f = fugacity
$\bar{g}$ = partial molar Gibbs energy
g = radial distribution function
H = Henry's constant
k = Boltzmann's constant
K = y_2/x_2
K_0, K_1, K_2, K_3 = functions given by Eqs. 5-9
P = total pressure
P_c = critical pressure
r = intermolecular distance
R = gas constant
T = absolute temperature
T_c = critical temperature
x = liquid-phase mole fraction
y = vapor-phase mole fraction
v = molar volume
ϵ = potential energy parameter
γ^* = liquid-phase activity coefficient
ϕ = vapor-phase fugacity coefficient
σ = molecular diameter
ξ = reduced density
ρ = density (molecules per unit volume)

LITERATURE CITED

Hankinson, R. W., and G. H. Thompson, "A New Correlation for Saturated Densities of Liquids and Their Mixtures," *AIChE J.*, **25**, 653 (1979).

Pierotti, R. A., "Aqueous Solutions of Nonpolar Gases," *J. Phys. Chem.*, **69**, 281 (1963).

Pierotti, R. A., "A Scaled Particle Theory of Aqueous and Nonaqueous Solutions," *Chemical Reviews*, **76**, 717 (1976).

Prausnitz, J. M., *Thermodynamics of Fluid-Phase Equilibria*, Chapter 5, Prentice-Hall (1969).

Prausnitz, J. M., E. A. Grens, T. F. Anderson, C. A. Eckert, R. Hsieh, and J. P. O'Connell, *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*, Appendix C, Prentice-Hall (1980).

Reiss, H., H. L. Frisch, and J. L. Lebowitz, "Statistical Mechanics of Rigid Spheres," *J. Chem. Phys.*, **31**, 369 (1959).

Reiss, H., H. L. Frisch, E. Helfand, and J. L. Lebowitz, "Aspects of the Statistical Thermodynamics of Real Fluids," *J. Chem. Phys.*, **32**, 119 (1960).

Wilhelm, E., and R. Battino, "The Solubility of Gases in Liquids," *J. Chem. Thermodynamics*, **3**, 371 (1971).

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Simultaneous Reactions of CO, NO and O_2 in a Tubular Reactor

N. JOTHI
and
A. VARMA

Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556

INTRODUCTION

Strict federal regulations on automotive exhaust emissions make it necessary to remove carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) by using so-called three-way catalysts. In automotive exhausts, CO and HC are reducing species, while NO_x and O_2 are oxidizing species. A desired characteristic of a three-way catalyst is that it preferentially favors reactions of the reducing species (i.e., CO and HC) with NO_x rather than with O_2. The actual number of reacting species and reactions possible in automotive three-way catalysis is very large; however, some basic factors involved in catalyst design can be understood by considering only the following two reactions:

$$2CO + O_2 \xrightarrow{k_1} 2CO_2 \tag{1}$$

$$2CO + 2NO \xrightarrow{k_2} 2CO_2 + N_2 \tag{2}$$

For the CO-NO-O_2 system, using an iridium catalyst, Tauster and Murrell (1976) found that under net oxidizing conditions, conversion of NO becomes independent of catalyst loading, and pointed out that this metal concentration-invariant behavior should apply to any catalyst provided that temperature or contact time were high enough for essentially complete CO conversion. Schlatter and Taylor (1977) also observed similar behavior using a rhodium catalyst. The former authors have also attempted to explain this behavior using approximate and numerical approaches (Tauster and Murrell, 1978).

In a recent paper, Hegedus et al. (1979) considered these reactions in an integral plug-flow reactor, under both rich (CO in excess) and lean (NO_x and O_2 in excess) conditions, when the catalyst is equally selective for both reactions ($k = 1$). In this note, we consider the case of *arbitrary* selectivity, and specifically cases where the catalyst is more selective for the second reaction—as with rhodium and iridium catalysts. For example, Tauster and Murrell (1976) found partition factors of 2·8 and 4·5 in favor of the second reaction for iridium catalysts. We also report analytic solutions for values of $k = 2$ and 3.

