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# Oxygen Inhibition in the Decomposition of NO on Metal Oxides and Platinum

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The decomposition of NO has been studied in a flow reactor on oxides of iron, cobalt, nickel, copper, and zirconium as well as on supported platinum at 780–960 Torr between 450 and 1000°C. The inlet gas contained from 1.5 to 15% NO and from 0 to 5% $O_2$. The exit gas was analyzed for NO, $N_2$, $O_2$, and $N_2O$. Above 450°C, $N_2$ and $O_2$ were the only products. For all catalysts, the reaction was first order with respect to NO, and $O_2$ had a strong inhibiting effect. From the kinetics, it appears that oxygen inhibition is due to equilibrated chemisorption of oxygen on sites required for the rate-determining process of NO chemisorption.

## INTRODUCTION

Published kinetic data agree on the difficulty of decomposing NO on catalysts

$$NO \rightleftarrows 1/2N_2 + 1/2O_2 \qquad (1$$

in spite of its thermodynamic instability (*1*) but disagree on a number of counts (Table 1). Some authors failed to mention the very important and interesting problem of the influence of oxygen on the rate of decomposition of NO (*2–4*). Other authors have given indications of an inverse dependence of the rate of decomposition upon the pressure of $O_2$ for several catalysts (*5–9*). Among these, Winter has proposed a kinetic expression accounting for the first order with respect to NO; however, his predicted inverse dependence upon the pressure of $O_2$ could not be tested with his experimental setup (*5*). Whereas some studies (*6–8*) purport the decomposition to be retarded by molecularly adsorbed oxygen, another study (*9*) indicates retardation by adsorbed oxygen atoms and further retardation by excess nitrogen in the system. However, no attempt has been made to determine the effect of $O_2$ on the rate, perhaps because of the experimental difficulties, especially the analysis of gas mixtures containing $N_2$, $O_2$, and NO.

It seemed, therefore, desirable to establish and understand the inhibition by oxygen on the rate of NO decomposition. We have also tried to explain the discrepancy in the reaction order with respect to the nitric oxide pressure reported in the literature. Finally, we have compared our rates to those reported by previous investigators.

## EXPERIMENTAL

The purity of the gases was as follows: He 99.995% (Liqiud Carbonic); premixed 10.12% NO in He 99.90% (typical impurities: 400 ppm $N_2$, 200 ppm $N_2O$, 250 ppm $CO_2$, 50 ppm $NO_2$ and less than 50 ppm $H_2O$, Matheson); premixed 10.5% $O_2$ in He 99.94% (impurities: less than 50 ppm $N_2$, Matheson); premixed 0.52% $N_2$ in He 99.995% (Matheson); and $H_2$ 99.93% (Liquid Carbonic). All hydrogen was purified by diffusion through a palladium membrane purifier manufactured by the Milton Roy Company.

The decomposition of NO was studied in a flow reactor at a total pressure of 780–960 Torr. Helium was used to dilute the NO and $O_2$ fed to the reactor. Streams of pure He, 10.12% NO in He and 10.5% $O_2$ in He were passed separately through

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TABLE 1
SUMMARY OF SOME PREVIOUS NO DECOMPOSITION STUDIES

| Authors | Catalyst | Reactor | Gas mixture | Temperature range, °C | Pressure, Torr | Reaction order with respect to NO | Reference |
|---|---|---|---|---|---|---|---|
| Fraser and Daniels | Metal oxides | Flow | 10% NO in He | 740–1040 | 760 | 0 | (*2*) |
| Yur'eva *et al.* | Transition metal oxides | Recycle | 100% NO | 250–750 | 100–380 | 2 | (*3*) |
| Shelef *et al.* | Supported Pt and oxides | Flow | 4–100% NO in He | 279–938 | 760 | ~1 | (*4*) |
| Winter | Oxides | Recycle | 100% NO | 330–870 | 50–400 | 1 | (*5*) |
| Bachman and Taylor | Pt wire | Batch | 100% NO | 1210 | 201–479 | 2 | (*6*) |
| Zawadski and Perlinsky | Pt-Rh wire | Batch | 100% NO | 860–1060 | 100 | 1 | (*7*) |
| Green and Hinshelwood | Pt wire | Batch | 100% NO | 882–1450 | 200–500 | 1 | (*8*) |
| Sakaida *et al.* | Supported Pt-Ni | Flow | 0.404 and 0.432% NO in $N_2$ | 427–538 | 1–15 atm | 2 | (*9*) |

flowmeters which were calibrated at a pressure of 200 Torr above atmospheric pressure at the downstream point. This pressure was maintained in most of the work. After the gas streams were metered, they were combined and passed through a glass tube filled with glass beads to mix the components of the reaction mixture. As a check of adequate mixing, the reaction mixtures at the inlet of the reactor were analyzed by gas chromatography, and these analyses showed that adequate mixing had been accomplished. The pressure drop in the reactor was measured with a manometer filled with mercury which was covered with Dow-Corning 200 silicone oil. The silicone oil was added to prevent the reaction of mercury with $NO_2$ formed.

