\mathrm{CO}). \tag{2}$$

For the sake of mathematical simplicity, it is further assumed that the concentration ratio of $O_2$ to NO is sufficiently high that the drain on CO due to the latter is negligible compared with that due to the former. This leads to

$$\frac{d(\mathrm{CO})}{dt} = 2\frac{d(\mathrm{O_2})}{dt} = -2k_2(\mathrm{O_2})(\mathrm{CO}) \tag{3}$$

and

$$(\mathrm{O_2}) = (\mathrm{O_2})_0 - \frac{(\mathrm{CO})_0}{2} + \frac{(\mathrm{CO})}{2}. \tag{4}$$

Introducing $\beta$ as twice the stoichiometric excess of $O_2$, i.e.,

$$\beta = 2(\mathrm{O_2})_0 - (\mathrm{CO})_0, \tag{5}$$

this can be inserted into Eq. (4) to give

$$(\mathrm{O_2}) = \frac{\beta + (\mathrm{CO})}{2}. \tag{6}$$

With the aid of Eq. (6), Eq. (3) can be integrated to give

$$(\mathrm{CO}) = \frac{\beta\,(\mathrm{CO})_0}{2(\mathrm{O_2})_0 e^{\beta k_2 t} - (\mathrm{CO})_0}. \tag{7}$$

Eq. (7) in turn can be substituted into Eq. (1) and the latter can be integrated, leading to

$$\ln\left[\frac{(\mathrm{NO})}{(\mathrm{NO})_0}\right] = \beta k_1 t - \frac{k_1}{k_2}\ln\left[\frac{2(\mathrm{O_2})_0 e^{\beta k_2 t} - (\mathrm{CO})_0}{\beta}\right]. \tag{8}$$

Equation (8) represents the general solution for the concentration of NO as a function of time, catalyst selectivity ($k_1/k_2$), and stoichiometric excess of $O_2$ ($\beta/2$).

At early stages of reaction, the conversion of NO can be simply described as a pseudo-first-order decay. This can be shown by differentiating Eq. (8),

$$\frac{d}{dt}\ln\left[(\mathrm{NO})/(\mathrm{NO})_0\right] = \frac{-\beta k_1(\mathrm{CO})_0}{2(\mathrm{O_2})_0 e^{\beta k_2 t} - (\mathrm{CO})_0}, \tag{9}$$

and taking the limit as $t \to 0$.

$$\lim_{t\to 0}\frac{d}{dt}\ln\left[(\mathrm{NO})/(\mathrm{NO})_0\right] = -k_1(\mathrm{CO})_0. \tag{10}$$

If a supported-metal catalyst is involved, Eq. (10) implies that the rate of NO conversion at the early stages of reaction will be proportional to the metal concentration, since $k_1$ will vary with the latter in a linear manner, assuming a constant degree of dispersion.

Kinetic partitioning is not manifest at low degrees of conversion since the supply of CO is ample for both oxidants. As catalytic activity and/or contact time increase, however, CO, being stoichiometrically deficient, becomes scarce. The two oxidants must now compete for the small amount of available reductant. The effect of this can be seen by examining the behavior of the system as (CO) → 0, i.e., as $t \to \infty$. The following result is derived:

$$\lim_{(\mathrm{CO})\to 0} \frac{(\mathrm{NO})}{(\mathrm{NO})_0} = \left(1 - \frac{(\mathrm{CO})_0}{2(\mathrm{O}_2)_0}\right)^{k_1/k_2}. \quad (11)$$

If Eq. (11) is compared with Eq. (10), a significant difference is noticed. Thus, the metal concentration of the assumed supported-metal catalyst has been implicitly eliminated from Eq. (11) since only a *ratio* of rate constants, both varying in the same manner with metal concentration, is involved. This ratio governs the kinetic partitioning of CO, which in turn controls the conversion of NO in this system.