BASIC EQUATIONS

Consider an isothermal plug-flow reactor, with simple bimolecular reaction kinetics and no diffusional limitations. To conserve space, the nomenclature of Hegedus et al. (1979) is used. In their notation, then, the relevant conservation equations in dimensionless form are:

$$\frac{dx}{dt} = kR(1 - x)(1 - y) + (S - R)(1 - x)w \tag{3a}$$

$$\frac{dy}{dt} = k(1 - x)(1 - y) \tag{3b}$$

$$\frac{dw}{dt} = -(1 - x)w \tag{3c}$$

with initial conditions at $t = 0$:

$$x = 0, \quad y = 0, \quad w = 1 \tag{4}$$

The various symbols are defined in the Notation. It is important, however, to note here that x and y are CO and NO conversions respectively, and w is the dimensionless O_2 concentration along the reactor length, t. Also by definition,

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Correspondence concerning this paper should be addressed to A. Varma.

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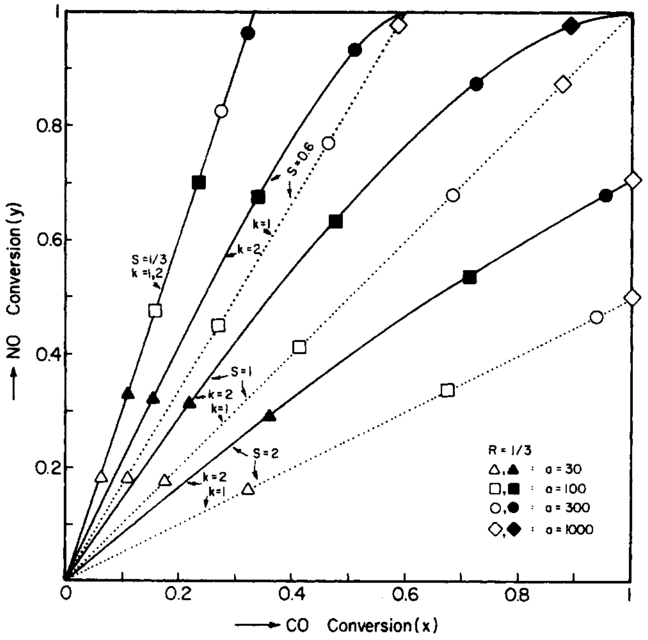

Figure 1. Effect of catalyst selectivity (*k*), active catalyst area (*a*), and inlet gas stoichiometry (*R*, *S*) on reactor performance.

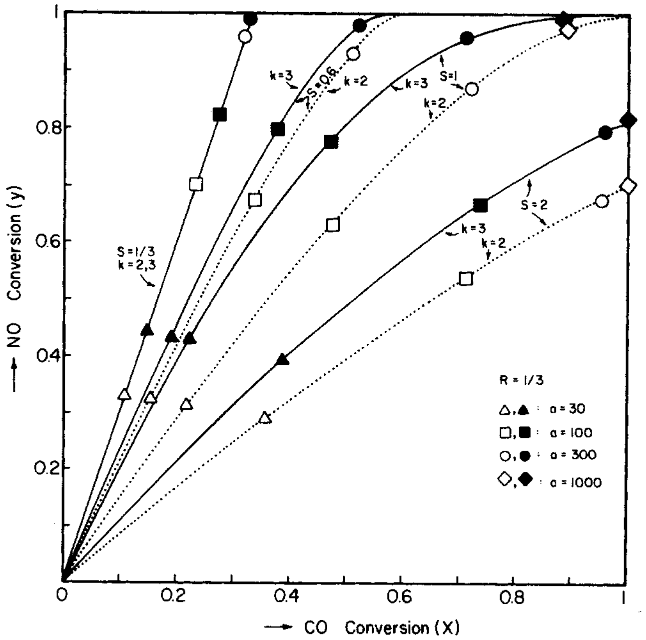

Figure 2. Effect of catalyst selectivity (*k*), active catalyst area (*a*), and inlet gas stoichiometry (*R*, *S*) on reactor performance.

$$S = [2C_{O_2,0} + C_{NO,0}]/C_{CO,0}, \quad R = C_{NO,0}/C_{CO,0} \tag{5}$$

and so $S \geq R$ always. x, y and w are limited by physical reasons to the range

$$0 \leq x,\ y,\ w \leq 1,$$

and it is apparent from Eqs. 3 that as t increases, x and y increase monotonically while w decreases.

