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The Catalytic Decomposition of Nitric Oxide by Metallic Oxides

II. The Effect of Oxygen

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The effect of O_2 upon the catalytic activity of 40 metallic oxides in the NO-decomposition reaction has been studied by working in a closed reaction system kept wholly above 400°C so as to minimize the formation of NO_2. In confirmation of the mechanism previously proposed it has been shown that in all cases O_2 retards the decomposition of NO by competing for the same surface centers.

INTRODUCTION

In Part I (1) we reported on the catalytic activity of 40 metallic oxides for the decomposition of NO to N_2 and O_2 under conditions where the O_2 was continuously removed as NO_2 by reaction with moist KOH pellets as the gases were circulated around a constant-volume reaction system.

The reaction mechanism proposed was

$$NO_{(gas)} \rightleftharpoons NO_{(ads)}, \qquad (1)$$

$$2NO_{(ads)} \rightarrow N_{2(gas)} + 2O_{(ads)}, \qquad (2)$$

$$2O_{(ads)} \rightleftharpoons O_{2(gas)}, \qquad (3)$$

with, in the cooler parts of the apparatus,

$$O_2 + 2NO \rightleftharpoons 2NO_2. \qquad (4)$$

From these reactions and from the detailed mechanism proposed it would be expected that gaseous O_2 in the neighborhood of the catalyst surface would poison the decomposition reaction because of the competition for sites between reactions (1) and (3), assuming that the same surface sites were involved in the two adsorption equilibria. This was not examined in the earlier paper because of experimental difficulty.

The present investigation, using the same catalysts, was performed in a static reaction system, provided with a capillary leak leading to the ionization region of a mass spectrometer, and the reaction was followed by monitoring mass 30, using argon as an internal standard.

The whole of the reaction system was kept at a minimum of 400°C, which, at the gas pressures employed, ensured that effectively no NO_2 was formed. O_2 thus accumulated in the system and by this means, and by the addition of O_2 during the reaction, the expected retardation by O_2 was demonstrated for all catalysts.

METHOD

a. Materials

The oxide samples and NO were as used in Part I, but the NO was diluted with 10% (v/v) of pure Ar which served as an internal mass-spectrometric standard. O_2 was prepared from $KMnO_4$ and purified by fractionation *in vacuo*.

b. Reaction System

The reaction vessel was of silica (connected by a graded seal to Hysil glass from which the remainder of the system was constructed) and was provided with a capillary leak which led to the ionization region of the mass spectrometer. The sample was pumped, and reactant gases admitted, through a 5 mm bore greaseless tap which operated by means of a Viton A diaphragm (supplied by Messrs. G. Springham & Co. Ltd., Harlow, Essex). The reaction vessel was surrounded by a furnace and the whole of the remainder of the reaction volume, including the Viton tap, was enclosed in a specially constructed oven kept at 400°C during kinetic measurements. An extension tool enabled the tap to be operated during kinetic runs without opening the oven. Thus the reaction system (of ca. 150 ml capacity) was essentially the same as that which we have used extensively in earlier work upon isotopic exchange reactions upon these oxides (*2*, *3*) except for the provision of means to maintain and operate the whole system at elevated temperatures.

c. Kinetic Measurements

The 40 oxides examined were the identical samples used in Part I; they were outgassed for 1 hr at ca. 10^{-5} Torr at the reaction temperature before each experiment: meanwhile the remainder of the system was heated to 400°C. The Viton tap was closed and the required quantity of reactant gas (NO + 10% Ar, with, when required, a known proportion of O_2) was measured out at room temperature in a gas burette and rapidly injected into the reaction system through the Viton tap which was then closed immediately. The reaction was followed by monitoring the change of mass 30 in the mass spectrometer using ^{40}Ar as internal standard. When required, the effect of additional O_2 during the reaction was determined by injecting further measured quantities of O_2. The reaction system was previously calibrated using N_2 and an external manometer under reaction conditions over the range of reaction temperatures employed so that, neglecting any adsorption, the pressures in the system could be calculated from the quantities of gas introduced. Experiments were performed at one temperature only, on each oxide; this temperature was usually towards the lower end of the range studied earlier (cf. Part I, Table 1).