The catalysts were confined in a quartz tube of 20 mm i. d. and supported by a quartz disc. The reactor, 160 mm in length, was preceded by a preheated zone which consisted of a 1.5 m quartz spiral. The reactor zone, 50–120 mm long, contained catalyst samples diluted with quartz chips and was heated by an electrical furnace. A chromel–alumel thermocouple covered with a ceramic shield was placed in a quartz well. This thermocouple, which was placed at the center of the reaction zone inside the reactor, could be raised or lowered along this zone. The desired temperature was maintained by an electronic controller.

To outgas the catalysts, the reactor was connected to a vacuum system consisting of a mercury diffusion pump backed by a mechanical pump and isolated from the reaction apparatus by a liquid nitrogen trap. The reactor was further protected from mercury vapor by means of a small trap filled with gold powder held in place by a minimum amount of Pyrex glass wool which had been boiled in concentrated nitric acid to remove oils. A vacuum of better than $10^{-5}$ Torr could be obtained.

The gases were analyzed before and after passing the catalyst by a gas chromatograph (Aerograph 1520) which was attached to the flow system, and the gas mixtures were sampled with two sampling valves. Our studies required the analysis of a mixture of NO, $O_2$, $N_2$, and $N_2O$.

The chromatographic column packing for the separation of oxides of nitrogen and air has typically been molecular sieve and microporous polymer packing (*10*). There are some major problems in the analysis of NO–$O_2$–$N_2$ mixtures: oxidation of NO in the porous solid phase (molecular sieve), the disproportionation of NO in the presence of $O_2$ on the molecular sieve to form $NO_2$ and $N_2O$ (*11*), reaction of NO and $O_2$ in gas phase to form $NO_2$, and extreme tailing of the NO peak which makes quantitative evaluation difficult.

In the experiments in which oxygen content was below 3.0%, we used a ¼-inch o. d. stainless steel column, of which 2 feet were filled with Porapak Q(100–120 mesh) and 6 feet with Linde molecular sieve 5A(50–100 mesh). A thermal conductivity detector with helium as carrier gas was used. The detector was operated at 120°C and a bridge current of 230 mA. The Porapak Q portion, which was located in the front portion of the column, helped us to solve partially the first two problems described above. The Porapak Q portion partly separated NO from other components of the gas mixture; hence, the reaction of NO and $O_2$ on the molecular sieve column was partially avoided. To avoid the gas phase reaction of NO with $O_2$, the helium flow rate was kept relatively high (50 $cm^3$/min), and the column temperature during the analysis was 65°C.

To overcome the fourth difficulty, the tailing of the NO peak, and to avoid the NO and $O_2$ reaction on the molecular sieve, the column was pretreated to saturate it with $NO_2$ by a variation of a technique described by Dietz (*12*). The column was evacuated at 250°C for 24 hr to remove water and activate the column. Then helium was introduced to eliminate any possibility of localized heating from NO adsorption. The column temperature was raised to 300°C, and NO was introduced into the column at the rate of 20 $cm^3$/min in order to saturate the column with NO. To prevent premature formation of adsorbed $NO_2$, it was necessary to have the column at 300°C. The saturation time for NO was about three hours. The temperature was lowered to 25°C while maintaining the NO flow rate for two hours. Then excess NO was removed by flushing briefly with helium, and $O_2$ was introduced at 20 $cm^3$/min for two hours, the column temperature being kept at 25°C. The oxygen possibly converted the adsorbed NO into more tightly held $NO_2$. With this pretreatment the $O_2$–$N_2$–NO separation was satisfactory with retention times of about 6.0, 8.5, and 11.5 min, respectively. As a check of the separation, a gas mixture was made containing 4.90% NO, 0.20% $N_2$, 1.10% $O_2$ with the balance consisting of helium and was passed through the empty reactor at 600°C to decompose any $NO_2$ formed; the analysis of the mixture showed 4.82% NO, 0.20% $N_2$, and 1.04% $O_2$ with no detectable $NO_2$. The amount of $N_2$ in the mixture, on which further calculations were based, could be determined to about ±2%. The tightly bound $NO_2$ molecules are believed to prevent further disproportionation and oxidation of the NO during the separation process.