Simple manipulations of Eqs. 3 and 4 reveal that they are equivalent to

$$y = 1 - w^k \tag{6a}$$

$$x = (S - R)(1 - w) + R(1 - w^k) \tag{6b}$$

where w is the solution of

$$\frac{dw}{dt} = -wF(w); \quad w(0) = 1 \tag{7}$$

and

$$F(w) \equiv Rw^k + (S - R)w + (1 - S) = 1 - x \tag{8}$$

The strategy is to first solve for $w(t)$ using Eq. 7; the corresponding x and y values are then obtained immediately from Eq. 6.

QUALITATIVE BEHAVIOR

The steady states of Eq. 7 are either $w = 0$ or w_s, where w_s satisfies $F(w_s) = 0$. Now, $F(w)$ has the properties:

$$F(0) = 1 - S, \quad F(1) = 1,$$

$$F'(w) = (S - R) + kRw^{k-1} > 0 \tag{9}$$

so that for $S < 1$ (i.e., net reducing feed) w_s does not exist, and the only steady state of Eq. 7 is $w = 0$. For $S > 1$ (i.e., net oxidizing feed) however, a *unique* w_s exists and then $w = 0$ and $w = w_s$ are the two steady states of the system. Note that $w = w_s$ corresponds to $x = 1$ (i.e., complete conversion of CO).

The dynamic behavior is then evident:

1. $S < 1$ (i.e., net reducing feed). As t increases, w decreases monotonically. Furthermore, as $t \to \infty$:

$$w \to 0, \quad y \to 1, \quad x \to S \tag{10}$$

Thus for a net reducing feed, if the contact time is high enough, the oxidants O_2 and NO are completely consumed, while CO is only partially converted.

2. $S > 1$ (i.e., net oxidizing feed). As $t \to \infty$;

$$w \to w_s, \quad y \to 1 - w_s^k, \quad x \to 1 \tag{11}$$

so that in a reactor with large enough contact time, a net oxidizing feed results in complete CO conversion; NO and O_2 are only partially converted.

It is important to note that since $0 < w_s < 1$, a large partition factor k will cause the NO conversion, y, to approach 1. Thus, in a long reactor, a large k will result in virtually complete NO conversion *even* with a net oxidizing feed—which is a consequence of the fact that larger k favor the CO-NO reaction over the CO-O_2 reaction.

The characteristics of a long reactor (i.e., one in which conversion of one of the reactants approaches completion) are therefore fully identified by the behavior analyzed above. For finite reactors, design equations relating conversions of various species with reactor length are required. For arbitrary k, Eq. 7 cannot be integrated analytically, and numerical techniques are then the only approach possible. For some special values of k, however, closed form solutions can be obtained, and these are now reported.

TABLE 1. PARAMETERS USED FOR FIGURES 1 AND 2

a	30-1000	cm² Catalyst/cm³ Reactor
L/v	0.03	s
$C_{CO,0}$	0.3	vol %
$C_{NO,0}$	0.1	vol %
$C_{O_2,0}$	0-0.25	vol %
k_1	5×10^6	cm³/mol · s at 500°C

ANALYTIC SOLUTIONS AND RESULTS

Analytic solutions can be obtained for $k = 1$, 2 or 3, and for the special case of $S = R$. Note that when $S = R$, the problem degenerates to the case of a *single* reaction, for there is no O_2 in the feed in that case.

