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The NO–CO Reaction in the Presence of Excess O_2 as Catalyzed by Iridium

In the course of the many investigations of prospective catalysts for control of automotive NO_x, a few authors have commented on the competition between the CO–NO and CO–O_2 reactions. Shelef *et al.* (*1*) reported that the latter reaction is predominant over a number of transition metal oxides as well as supported Pt. Baker and Doerr found the same for copper chromite (*2*) and copper oxide–cobalt oxide alumina (*3*). Bauerle *et al.* (*4*), however, found 75% reduction of NO by CO over 0.5% Rh/alumina in the presence of a 102% stoichiometric excess of oxidants (NO + O_2).

In the present work we have found 90% conversion of NO, in the presence of 75% excess of oxidants, over Ir/alumina catalysts containing either 0.1 or 0.001% Ir. The more dilute catalyst requires higher temperature to achieve complete removal of CO, but the partitioning of CO between NO and O_2 is, to first approximation, independent of space velocity and iridium content.

The catalysts were prepared by incipient wetness impregnation of η-alumina with H_2IrCl_6 solution, followed by drying @ 120°C and *in situ* reduction by H_2 @ 500°C. The catalyst (1.0 g) was charged as a 20/40 mesh pressed powder, mixed with 5 cc 20/40 mesh alumina beads, into a 25 mm i.d. Vycor reactor. A preheater zone consisted of 25 cc alumina beads. CO (10% in helium), O_2 (10%), and NO (2%) were supplied from cylinders and diluted with helium in a blending manifold to provide an inlet gas composition of 0.2% NO, 1.0% CO, 0.75% O_2; total flow = 100 liters/hr. Effluent gas was analyzed for N_2, CO, and O_2 with a Perkin-Elmer 900 gas chromatograph using a 13X molecular sieve column (8 ft) operating at -10°C. In addition, a portion of effluent gas was continuously monitored for NO by means of a chemiluminescent gas analyzer obtained from Thermo Electron Co., Waltham, Mass. Material balance of NO converted and N_2 formed agreed to within 5% for both catalysts, indicating little if any formation of N_2O or NO_2.

Preliminary experiments indicated the desorption of O_2 from 2% Ir/Al_2O_3 to be undetectable at $T \leqslant 700$°C. In contrast a significant amount of CO desorption occurred below 400°C. It will be assumed that adsorbed oxygen is the predominant surface species, under our experimental conditions of excess O_2, on the catalytically active part of the iridium surface, and that its reaction with gaseous CO [analogous to the mechanism found by Ertl and Koch (*5*) for CO oxidation over Pd], generates free surface sites according to

$$O_a + CO \xrightarrow{k_1} CO_2 + \square. \qquad (1)$$

Here $\square$ denotes such a site and the subscript denotes an adsorbed species. These sites are available for the chemisorption of NO and O_2, the adsorption of NO leading ultimately to the formation of N_2 and O_a.

In terms of this model, the relative rates of NO and O_2 adsorption onto sites made available by reaction (1) is of critical importance. This determines the partitioning of CO between the two oxidants, and thus the conversion of NO under lean (excess oxygen) conditions.

Setting the steady-state rates of NO and O_2 consumption equal to their chemisorption rates, we obtain

$$\frac{-d(\mathrm{NO})}{dt} = k_2(\mathrm{NO})(1-\theta), \qquad (2)$$

$$\frac{-d(\mathrm{O_2})}{dt} = k_3(\mathrm{O_2})(1-\theta)^n, \qquad (3)$$

where θ = fractional active-surface concentration of O_a, NO adsorption is assumed to require a single site, and the exponent gives the number of statistically independent sites involved in the rate-determining step of O_2 chemisorption. The partition equation may then be written as

$$\frac{d\ln(\mathrm{NO})}{d\ln(\mathrm{O_2})} = \frac{k_2}{k_3}\cdot\frac{1}{(1-\theta)^{n-1}}. \qquad (4)$$

If one assumes $\theta \ll 1$, which follows from the supposition $k_1 \gg k_2, k_3$, the value of n becomes unimportant and Eq. (4) reduces to

$$\frac{d\ln(\mathrm{NO})}{d\ln(\mathrm{O_2})} = \frac{k_2}{k_3}. \qquad (5)$$

We have observed, however, that the adsorption of O_2 onto Ir/Al_2O_3 is rapid even at ambient temperature up to approximately monolayer coverage. In view of this and the above-mentioned tenacious retention of O_2, it seems reasonable to assume $k_2, k_3 \gg k_1$. This implies that Eq. (1) is the rate-limiting step for both the CO–NO and CO–O_2 reactions. In this situation the inequality $1 - \theta \ll 1$ prevails and the value of n in Eq. (4) is pertinent. For the present we *assume* $n = 1$ (this point will be returned to) and adopt Eq. (5) as the partition equation.

The partition curve for 0.1% is shown in Fig. 1. A partition factor of 2.8 is indicated; thus a given NO molecule has a 2.8-fold higher probability of adsorbing onto a surface site than a given O_2 molecule. The catalyst, in this fundamental sense, is selective.