In the experiments in which oxygen content was above 3.0%, the same column was used, but the helium flow rate and column temperature were suitably decreased to improve the separation of $N_2$ and $O_2$. Although under these conditions NO–$O_2$ reactions may have occurred on the chromatographic column, these reactions did not interfere with the analysis since the calculation of the rates was based on analysis for nitrogen alone. Furthermore, the oxygen formed by NO decomposition was superimposed on the large oxygen peak and in some cases could not be measured.

A second column, 6 feet by ¼ inch o. d. stainless steel tubing packed with Porapak Q(80–100 mesh), was used to separate $N_2O$ from the rest of the gas mixture. This column was maintained at 65°C.

The catalysts used were unsupported $Fe_2O_3$, $Co_3O_4$, NiO, CuO, $ZrO_2$–$Sc_2O_3$, $ZrO_2$–CaO, transitional $Al_2O_3$, and platinum supported on $\gamma$-$Al_2O_3$ (Pt/$Al_2O_3$). Reagent grade $Co_3O_4$, $Fe_2O_3$, NiO, and CuO were obtained from Baker Chemical Co. Other samples of NiO and CuO were prepared by dehydration of pure nickel and copper hydroxides under vacuum

($10^{-5}$ Torr) at 750°C. The hydroxides themselves were prepared from aqueous solutions of the nitrates by the method described by Merlin and Teichner (*13*). Reagent grade $Ni(NO_3)_2$ and $Cu(NO_3)_2$ were obtained from Baker and Adamson Corp. Zirconium oxide stabilized with 8 wt % $Sc_2O_3$ and $ZrO_2$ stabilized with 10 wt % CaO were provided by Electrochemistry Inc. Transitional $Al_2O_3$ was supplied by Kaiser Chemicals. A 0.6 wt % Pt/$\gamma$-$Al_2O_3$ catalyst was obtained from Cyanamid-Ketjen N. V.

Surface areas of the catalysts before and after use were determined according to the $N_2$ BET method. The platinum surface of the supported platinum catalysts was measured by the method of Benson and Boudart (*14*). The dispersion, D, defined as the ratio of the number of surface platinum atoms to the total number of platinum atoms, was converted to average particle size as in Ref. (*14*). The platinum surface decreased by a factor of 19.5 while the catalyst was heated to 720°C for 12 hr under an oxygen atmosphere.

The catalysts were subjected to X-ray line broadening studies. A sample of the catalyst powder was pressed into a depression in a glass slide and placed in a Picker diffractometer. Copper $K\alpha$ radiation, filtered by 10 $\mu$ nickel, was introduced through a 1° beam slit, a 4° Soller slit, a 0.2° receiving slit and a 4° Soller slit, and the counting rate was recorded as a function of scanning angle.

All reactions were carried out at or above 450°C where any nitrogen dioxide formed from the gas phase reaction of NO and $O_2$ in the cool parts of the system before entering the preheater would be decomposed almost completely to nitric oxide and oxygen in the preheater coil. The composition of the gas mixture before entering the reactor was checked by gas chromatography, and no NO disappearance could be detected at this point.

The equilibrium constant $K_p$ (atm) for the reaction:

$$2NO_2 \rightleftarrows 2NO + O_2 \qquad (2)$$

is given by the expression (*15*):

$$\log_{10} K_p = (-5749/T) + 1.7 \log_{10} T - 0.0005T + 2.839, \qquad (3)$$

where $T$ is the temperature in K. Using (3) and assuming an initial concentration of 5% for both NO and $O_2$ in He at a total pressure of 960 Torr, we calculated the equilibrium composition of the gas mixture at 600 and 700°C. The $NO_2$ content of the gas mixture at equilibrium was calculated to be 0.43% and 0.20% at 600 and 700°C, respectively, which are small compared to the NO concentration of 5%. This calculation agrees with the experimental evidence concerning the undetectable amount of NO reacted in the gas phase.

The oxide catalysts were first outgassed ($10^{-5}$ Torr) at 20 K above the highest temperature to be studied for 24 hr to remove water, cooled to the first reaction temperature and left in contact with a flow of oxygen for 12 hr to remove possible impurities (mainly carbon) and to stabilize the catalysts. The catalysts were then cooled to below 200°C and flushed with a flow of helium for 30 min to clean the system of oxygen before the reactants were introduced into the reactor. The temperature of the reactor was then raised to the desired value. Following a series of runs, catalysts were checked for any change that might have occurred by returning to flow condition used in an earlier run. The activity for all of the catalysts except for $Co_3O_4$ at 700°C dropped by a factor of less than 10% during the first 2–8 hr of experiments. The special case of $Co_3O_4$ will be discussed later. After this time no further change was noticed, and all kinetic data were taken during the period of constant activity.