Case 1: $k = 1$. This is the case considered by Hegedus et al. (1979), and the complete solution is:

$$x = S(1 - w), \quad y = 1 - w, \tag{12a}$$

$$w = \frac{(1 - S)\exp[(S - 1)t]}{1 - S\exp[(S - 1)t]} \tag{12b}$$

The phase plane of NO conversion (y) vs. CO conversion (x) then simply consists of straight lines:

$$y = x/S \tag{13}$$

and various points on these lines correspond to various values of the parameter t. The qualitative behavior described by Eqs. 10 and 11 for arbitrary k, can again be seen from Eqs. 12 for this special value of k.

Some calculations for a typical case in automotive catalysis, utilizing the same parameters as those of Hegedus et al. (1979) given in Table 1, are shown in Figure 1.

Case 2: $k = 2$. Values of x and y are given in terms of w by Eq. 6 with $k = 2$, and w is the solution of

$$\frac{dw}{dt} = -w[Rw^2 + (S - R)w + (1 - S)]$$
$$= -Rw(w - w_-)(w - w_+) \tag{13}$$

with initial condition: $w(0) = 1$, where

$$w_\pm = -[(S - R) \pm \{(S + R)^2 - 4R\}^{1/2}]/2R \tag{14}$$

It can readily be shown that $w_\pm$ are always real when $S > 1$. For $S < 1$, however, $w_\pm$ are a complex conjugate pair for values of R in the range

$$R_- < R < S \tag{15}$$

and real otherwise, where

$$R_- = (2 - S) - 2(1 - S)^{1/2} \tag{16}$$

The complete solution of Eq. 13 is:

A. *$w_\pm$ real*

$$t = \frac{1}{R}\, ln\left[\frac{1}{w^{p1}}\left\{\frac{1 - w_+}{w - w_+}\right\}^{p2}\left\{\frac{1 - w_-}{w - w_-}\right\}^{p3}\right] \tag{17}$$

B. *$w_\pm$ complex*

$$t = \frac{1}{R(q_1^2 + q_2^2)}\left[ln\left(\frac{1}{w}\right) + \frac{1}{2}\, ln\left\{\frac{(w - q_1)^2 + q_2^2}{(1 - q_1)^2 + q_2^2}\right\} + \frac{q_1}{q_2}\left\{\tan^{-1}\left(\frac{1 - q_1}{q_2}\right) - \tan^{-1}\left(\frac{w - q_1}{q_2}\right)\right\}\right] \tag{18}$$

where the p_i and q_i are constants, given by

$$p_1 = \frac{R}{1 - S}, \quad p_2 = \frac{Rw_+ - (R - S)}{(S - 1)(w_+ - w_-)},$$
$$p_3 = \frac{(R - S) - Rw_-}{(S - 1)(w_+ - w_-)} \tag{19}$$
$$q_1 = (R - S)/2R, \quad q_2 = [4R - (S + R)^2]^{1/2}/2R$$

The w-t relations are implicit in w; the easiest way to evaluate them is, given R and S, to assume a value of $w[0 < w < 1$ for $S < 1$, and $w_+ = w_s < w < 1$ for $S > 1]$ and find the corresponding t from Eq. 17 or 18 depending on whether $w_\pm$ are real or complex. Once w is known, x and y are directly obtained from Eq. 6.

Note from Eq. 3:

$$\frac{dy}{dx} = \frac{1}{R + [(S - R)/kw^{k-1}]} \tag{20}$$

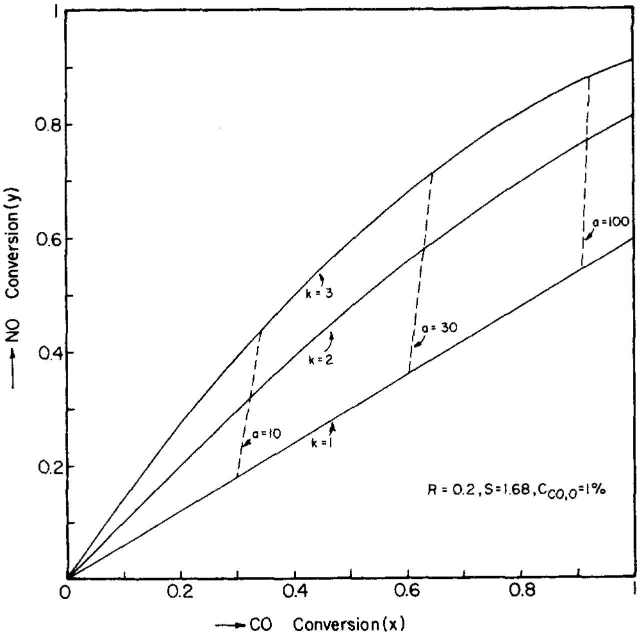

Figure 3. Effect of catalyst selectivity (k) on reactor performance, corresponding to experimental inlet gas composition of Tauster and Murrell (1976).

Since w decreases monotonically as t increases, and $k > 1$, dy/dx decreases as t increases. The trajectories in the phase plane are therefore convex, and for $S \geq 1$ approach their final values with zero slope—as shown in Figure 1. As is intuitively proper, for equal values of the other parameters, more NO and CO conversions occur when $k = 2$ than when $k = 1$.

Case 3: $k = 3$. The solution of Eq. 7 in this case is

$$t = \frac{ln\, w}{R\overline{w}(r_+^2 + r_-^2 - r_+r_-)} - \frac{ln[(w - \overline{w})/(1 - \overline{w})]}{3R\overline{w}(r_+^2 + r_-^2 + r_+r_-)} - \frac{1}{3R[(r_+^2 + r_-^2)^2 - (r_+r_-)^2]}\left[\overline{w}\, ln\left\{\frac{w^2 + w\overline{w} + r_+^2 + r_-^2 - r_+r_-}{1 + \overline{w} + r_+^2 + r_-^2 - r_+r_-}\right\} + \frac{2\sqrt{3}r_+r_-}{r_+ - r_-}\left\{\tan^{-1}\left(\frac{2w + \overline{w}}{\sqrt{3}(r_+ - r_-)}\right) - \tan^{-1}\left(\frac{2 + \overline{w}}{\sqrt{3}(r_+ - r_-)}\right)\right\}\right]$$

where

$$r_\pm = [\alpha \pm (\alpha^2 + \beta^3)^{1/2}]^{1/3}, \quad \overline{w} = r_+ + r_- = w_s$$
$$\alpha = (S - 1)/2R, \quad \beta = (S - R)/3R \tag{22}$$

As with $k = 2$, the relationship is implicit in w, and exactly the same strategy can be employed to construct the phase plane. A representative set of calculations is shown in Figure 2, where the curves for $k = 2$ are also shown for comparison.

Case 4: $S = R$. In this case, also considered by Hegedus et al. (1979), there is no O_2 in the feed and so CO-NO is the only reaction possible. The phase plane consists of straight lines:

$$y/x = 1/S \tag{23}$$

where

$$y = \frac{1 - \exp[(1 - S)\theta]}{S - \exp[(1 - S)\theta]} \tag{24a}$$

and

$$\theta = 2ak_2C_{CO,0}(z/v) \tag{24b}$$

provide the reactor length required for a specified conversion level. Figures 1 and 2 show calculations for this case for various values of k_2.

DISCUSSION

Figures 1 and 2 reveal that under oxidizing conditions ($S > 1$), the eventual conversion of NO (i.e., when CO conversion = 1) increases as k increases, as would be expected. The phase plane diagram shown in Figure 3 corresponds to the experimental feed compositions of Tauster and Murrell (1976). The curves are themselves independent of k_1; however, lines of constant catalyst area (a) depend on k_1, and for Figure 3 the value shown in Table 1 is used.

At complete CO conversion, NO conversions of 59.5%, 81.2% and 91% are realized for $k = 1$, 2 and 3, respectively. It is worth noting that Tauster and Murrell (1976) did observe NO conversions in excess of 90% in their experiments.