The effect of kinetic partitioning as (CO) → 0 can be derived more directly by combining Eqs. (1) and (2) to obtain the partition equation:

$$\frac{d \ln (\mathrm{NO})}{d \ln (\mathrm{O}_2)} = \frac{k_1}{k_2}. \quad (12)$$

Integrating and substituting Eq. (6) yields

$$\ln\left(\frac{(\mathrm{NO})}{(\mathrm{NO})_0}\right) = \frac{k_1}{k_2} \ln\left(\frac{\beta + (\mathrm{CO})}{2(\mathrm{O}_2)_0}\right). \quad (13)$$

The limit as (CO) → 0 is easily obtained, giving

$$\lim_{(\mathrm{CO})\to 0} \frac{(\mathrm{NO})}{(\mathrm{NO})_0} = \left(1 - \frac{(\mathrm{CO})_0}{2(\mathrm{O}_2)_0}\right)^{k_1/k_2} \quad (14)$$

identical to Eq. (11). Different mechanisms may lead to a partition equation of the same form as Eq. (12). For example, assuming the NO–CO $O_2$ system to react via Langmuir–Hinshelwood kinetics with reversible adsorption of all reactants onto common sites leads to this same form. As the system contains only a *ratio* of rate constants, the metal-concentration-invariant nature of the end result is ensured.

## EFFECT OF CATALYST SELECTIVITY ON NO CONVERSION UNDER LEAN CONDITIONS

The selectivity parameter of the catalyst, $\alpha$, equal to $k_1/k_2$, can be seen from Eq. (14) to exert a strong influence on NO conversion. Thus, under lean (excess $O_2$) conditions and with a sufficiently high value of $k_2 t$ so that (CO) approaches zero, there will be an exponential dependence of $(\mathrm{NO})/(\mathrm{NO})_0$ on $\alpha$.

Figure 1 illustrates this by plotting the amount of unconverted NO versus initial $O_2$ concentration assuming $(\mathrm{CO})_0 = 1.5\%$ and $(\mathrm{NO})_0 = 0.1\%$. These values are in the range of those occurring in automotive exhaust. The assumption made earlier that reaction of NO with CO represents a negligible drain on the latter is suspended. The

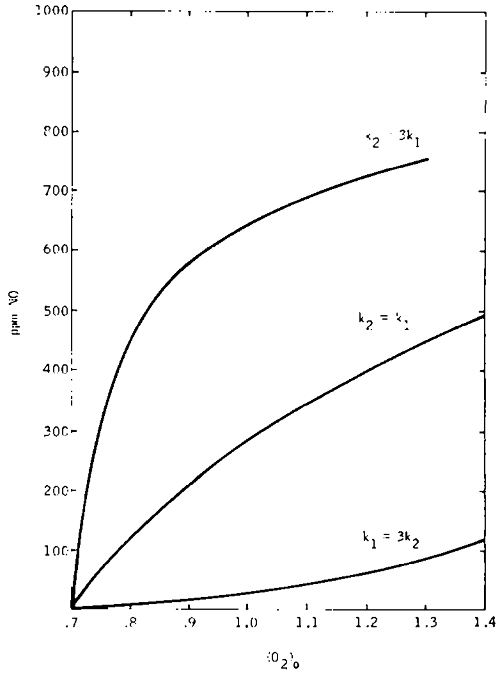

FIG. 1. Effect of catalyst selectivity on NO conversion under lean conditions. CO is assumed to be completely converted. Initial concentrations: $(\mathrm{CO})_0 = 1.5\%$; $(\mathrm{NO})_0 = 0.1\%$; $(\mathrm{O}_2)_0$, variable.

equation

$$(O_2) = (O_2)_0 - \frac{(CO)_0}{2} + \frac{(NO)_0}{2} - \frac{(NO)}{2} \qquad (15)$$

is used for substitution into the integrated form of Eq. (12) and this is solved numerically for (NO).