The supported platinum catalyst was first reduced at 425°C in hydrogen for 10 hr and left in contact with a flow of oxygen for 2 hr at 600°C (for $D = 0.34$) and 12 hr at 720°C (for $D = 0.037$), respectively. The catalysts were then cooled to reaction temperature and reactants were introduced into the reactor. The platinum surface of the supported platinum catalysts did not change during the experiments.

In order to study the possible direct chemical reaction of NO with some of the catalyst surfaces the standard pretreatment described above was changed; the stabilization in oxygen was omitted.

The rate of reaction $r$ for the stoichiometric Eq. (1), characterized by its extent of reaction $\xi$ (mol), is defined in molecular units as:

$$r = \frac{N}{A} \cdot \frac{d\xi}{dt} \qquad (4)$$

where $r$ is expressed in $\mathrm{cm^{-2}sec^{-1}}$, $A$ is the surface area of the catalyst and $N$ is Avogadro's number (*16*).

In our differential flow reactor, $r$ is obtained directly, as for a well stirred reactor, by the relation:

$$r = (N/A)2\bar{n}(x_f - x_i) \qquad (5)$$

where $\bar{n}$ is the total molar flow rate (mol $\mathrm{s^{-1}}$) and $x_f$ and $x_i$ are the mole fractions of either $N_2$ or $O_2$ at exit and at entrance of the reactor, respectively.

In the calculation of the rate for $Pt/Al_2O_3$ only the surface area of the platinum metal was used; the support contributed about a maximum of 4% to the total NO decomposition as determined by blank runs on a similar alumina. The rates were corrected for this support contribution.

## RESULTS

### *Kinetics*

Preliminary runs were made at 600°C on the $Co_3O_4$ catalyst to determine the effect of the concentration of $O_2$ on the rate of decomposition of NO. The decomposition rate decreased by a factor of about 4 when 5.2% $O_2$ was present in the feed. Such strong inhibition ruled out the normal procedure of arriving at the kinetics, namely, varying the partial pressure of NO in the feed; the inhibiting effect of the oxygen produced by the reaction did not allow the differential reactor concept to be employed for the catalysts with high activity. Consequently, the dependence of the reaction rate upon the pressure of oxygen was first determined for all the catalysts except transitional $Al_2O_3$ at a total pressure of 780–960 Torr and temperatures from 450 to 1000°C by varying the amount of oxygen in the feed at constant NO pressure. The results indicated a linear dependence of the inverse rate on oxygen pressure. Plots of the data in this form at approximately constant NO concentration (5%) for $Co_3O_4$ and $Pt/Al_2O_3$ ($D = 0.037$) at 600°C are shown in Fig. 1. However, plots of reciprocal rate vs square root of oxygen concentration did not fit the data at all. Extrapolated values of the rates of NO decomposition at 0% $O_2$ were obtained from Fig. 1 and similar plots for the other catalysts (*17*). In all of the experiments, the nitric oxide fractional conversion was kept below 10%; therefore, the contribution of the oxygen formed to the total oxygen concentration was negligible.

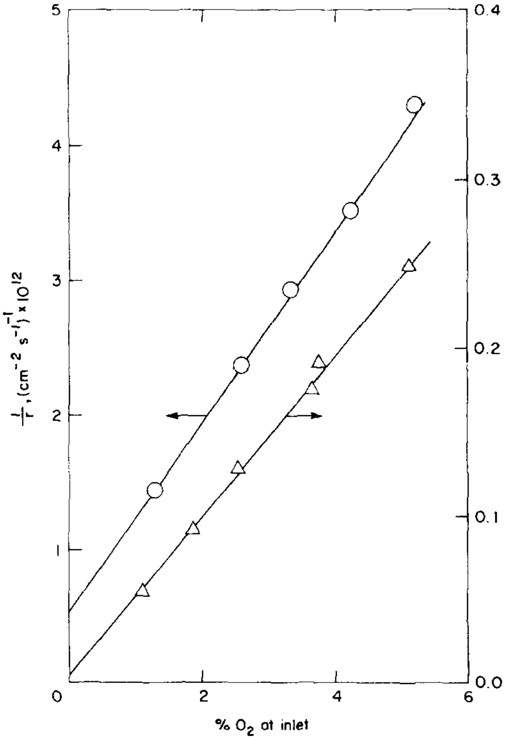

FIG. 1. Effect of Oxygen on the rate of decomposition of NO. % NO at inlet ≈ 5; ○, $Co_3O_4$ (600°C); △, $Pt/Al_2O_3$ (D = 0.037, 600°C).