Initial pressures of 20–60 Torr of NO were employed, with, in a number of cases, the introduction of 10–40 Torr of O_2 either at the start of the reaction or at various times during the decomposition of the NO; experiments were usually terminated before 30% of the NO had decomposed.

d. Dissociation of NO_2

The experimental procedure is valid only if the equilibrium of the reaction

$$2NO_2 \rightleftharpoons 2NO + O_2 \qquad (5)$$

lies well to the right at the temperature of the coldest part of the reaction system (ca. 400°C) at the gas pressures employed. If at equilibrium the concentrations of NO_2, NO and O_2 are respectively $(a - x)$, x and $x/2$ g-moles/liter and the total pressure in the system is P atmospheres, writing $y = x/a$ the equilibrium constant, K_p, is given by

$$K_p = \frac{(P_{NO_2})^2}{(P_{NO})^2 P_{O_2}} = \frac{2(1-y)^2(1+y/2)}{Py^3}. \qquad (6)$$

Using published values for ΔG_T for NO and NO_2 (*4*) we find

$$\log_{10} K_p = \frac{13860}{4.574T} - \frac{0.81 \log_{10} T}{1.98} + \frac{0.715 \times 10^{-3}T}{4.574} - \frac{6.35 \times 10^4}{4.574T^{-2}} - \frac{15.90}{4.574}, \qquad (7)$$

from which K_p may be calculated at any temperature. This equation is presumably to be preferred to the older one, due to Bodenstein, used recently by Amirnazmi, Benson and Boudart (*5*). Values of K_p are summarized in Table 1.

Clearly under our experimental conditions, with P_{NO} initially always less than 0.1 atm, and P_{O_2} initially zero or at most ca. 0.05 atm, the partial pressure of NO_2 at ca. 673°K will be negligibly small. No mass 46 was detected in the mass spec-

TABLE 1
DISSOCIATION OF NO_2

T (°K)	K_P	% Dissociation		
	P(atm):	1	0.1	0.01
700	0.604	71.3	88.9	91.3
600	3.104	55.0	77.0	89.5
500	31.7	32.3	60.2	77.0

trometer during the kinetic runs (the instrument being operated under conditions which would reveal the presence of less than 1 part in 1000 of NO_2).

KINETICS

In Part I we assumed that the rate-determining step in the decomposition of NO was the reaction of one molecule with a pair of adjacent surface anion vacancies each containing a trapped electron, a surface R_2 center:

$$(e^-|\square_s^-)_1(e^-|\square_s^-)_2 + NO_{(gas)} \xrightarrow{k_e} (NO^-|\square_s^-)_1 + (e^-|\square_s^-)_2 \quad (8)$$

followed rapidly by the reaction of a second molecule of NO with the surface F-center so formed and then by the reaction of the two neighboring adsorbed NO species:

$$(NO^-{}_1\square_s^-)| + (NO^-|\square_s^-)_2 \rightarrow N_{2(gas)} + (O^-|\square_s^-)_1 + (O^-|\square_s^-)_2. \quad (9)$$

Oxygen retardation was assumed to occur by competition for the R_2-center by means of Eq. (8) and the adsorption–desorption equilibrium of O_2:

$$(O^-|\square_s^-)_1 + (O^-|\square_s^-)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_{2(gas)} + (e^-|\square_s^-)_1(e^-|\square_s^-)_2. \quad (10)$$