The value of $(O_2)_0$ at the stoichiometric point is 0.7%, and as $(O_2)_0$ increases beyond this, the conversion of NO is lowered. With a selective catalyst, e.g., one characterized by a value of $\alpha = 3$, a conversion of almost 90% can still be obtained with a 100% stoichiometric excess of $O_2$. Contrastingly, with a selectivity parameter of $\frac{1}{3}$, even a 10% excess of $O_2$ lowers the NO conversion to 60%. It is thus apparent that a modest change in the ratio $k_1/k_2$ of a catalyst, e.g., brought about by a promotor, support-interaction or selective poison, can lead to a significant increase or decrease in the ability of the catalyst to promote NO reduction under lean conditions.

## PARTITIONING IN ACTIVITY-CONTROLLED AND SELECTIVITY-CONTROLLED REGIMES

The effect of kinetic partitioning on a competitive reaction system will depend upon the relative concentration of the partitioned species and on its overall degree of conversion. To pursue this in a quantitative manner, we consider the generalized reaction system $A_1$, $A_2$, and B in which the irreversible reactions

$$A_1 + B \xrightarrow{k_1} (\text{Products})_1 \qquad (16)$$

and

$$A_2 + B \xrightarrow{k_2} (\text{Products})_2 \qquad (17)$$

occur. In contrast to the usual type of partitioning (e.g., that of a solute between two solvents), the kinetic partitioning of B will not involve thermodynamic parameters but rather the initial concentrations of the competing reactants $A_1$ and $A_2$ and the rate constants of their respective reactions with B over the particular catalyst employed.

Although kinetic partitioning will occur under all conditions, its effect on the performance of the catalyst, for example, on the conversion of $A_1$, will depend upon the regime of operation. Let us again make the simplifying assumption that $(A_2)_0 \gg (A_1)_0$ so that the consumption of B is essentially due only to $A_2$. We wish to examine the effect of kinetic partitioning on the conversion of $A_1$ as the catalytic activity and/or contact time are increased over a wide range. For the present discussion, changes in catalytic activity will be considered to relate to changes in concentration of the active phase. The situation in which an increase in activity is because of a rise in temperature will be discussed subsequently. Assuming the reactions represented by Eqs. (16) and (17) to be first order with respect to each species, a treatment analogous to that given above leads to

$$\ln\left[\frac{(A_1)}{(A_1)_0}\right] = \beta k_1 t - \alpha \ln\left(\frac{(A_2)_0 e^{\beta k_2 t} - (B)_0}{\beta}\right), \qquad (18)$$

equivalent to Eq. (8), in which $\beta = (A_2)_0 - (B)_0$ and $\alpha = k_1/k_2$. Figure 2 shows a plot of $\log_{10}(-\ln[(A_1)/(A_1)_0])$ vs $\log(k_1(B)_0 t)$ assuming five different values of $\alpha$ and/or $\beta$. Curve A corresponds to $k_2 = 0$, i.e., a total *absence* of partitioning. In this limiting case the analysis simplifies to

$$\ln\left[\frac{(A_1)}{(A_1)_0}\right] = -k_1(B)_0 t. \qquad (19)$$

Any deviation from the straight line of Curve A reflects the influence of kinetic partitioning.

Curve B represents a stoichiometric excess of B ($\beta < 0$). Although Curve B diverges from Curve A for sufficient degrees of conversion of $A_1$, it never approaches a limiting value. This is in accordance with the fact that

$$\lim_{\substack{t\to\infty \\ \beta<0}} \ln [(A_1)/(A_1)_0] = \beta k_1 t \qquad (20)$$

and thus the conversion of $A_1$ constantly increases along with $k_1t$.

Curves C through E relate to cases in which B is stoichiometrically deficient ($\beta > 0$). This can lead to situations in which kinetic partitioning exerts a dominant effect on the reaction. Figure 2 shows, however, that at low values of $k_1(B)_0t$ this is not so, as Curves A through E are coincidental there. This reflects the fact that

$$\lim_{t\to 0} \ln [(A_1)/(A_1)_0] = -k_1(B)_0t \qquad (21)$$

for any $\alpha$ or $\beta$.