The extrapolated values of rates of NO decomposition at zero $O_2$ concentration [Fig. 1 and similar figures in Ref. (*17*)] were obtained for several NO concentrations, and the slope of the line obtained by plotting these rates vs nitric oxide concentration gave the order of the reaction. Four sets of data for the determination of the reaction order are shown in Fig. 2 for NiO, $ZrO_2$–$Sc_2O_3$, CuO and $Co_3O_4$. The dependence of the reaction rate upon the initial concentration of NO was determined for all the catalysts, and in each case the reaction order with respect to NO concentration was 1.0 ± 0.1.

After inspection of Figs. 1 and 2, and similar plots which are shown elsewhere (*17*), it was concluded that the rate $r$ could be adequately represented by the expression

$$r = N\,k(\mathrm{NO})/1 + \alpha K(\mathrm{O_2}) \tag{6}$$

where $r$ is the NO decomposition rate from Eq. (5) in $cm^{-2}sec^{-1}$, (NO) and ($O_2$) are molar concentration of NO and $O_2$ in mole $cm^{-3}$, $k$ is a reaction rate constant in cm $sec^{-1}$, $K$ is an adsorption equilibrium constant in $atm^{-1}$, and $\alpha$ is a conversion factor in atm $mole^{-1}cm^3$. It must be noted that values of $K$ did not depend on NO concentration when the latter was varied as described above.

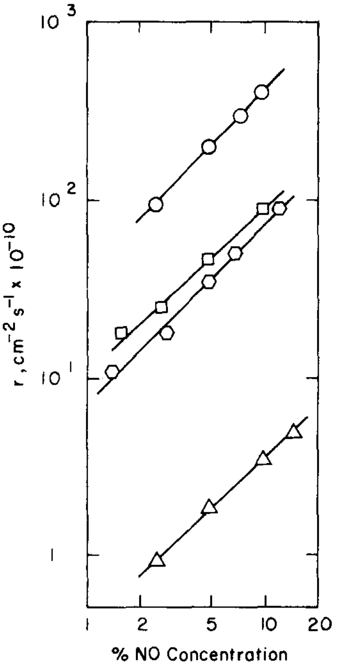

FIG. 2. Effect of NO on its initial rate of decomposition. ○, $Co_3O_4$ (600°C, 960 Torr); □, CuO (*600°C, 960 Torr*); △, NiO (700°C, 780 Torr); ⬡, $ZrO_2$ (900°C, 960 Torr).

The values of $k$ and $K$ obtained from Fig. 1 and similar plots for the other catalysts at various inlet concentrations of NO are given in Table 2. Values are listed for two cobalt oxide samples; one was treated in NO at 600°C, and the other was treated in NO at 700°C and had lost part of its activity. The reaction rate constants (at 700°C) are shown in decreasing order. The values of $k$ and $K$ for $ZrO_2$ are listed at 900 and 1000°C, as we could not determine the fractional conversion of NO at 700°C due to the very small surface area of $ZrO_2$.

Arrhenius and van't Hoff plots, shown in Fig. 3, were prepared from the values of $k$ and $K$ for $Co_3O_4$ at 450, 500, 550, and 600°C and for $Pt/Al_2O_3$ ($D$ = 0.037) at 600, 650, and 700°C. The rate and ad-

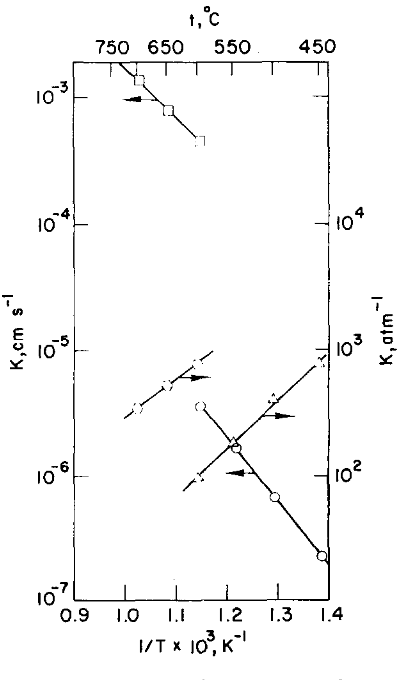

FIG. 3. Temperature dependence of rate and adsorption parameters. ○△, $Co_3O_4$; □⬡, $Pt/Al_2O_3$ ($D$ = 0.037).

sorption constants can be written as:

$$k = A\exp(-E/RT) \quad (7)$$

$$K = \exp(\Delta S^\circ/R)\exp(-\Delta H^\circ/RT) \quad (8)$$

where $A$ is the pre-exponential factor of the rate constant in cm $s^{-1}$, $E$ is the activation energy in kcal $mole^{-1}$, $\Delta S^\circ$ is the standard entropy of adsorption in cal $mole^{-1}K^{-1}$, and $\Delta H^\circ$ is the standard enthalpy of adsorption in kcal $mole^{-1}$. We obtained the values of $A$, $E$, $\Delta H^\circ$, and $\Delta S^\circ$ from the plots of Fig. 3 and the results in Table 2. These values together with the values for CuO and the apparent activation energy for $Co_3O_4$ which had been heated to 700°C in NO are listed in Table 3.