If v is the number of R_2-centers, a the number of O^- ion pairs, and N is the total number of active surface "sites," all per square centimeter of surface,

$$N = a + v. \quad (11)$$

At equilibrium we have

$$k_1 a = k_2 v P_{O_2} + k_e v P_{NO} \quad (12)$$

or

$$v = \frac{k_1 a}{k_2 P_{O_2} + k_e P_{NO}}. \quad (13)$$

From Eqs. (11) and (13)

$$v = \frac{N k_1}{k_2 P_{O_2} + k_e P_{NO} + k_1}. \quad (14)$$

Now

$$-\frac{d[NO]}{dt} = k_e A v P_{NO}, \quad (15)$$

where A is the catalyst area (cm^2)

$$= \frac{N k_1 k_e A P_{NO}}{k_2 P_{O_2} + k_e P_{NO} + k_1} \quad (16)$$

or, when $k_2 P_{O_2} \gg k_e P_{NO}$

$$-\frac{d[NO]}{dt} = \frac{k_1 k_e A N P_{NO}}{k_1 + k_2 P_{O_2}}. \quad (17)$$

The derivation of (17) is given in full here because the statement that this equation is only correct when $k_2 P_{O_2} \gg k_e P_{NO}$ was, by an error in transcription, omitted from the printed text of Part I. In fact calculations based on the published kinetic parameters for NO decomposition (*1*) (i.e., effectively $k_e P_{NO}$ at zero P_{O_2}), and isotopic oxygen exchange with the surface (*3*) (i.e., $k_2 P_{O_2}$), show that only in the case of 6 of the oxides is $k_2 P_{O_2} \approx k_e P_{NO}$: these oxides are SrO, Al_2O_3, Rh_2O_3, Ho_2O_3, Tm_2O_3 and Yb_2O_3. In all other cases $k_2 P_{O_2} \gg k_e P_{NO}$. These calculations refer to the middle of the temperature ranges over which the NO decomposition was studied (Part I, Table 1).

We may rewrite Eq. (17) as

$$\frac{P_{NO}}{R} = A' + B P_{O_2}, \quad (18)$$

where A' and B are constants for each oxide at a fixed temperature and reaction volume and R is the rate of disappearance of NO. Equation (18) has been used to test the effect of O_2 upon the reaction.

RESULTS

All the oxides, tested by means of Eq. (18), showed retardation by O_2. Figures 1 and 2 show typical plots for a number of catalysts. It is of interest that, as can be seen for example in the cases of Cr_2O_3, HfO_2, Nd_2O_3, Gd_2O_3 and Sc_2O_3, the retardation initially is often very pronounced and only at P_{O_2} above ca. 2 to 4 Torr is the straight-line relationship of Eq. (18) reasonably satisfactory. This is probably due to the greater susceptibility to poisoning of the most active sites, or to saturation of oxygen-deficient sites produced by outgassing, and indicates, as would be expected for a reaction which can occur at random over the whole catalyst surface, a marked surface heterogeneity. The differ-

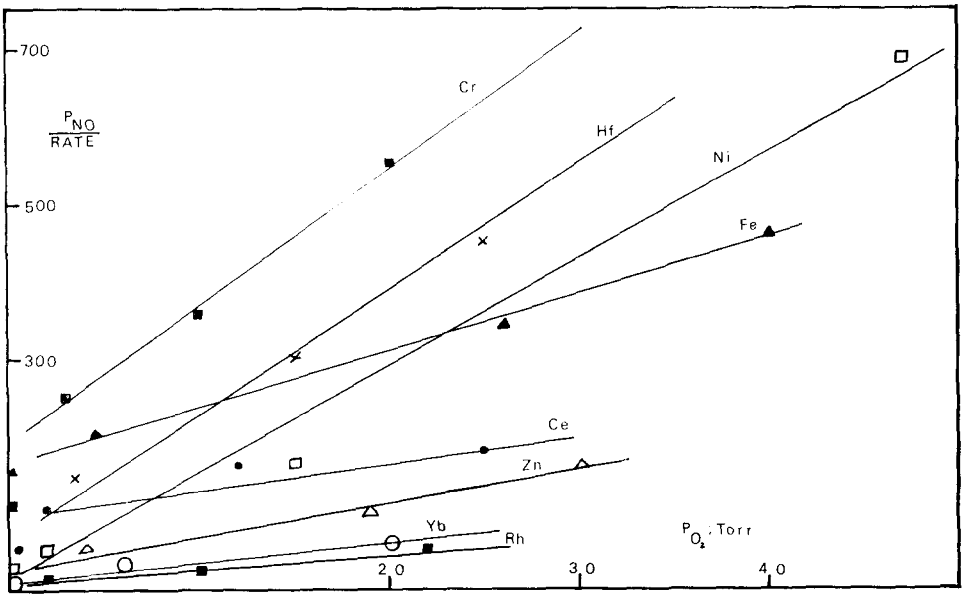

FIG. 1. Effect of added O_2 on the rate of NO decomposition (ordinates in arbitrary units).

