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Effect of Catalyst Loading on the Simultaneous Reactions of NO, CO, and O_2

Recent experimental studies by Tauster and Murrell (*1*) and by Schlatter and Taylor (*2*) showed that under certain operating conditions the conversion of NO may become independent of catalyst noble metal surface area in integral reactors during the simultaneous reactions of NO, CO, and O_2. In a recent theoretical paper Tauster and Murrell (*3*) considered a simplified model of this reaction system to identify the conditions under which this behavior can occur. Their analysis assumed simple bimolecular kinetics and a large initial excess of O_2 ("lean limit"). The purpose of this note is to provide an analysis of this reaction system using an integral reactor and allowing the inlet O_2 concentration to vary so that it covers both the O_2-deficient (rich) and the O_2-excess (lean) regions.

We consider an isothermal, plug-flow integral reactor in which there are no diffusion limitations (the actual experimental system, of course, is nonisothermal, with finite diffusion interferences; nevertheless, as we will see, it is informative to consider this simpler picture).

The reactions of interest are:

$$2\mathrm{CO} + \mathrm{O}_2 \xrightarrow{k_1} 2\mathrm{CO}_2, \tag{1}$$

$$2\mathrm{CO} + 2\mathrm{NO} \xrightarrow{k_2} 2\mathrm{CO}_2 + \mathrm{N}_2. \tag{2}$$

Assuming simple bimolecular kinetics (which may or may not be true for the experimental system; again, this will not change our qualitative conclusions), as Tauster and Murrell (*3*) did, we obtain the following conservation equations:

$$-v\frac{dC_{\mathrm{CO}}}{dz} - 2ak_1C_{\mathrm{CO}}C_{\mathrm{O}_2} - 2ak_2C_{\mathrm{CO}}C_{\mathrm{NO}} = 0, \tag{3}$$

$$-v\frac{dC_{\mathrm{NO}}}{dz} - 2ak_2C_{\mathrm{CO}}C_{\mathrm{NO}} = 0, \tag{4}$$

$$-v\frac{dC_{\mathrm{O}_2}}{dz} - ak_1C_{\mathrm{CO}}C_{\mathrm{O}_2} = 0, \tag{5}$$

$$C_{\mathrm{CO}}(0) = C_{\mathrm{CO},0}, \tag{6}$$

$$C_{\mathrm{NO}}(0) = C_{\mathrm{NO},0}, \tag{7}$$

$$C_{\mathrm{O}_2}(0) = C_{\mathrm{O}_2,0}. \tag{8}$$

Due to the large excess of inert diluent (N_2), v is constant.

The course of these reactions can be conveniently displayed in the plane of NO conversion versus CO conversion. Let us define these conversions, and other dimensionless variables, as follows:

$$x = 1 - (C_{\mathrm{CO}}/C_{\mathrm{CO},0}), \tag{9}$$

$$y = 1 - (C_{\mathrm{NO}}/C_{\mathrm{NO},0}), \tag{10}$$

$$w = C_{\mathrm{O}_2}/C_{\mathrm{O}_2,0}, \tag{11}$$

$$t = ak_1C_{\mathrm{CO},0}(z/v), \tag{12}$$

$$k = 2k_2/k_1, \tag{13}$$

$$R = C_{\mathrm{NO},0}/_{\mathrm{CO},0}. \tag{14}$$

The oxidizing or reducing nature of the

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feedstream is characterized by the stoichiometry number which is defined by

$$S = (2C_{O_2,0} + C_{NO,0})/C_{CO,0}. \quad (15)$$

The conservation equations now become

$$dx/dt = Rk(1-x)(1-y) + (S-R)(1-x)w, \quad (16)$$

$$dy/dt = k(1-x)(1-y), \quad (17)$$

$$dw/dt = -(1-x)w. \quad (18)$$

When $t = 0$, $x = y = 0$, and $w = 1$. As t increases, x and y increase and w decreases. Note that $[x - Ry + (S-R)w]$ is independent of t, and that, due to the above initial conditions, it is equal to $(S - R)$. Thus,

$$x = Ry + (S-R)(1-w). \quad (19)$$

Also, by dividing Eq. (17) by Eq. (18), we see that

$$dy/dw = -k(1-y)/w, \quad (20)$$

or

$$y = 1 - w^k, \quad (21)$$

$$x = S(1-w) + R(w - w^k). \quad (22)$$

Equations (21) and (22) give the reaction path on the $x - y$ plane, by letting w vary from 1 to 0. When $k = 1$, *or* when $S = R$, reaction paths are straight lines, while reaction paths for $k \neq 1$ *and* $S > R$ are curved.

Table 1 shows the parameter values selected for the calculations. The ratio of k_1 and k_2 was chosen so that the CO conversion and the NO conversion are equal at the stoichiometric point ($S = 1$). The residence time, L/v, was selected to resemble typical experimental conditions in automotive exhaust catalysis. The catalyst's active surface area, a, is varied within physically realistic limits. The inlet CO and NO concentrations were fixed, and only the inlet O_2 concentration was varied.

TABLE 1

Parameters Used in the Computations

a (cm^2 catalyst/cm^3 reactor)	30 to 3000
(L/v) (s)	0.03
$C_{CO,0}$(vol.%)	0.3
$C_{NO,0}$(vol.%)	0.1
$C_{O_2,0}$(vol.%)	0 to 0.25
$2k_2/k_1 = k$	1
k_1	5×10^6

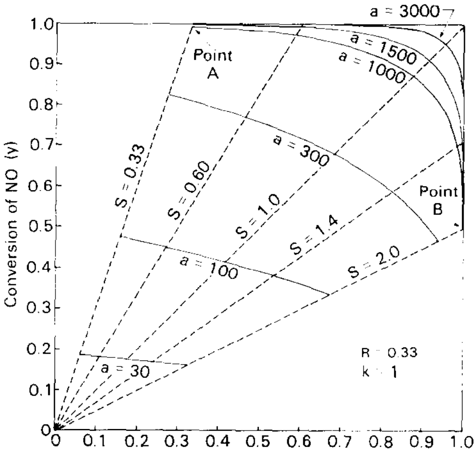

FIG. 1. Effects of active surface area and inlet stoichiometry on catalyst performance.

Figure 1 shows the reaction paths (dashed lines). $R = 0.33$ and $k = 1$, while S varies between 0.33 ($C_{O_2,0} = 0$) and 2 ($C_{O_2,0} = 0.25$). Curves of constant catalyst active surface area (solid lines in Fig. 1) are obtained by integrating Eq. (18) to get $w(t)$ and determining the resulting x and y using Eqs. (21) and (22) at constant t, k, and R, for various values of S.

The conversions of both NO and CO increase at $S = 1$ as the catalyst's active surface area, a, is increased. When $S < 1$, the conversion of CO is independent of a, as long as the conversions of NO and O_2 are complete (point A in Fig. 1). Similarly, when $S > 1$, the conversion of NO is independent of a, as long as the conversion of CO is complete (point B in Fig. 1).

APPENDIX: NOMENCLATURE

a (cm^2 catalyst/cm^3 reactor)	Catalyst active surface area

C (mol/cm^3)	Concentrations
k_1, k_2	Rate constants
L (cm)	Reactor length
v (cm/s)	Superficial gas velocity
z (cm)	Distance from reactor inlet

The dimensionless variables x, y, w, t, k, R, and S are defined in the text.

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