The different methods of preparing the copper oxide and nickel oxide catalysts (one sample was calcined in vacuum at 750°C, the other in air at 800°C) caused only small changes in their performance under stationary state conditions. Zirconium oxides stabilized with scandium oxide or calcium oxide were almost indistinguishable for the decomposition of nitric oxide.

A significant reduction in platinum surface area occurred on $Pt/Al_2O_3$ as a result of carrying out the reaction at 720°C for varying periods of time. Crystal growth was verified by taking electron micrographs on catalyst samples. On heating the catalyst in oxygen under conditions known

TABLE 2

Rate and Adsorption Equilibrium Constants $k$(cm $sec^{-1}$) and $K$($atm^{-1}$)

| Catalyst | % NO in feed | $k$ | | $K$ | |
|---|---|---|---|---|---|
| | | 600°C | 700°C | 600°C | 700°C |
| $Pt/Al_2O_3$ | 1.3 | $4.3 \times 10^{-4}$ | $1.5 \times 10^{-3}$ | $7.6 \times 10^{2}$ | $3.6 \times 10^{2}$ |
| | 2.5 | 4.3 | 1.5 | 7.6 | 3.6 |
| | 5.0 | 4.4 | 1.4 | 7.6 | 3.5 |
| | 7.5 | 4.4 | 1.5 | 7.7 | 3.7 |
| $Co_3O_4$ [a] | 2.5 | $3.6 \times 10^{-8}$ | | $1.0 \times 10^{2}$ | |
| | 5.0 | 3.6 | | 1.0 | |
| | 7.5 | 3.7 | | 1.0 | |
| | 10 | 3.7 | | 1.0 | |
| $Co_3O_4$ [b] | 5.0 | | $1.2 \times 10^{-6}$ | | $0.9 \times 10^{2}$ |
| CuO | 1.6 | $8.4 \times 10^{-8}$ | | $2.3 \times 10^{2}$ | |
| | 2.5 | 8.6 | $1.4 \times 10^{-6}$ | 2.4 | $1.3 \times 10^{2}$ |
| | 5.0 | 8.6 | 1.4 | 2.4 | 1.3 |
| | 10 | 8.8 | | 2.5 | |
| NiO | 2.5 | | $4.5 \times 10^{-8}$ | | $1.0 \times 10^{2}$ |
| | 5.0 | | 4.7 | | 1.1 |
| | 10 | | 5.1 | | 1.1 |
| | 15 | | 4.9 | | 1.2 |
| $Fe_2O_3$ | 2.5 | | $2.9 \times 10^{-8}$ | | $0.6 \times 10^{2}$ |
| | 5.0 | | 3.1 | | 0.6 |
| | 10 | | 3.2 | | 0.7 |
| | 15 | | 3.3 | | 0.7 |
| | | 900°C | 1000°C | 900°C | 1000°C |
| $ZrO_2$ | 1.4 | $1.0 \times 10^{-6}$ | $2.8 \times 10^{-6}$ | | |
| | 2.9 | 1.0 | | ~0.7 | |
| | 5.0 | 0.9 | 2.5 | | ~0.1 |
| | 7.1 | 0.9 | | ~0.7 | |
| | 12.5 | 0.9 | 2.6 | | |

[a] Heated to 600°C in NO.

[b] Heated to 700°C in NO.

TABLE 3

PARAMETERS OF RATE AND ADSORPTION EQUILIBRIUM CONSTANTS

| Catalyst | $A$, cm sec$^{-1}$ | $E$, kcal mole$^{-1}$ | $-\Delta H°$, kcal mole$^{-1}$ | $-\Delta S°$, cal mole$^{-1}$ K$^{-1}$ | $E - \Delta H°$, kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| $Pt/Al_2O_3$ | 19 | 18.4 | 14.0 | 2.85 | 32.4 |
| $Co_3O_4$ [a] | 1.6 | 22.5 | 17.4 | 10.8 | 39.9 |
| $Co_3O_4$ [b] | | 11.1 | | | |
| CuO | $10^{-4}$ | 8.2 | 10.3 | 1.0 | 18.5 |
| $Co_3O_4$ [c] | | 28.3 | | | |
| $Co_3O_4$ [d] | | 29.0 | | | |
| $Pt/Al_2O_3$ [c] | | 20.1 | | | |

[a] Heated to 600°C in NO.
[b] Heated to 700°C in NO.
[c] Shelef *et al.* (*4*).
[d] Yur'eva *et al.* (*3*).

to promote growth of the platinum crystallites, there was no noticeable effect on the initial rate of nitric oxide decomposition. Two samples of $Pt/Al_2O_3$ catalysts, sintered at 600°C and 720°C, respectively, were examined. The supported platinum dispersions were 0.39 and 0.037 which correspond approximately to 27 and 280 Å platinum crystallite size, respectively.