Schlatter and Taylor (1977), and Tauster and Murrell (1976) had experimentally noted that under oxidizing conditions ($S > 1$), NO conversion (y) becomes independent of catalyst loading as long as CO conversion (x) is close to 1. Hegedus et al. (1979) remarked about this point for $k = 1$, and also that under net reducing conditions ($S < 1$), CO conversion becomes independent of the catalyst area when NO conversion is close to 1. Both these features can also be seen for $k = 2$ and 3 in Figures 1 and 2. Note that this independence occurs at relatively lower catalyst areas when k is larger; i.e., as the catalyst becomes more active in general, as well as more selective for NO.

In conclusion, it is worth remarking that the analysis presented in this work is general, and applies to other competitive reaction systems as well.

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NOTATION

a = active catalyst area
C = species concentration
F = function, defined by Eq. 8
k = catalyst partition factor, $2k_2/k_1$
k_1, k_2 = rate constants
L = reactor length
p_i = constants, defined by Eq. 19
q_i = constants, defined by Eq. 19
$r_\pm$ = constants, defined by Eq. 22
R = constant, $C_{NO,0}/C_{CO,0}$
S = stoichiometry number, $(2C_{O_2,0} + C_{NO,0})/C_{CO,0}$
t = dimensionless reactor length, $ak_1C_{CO,0}(z/v)$
v = fluid velocity
w = dimensionless O_2 concentration, $C_{O_2}/C_{O_2,0}$
$\bar{w}$ = constant, defined by Eq. 22
$w_\pm$ = constants, defined by Eq. 14
x = CO conversion, $1 - (C_{CO}/C_{CO,0})$
y = NO conversion, $1 - (C_{NO}/C_{NO,0})$
z = distance from reactor inlet

Greek Letters

α = constant, defined by Eq. 22
β = constant, defined by Eq. 22
θ = dimensionless reactor length when $S = R$

Subscripts

0 = inlet value

LITERATURE CITED

Hegedus, L. L., R. K. Herz, S. H. Oh, and R. Aris, "Effect of Catalyst Loading on the Simultaneous Reactions of NO, CO and O_2," *J. Catalysis*, **57**, 513 (1979).

Schlatter, J. C. and K. C. Taylor, "Platinum and Palladium Addition to Supported Rhodium Catalysts for Automotive Emission Control," *J. Catalysis*, **49**, 42 (1977).

Tauster, S. J. and L. L. Murrell, "The NO-CO Reaction in the Presence of Excess O_2 as Catalyzed by Iridium," *J. Catalysis*, **41**, 192 (1976).

Tauster, S. J. and L. L. Murrell, "Kinetic Partitioning in Competitive Reaction Systems," *J. Catalysis*, **53**, 260 (1978).

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Bubble Nucleation Studies

Part I: Formation of Bubble Nuclei in Superheated Water by Bursting Bubbles

THEODORE BERGMAN

and

RUSSELL MESLER

University of Kansas
Lawrence, KS

The development of a thorough understanding of nucleate boiling requires, among other things, an explanation of the source of the nuclei from which the vapor bubbles grow. Experiments have shown that for boiling in thin liquid films a new mechanism operates to produce bubble nuclei, Mesler & Mailen (1977). The experiment reported here gives further information on this new mechanism when the boiling is not confined to a thin film.

Nucleate boiling is an efficient means to transfer heat that relies on bubbles to augment heat transfer. Bubbles live only a transient existence in nucleate boiling. They grow from tiny nuclei and reach a size that causes them to break, either individually or after joining other bubbles, into the vapor region above the liquid surface. Boiling depends on a source of bubble nuclei for if there are no bubbles there is no boiling. Bubbles start their growth from something very small usually termed a nucleus. In experiments which minimize the presence of nuclei quite high liquid superheats are achieved without ebullition. The usual explanation of a nucleus is that it is a tiny bit of gas or vapor trapped in a crack or pit on the solid surface, Cole (1974). The gas nuclei may come from some gas that remains of that covering the surface before it was wet and the vapor nuclei may come from the remainder of a previously departed bubble which has stayed attached to the solid surface. Nowhere in the literature on nucleate boiling has there been found mention that nuclei might originate in the liquid during boiling because of the complicated motions of interacting vapor and liquid.

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