ent slopes recorded for the various oxides have no particular significance as they depend upon the temperature chosen for the experiment.

DISCUSSION

The present work was performed at temperatures covered by the data reported in Part I, although the initial pressures of NO were much less than those used earlier (ca. 1/10th), and the retardation by O_2 observed for all oxides provides confirmation of the general correctness of the reaction scheme proposed in Part I. This conclusion is of course reinforced by the other experimental evidence adduced in the

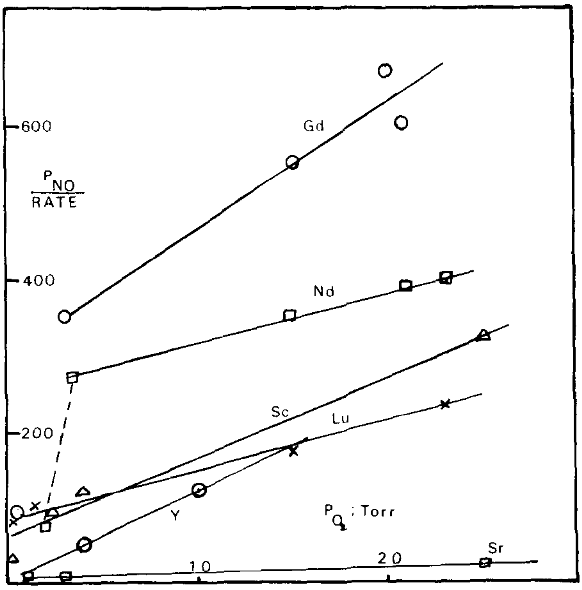

FIG. 2. Effect of added O_2 on the rate of NO decomposition (ordinates in arbitrary units).

earlier paper, namely the first-order dependence upon P_{NO} and the general relationships, predicted by the derived kinetic expressions, with both the N_2O decomposition and the O_2-exchange reaction.

The present series of two papers upon the NO decomposition and the earlier papers (*3*, *6*) upon the N_2O decomposition and isotopic oxygen exchange furnish a satisfactory general correlation, over a wide range of oxides (which includes almost all the simple oxides which are stable compounds under the experimental conditions), between three simple reactions in which a common desorption step, that of O_2, plays an important part. The wide range of the correlations we have demonstrated only exists, in our opinion, because of the close similarity between the decomposing reaction complexes in the two decomposition reactions (*1*) and because all three reactions involve only one, relatively simple, desorption stage. It has also been more readily apparent because of the employment of the same catalyst samples throughout and because of close attention to experimental detail, in particular the preconditioning and outgassing procedures adopted. It is unlikely that other examples of similar range and simplicity will be discovered upon oxide catalysts but from our results we conclude that studies, of more complex reactions, designed to eliminate the influence of crystal structure, i.e., by detailed studies within a series of catalysts of a constant crystal form, will prove of value.

In a similar vein we would comment that past attempts to draw up general correlations of patterns of oxide catalyst activity with particular chemical or physical properties [for example semiconductor type (*7*, *8*) or the oxygen-bonding energy (*9*)] have been of limited use partly because of lack of experimental data but principally because variations of such things as crystal type and metal valency have generally been ignored. Correlations undoubtedly exist but will be most marked (and most instructive) in iso-valent and iso-structural series, if only because many properties vary in a systematic manner therein. Concentration of attention in this manner may help to eliminate extraneous matter and uncover useful basic information on the important factors governing catalytic reactivity in this class of compounds.

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