Figure 4 is a plot of the turnover number for NO decomposition (molecules reacting per second per surface metal atom) extrapolated to zero oxygen pressure vs 1/T at 5% initial nitric oxide concentration. The values of the turnover at 600°C were 0.18 and 0.17 sec$^{-1}$ for the $Pt/Al_2O_3$ catalysts with dispersion of 0.037 and 0.39, respectively. The absence of any significant change in turnover number as the amount of surface metal was increased tenfold is a convincing test of the lack of influence of pore diffusion under these conditions (*18*). As platinum was the most active catalyst for the decomposition of NO and supported platinum catalysts were by far the ones with the smallest pores, it

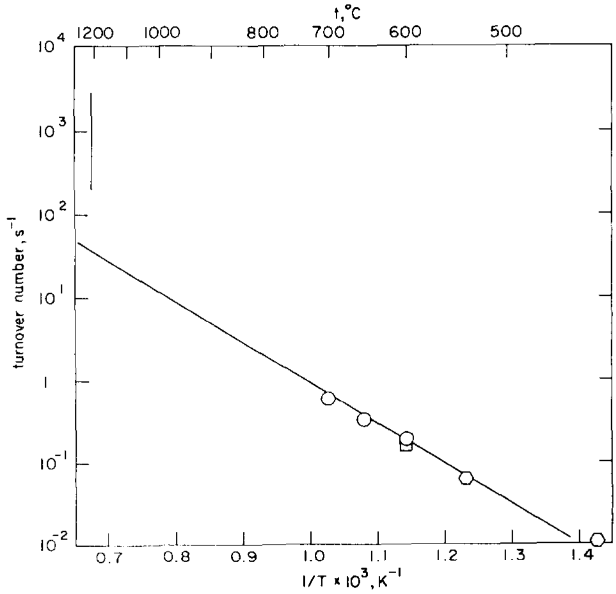

FIG. 4. Activity of Pt catalysts. O, D = 0.037; □, D = 0.39; ⬡, Sakaida *et al.* (*9*); |, Bachman and Taylor (*6*).

is conservative to assume that rates on the other catalysts were not influenced by mass transport.

### *Nonstationary State Condition of the Catalysts*

In those experiments where we studied the possible direct chemical reaction of NO with the catalyst $Co_3O_4$, CuO, and $Fe_2O_3$ were outgassed ($10^{-5}$ Torr) at 600, 600, and 700°C, respectively. Upon contacting these catalysts with 10.12% NO in helium, chromatographic analysis of the products indicated a deficiency of oxygen in the gas phase. The reoxidation of the catalysts by NO resulted in an additional disappearance of NO as indicated by high conversions compared to the stationary state conversion. For cobalt oxide, the ratio of the initial conversion of NO to the stationary state conversion of NO was about 15, a higher ratio than for the other oxides. The reoxidation time was less than 10 min for $Co_3O_4$, CuO, and $Fe_2O_3$. The concentration of oxygen at the exit of the reactor was almost the same as under stationary state condition of the catalysts.

Because cobalt oxide showed unusually high activity at 600°C, an experiment was performed to determine its activity at 700°C. After determination of the rate of decomposition of NO at 600°C, the temperature was raised to 700°C in flowing reactant gas (5% NO in He). The catalyst yielded a stationary state NO conversion of 6.2% compared to an initial NO conversion of 55%. An X-ray diagram of this sample indicated two phases, CoO and $Co_3O_4$.

## DISCUSSION

The kinetic data were found to obey Eq. (6), which can be obtained as explained elsewhere (*19*) by postulating only two elementary processes:

$$NO + * \rightarrow NO* \qquad (I)$$

$$O_s + O* \leftrightarrow O_2 + * \qquad (II)$$

with the assumptions that the adsorption of NO on a site * is the rate-determining process (I) with rate constant $k$ and that among all adsorbed species, O* is the most abundant with a concentration determined by the equilibrium (II) with a constant $K$. By $O_s$ we denote surface mobile oxygen.