In the regime of low values of $k_1(B)_0t$, the conversion of $A_1$ may be said to be *activity-controlled*. One might demonstrate this, for instance, by sintering the catalyst, which would lower $k_1$ and therefore the conversion of $A_1$ under fixed conditions. As $k_1(B)_0t$ becomes greater, however, Curves C through E increasingly diverge from Curve A. This signifies transition into a new regime in which the conversion of $A_1$ may be said to be *selectivity-controlled*. As the asymptotic value is approached, this conversion becomes metal-concentration-invariant (assuming a supported-metal catalyst), since a decrease in $k_1$ resulting from a lower metal concentration or from sintering of the original catalyst is without effect unless sufficient to return the catalyst to the activity-controlled regime. Conversion of $A_1$ in the selectivity-controlled regime will be adversely affected by lowering $\alpha$ (compare Curves C and E) or increasing $\beta$ (compare Curves C and D).

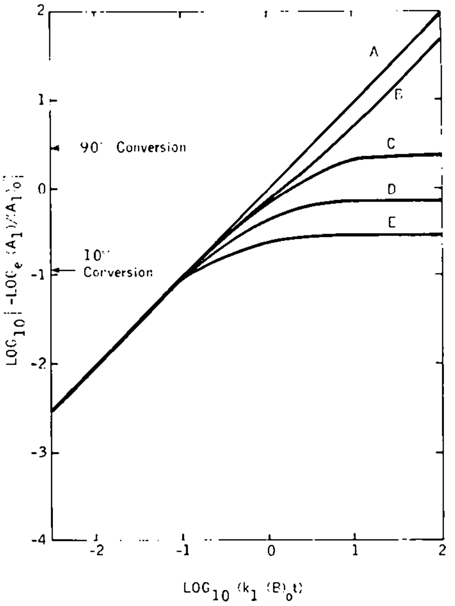

FIG. 2. Effect of kinetic partitioning in activity-controlled and selectivity-controlled regimes. Curves: (A) $k_2 = 0$; (B) $\alpha = \frac{1}{3}$, $\beta = -(B)_0/2$; (C) $\alpha = 3$, $\beta = (B)_0$; (D) $\alpha = 3$, $\beta = 4(B)_0$; (E) $\alpha = \frac{1}{3}$, $\beta = (B)_0$. Calculations are based on Eq. (18). Variation in $k_1(B)_0t$ is assumed *not* to be due to change in temperature unless $d\alpha/dT = 0$ (see text). Ordinate values corresponding to 10 and 90% conversion are indicated.

Let us now consider the situation in which $k_1(B)_0t$ increases as the result of rising temperature. If the selectivity parameter $\alpha$ is essentially temperature independent, the change in conversion of $A_1$ resulting from increasing $k_1$ (assuming $\beta > 0$) will lead to a curve of the same form as Curves C through E shown in Fig. 2. Thus, it will progress through an activity-controlled zone into a selectivity-controlled zone in which $(A_1)/(A_1)_0$ will be independent of further temperature increase. Temperature-independent partitioning was indicated in the iridium-catalyzed NO–CO–$O_2$ system (1), in which the selectivity parameter was interpreted as the ratio of the chemisorption rate constants of NO and $O_2$ on the iridium surface. As these chemisorptions may be assumed to be nonactivated, a negligible temperature-dependence of the partitioning would be expected.

In the case of a temperature-insensitive $\alpha$, a low metal concentration can be compensated by an increase in temperature. In the system described in Ref. (*1*), for example, a 100-fold diminution in metal concentration could be compensated by a 100°C increase in temperature.

For the more general case of $\alpha$ varying with temperature, the effectiveness of raising temperature to compensate for low metal concentration will of course depend upon whether $d\alpha/dT$ is positive or negative. If sufficiently negative, such compensation will not be possible, whereas if $d\alpha/dT$ is positive, higher temperature will be advantageous for any metal concentration.

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