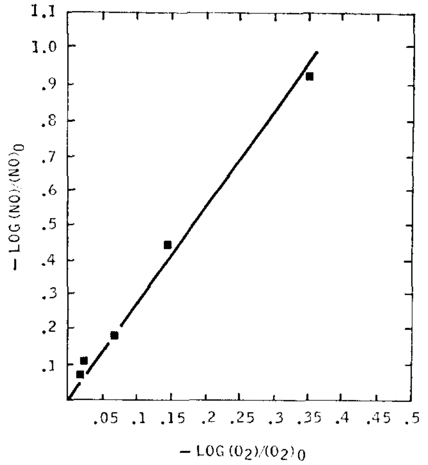

FIG. 1. Partition curve for 0.1% Ir/Al_2O_3. Inlet concentrations: $(NO)_0 = 0.20\%$, $(CO)_0 = 1.00\%$, $(O_2)_0 = 0.74\%$. Partition factor = 2.8.

A partition curve as in Fig. 1 has a definite terminus representing the extinction of CO, after which no further conversion of NO or O_2 can occur. This is a function of the partition factor and the various inlet concentrations. In Fig. 1 this is shown to amount to 90% reduction of NO.

The partition curve for 10 ppm Ir/Al_2O_3 is shown in Fig. 2, Curve a. It is obvious that no straight line can be drawn, but the curve suggests that a uniform displacement applied to the abcissa values would be helpful. Curve b is derived by shifting all points on Curve a leftward by 0.030 log units. The physical interpretation of such a correction is the assumption that a small amount of oxygen (~7%) reacts with CO in the preheater section of the reactor. Indeed, experiments made without any iridium catalyst revealed that small amounts of "blank" CO-oxidation did occur, although it varied somewhat from run to run and proved difficult to eliminate entirely. This could presumably be accomplished, however, with a larger ratio of catalyst to preheater zone.

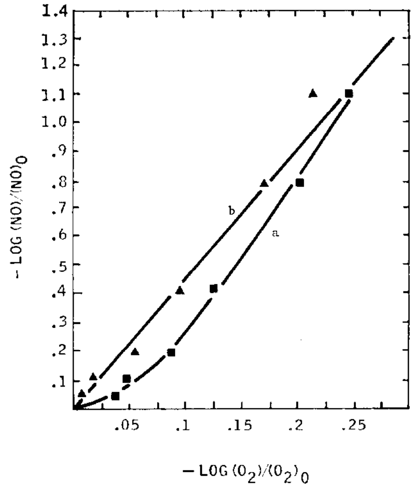

FIG. 2. Partition curve for 0.001% Ir/Al_2O_3. Inlet concentrations: $(NO)_0 = 0.20\%$, $(CO)_0 = 0.97\%$, $(O_2)_0 = 0.75\%$. (a) Uncorrected data; (b) data corrected for assumed preheater reaction of 7% of $(O_2)_0$ (see text). Partition factor, Curve (b) = 4.5.

From Fig. 2, Curve b, a partition factor of 4.5 for 10 ppm Ir/Al_2O_3 is derived. The predicted terminal NO conversion is 96%, and if the above-mentioned degree of preheater CO oxidation is taken into account, this is reduced to 95%. The value actually obtained was 92% and when the temperature was increased by 75°C, this was significantly reduced. Obviously, the assumption made above of an approximately constant amount of preheater CO oxidation is only viable over a limited temperature range.

It may appear surprising that a 10 ppm Ir/Al_2O_3 catalyst achieves about the same degree of NO reduction, operating at the same space velocity, as a catalyst which contains 100 times as much iridium. To explain this, one must consider the fact that the temperature required for a given degree of conversion of any of the reactants—CO, O_2, or NO—is about 100°C higher for the more dilute catalyst. Extinction of CO, for example, occurs at ~400°C for 1000 ppm Ir/Al_2O_3 and at ~500°C for 10 ppm Ir/Al_2O_3. However, regardless of the activity of the catalyst, provided only that this is sufficient, under the given experimental conditions, to bring about complete removal of CO, the NO conversion will depend solely upon the *partitioning* of the CO between O_2 and NO. There is no reason to expect this partitioning to be less favorable for a more dilute catalyst.

This conclusion is, of course, a general one for competitive reaction systems in which a species which is present in stoichiometric deficiency is partitioned between two reactants. Under certain circumstances, however, it may be invalidated. To illustrate with reference to the present case, the 10 ppm Ir/Al_2O_3 catalyst achieves parity with the more concentrated one by operating at a higher temperature at which, due to a greater rate constant for reaction of CO with adsorbed oxygen, its deficiency of iridium is compensated by a greater concentration of free surface sites. If O_2 chemisorption were to require two statistically independent sites, the partition equation would be written

$$\frac{d \ln (\mathrm{NO})}{d \ln (\mathrm{O_2})} = \frac{k_2}{k_3} \cdot \frac{1}{1-\theta}, \tag{6}$$

and such an increase in the concentration of free sites would depress the selectivity for NO reduction. As this is contrary to fact, a value of $n = 1$ in Eq. (3) is supported.

As we have seen, the partition factor for 0.001% Ir/Al_2O_3 is significantly greater than that of 0.1% Ir/Al_2O_3 (4.5 vs 2.8). This may tentatively be ascribed to a difference in iridium crystallite size between the two catalysts. It is conceivable that the properties of ultrasmall crystallites are somewhat altered with respect to larger ones, and the adsorption of oxygen on such crystallites might be affected to a greater degree than that of NO.

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