To be physically meaningful, the parameters of Table 3 must satisfy certain conditions: $A < 10^4$ cm sec$^{-1}$, $-\Delta H° > 0$ and $0 < -\Delta S° < S_g°$ where $S_g°$ is the standard entropy of $O_{2(g)}$ (at 1 atm) (*19*). These conditions being satisfied, the constants $k$ and $K$ can be used with some degree of confidence to compare the catalytic behavior of various samples.

From the values of these constants at 700°C (Table 2), it appears that the difference in activity among various catalysts is caused by a variation of the rate constant $k$ (by $5 \times 10^4$) rather than by a change in the equilibrium constant $K$ (by about 6). Besides, there does not seem to be any correlation between variations of $k$ and $K$ for all the catalysts although it is clear that both $k$ and $K$ are large for Pt (the most active catalyst by far) and small for all the oxides listed. This is typical of a Brønsted–Polanyi relation (*16*), and it might be interesting to examine its validity in further work on the decomposition of NO.

Heating $Co_3O_4$, CuO, and $Fe_2O_3$ in vacuum at high temperatures caused partial reduction of the oxides and at the same time the formation of more active catalysts. Shelef *et al.* (*4*) found a similar phenomenon for the NO decomposition on reduced $Co_3O_4$. These observations can be understood by the following arguments.

During the NO decomposition in the presence of an excess of $O_2$ on metal oxides, one must extend the quasi-equilibrium reaction (II) to the bulk

$$O* \leftrightarrow O_B \qquad (III)$$

where $O_B$ denotes bulk oxygen in the lattice.

When the decomposition of NO is carried out on the oxygen deficient oxides, reaction (III) proceeds to the right until equilibrium is reached, but the quasi-equilibrium reaction (II) is not disturbed as shown by the approximate equality of the oxygen production under nonstationary and stationary state conditions of the catalysts. Therefore, during an induction period the total rate of NO decomposition is higher until it reaches the stationary value. After this induction period, reaction (III) is in equilibrium, and the rate of decomposition of NO is due to process (I) alone.

We shall now compare our data to those of others, first for the oxide catalysts, then for platinum. For the oxides, Table 4 gives our experimental results and the extrapolated rates of other authors. The rates are expressed as turnover numbers ($sec^{-1}$) at 48 Torr initial pressure of NO. Extrapolation of the available data to zero concentration of $O_2$ could not be done for the work of some authors. To obtain extrapolated rates in each case, we have used published kinetic parameters and rate expressions, as reported by individual authors. In the calculation of the turnover numbers, it was arbitrarily assumed that there were $10^{15}$ sites/cm$^2$. The extrapolated decomposition rates were generally higher for Yur'eva *et al.* (*3*) and Winter (*5*) than for us. This discrepancy in the rates of NO decomposition could be partly due to the nonstationary state phenomenon which was discussed earlier as these authors were unable to monitor the appearance of $O_2$. Thus the question can be raised whether stationary state was reached in their experimental work.

By contrast, the extrapolated decomposition rate of NO on $Co_3O_4$ according to Shelef *et al.* (*4*) appeared at first lower than our experimental result. The Arrhenius plot of Shelef *et al.* for the unsupported cobalt oxide showed a definite curvature, which we ascribe to oxygen inhibition at high conversion. Therefore, a second attempt was made to calculate the extrapolated rate from the data of Shelef *et al.* by using our rate expression (6), our kinetic parameters and zero concentration of oxygen, and by taking into account the curvature of the Arrhenius plot. This time the turnover number, $2.9 \times 10^{-3}$ $sec^{-1}$, was in good agreement with ours. One important point to note from Table 3 is that the apparent activation energies for $Co_3O_4$ reported by Shelef *et al.* (*4*) and Yur'eva *et al.* (*3*) lie between our true activation energy and the total maximum apparent activation energy of the overall reaction, $E - \Delta H°$, as expected from the expression (6) for large inhibition by oxygen.

Let us now discuss results on platinum catalysts. The two platinum catalysts, Pt/$Al_2O_3$ ($D = 0.037$), Pt/$Al_2O_3$ ($D = 0.39$) showed good activity compared to the metallic oxides (Table 2). A comparison between rates, expressed as turnover numbers, obtained from the experiments employing different types of reactors, wide temperature and pressure ranges and different metal crystallite sizes can yield useful information. We calculated the initial nitric oxide decomposition rate of Bachman and Taylor (*6*) at 342 Torr and 1210°C, and the calculated rate was then extrapolated to 48 Torr initial nitric oxide pressure by using their proposed rate expression. The result of this calculation is

TABLE 4

DECOMPOSITION OF NO ON METALLIC OXIDES: TURNOVER NUMBER, N $sec^{-1}$ AT 48 TORR NO AND INITIAL CONDITION WITHOUT $O_2$

| | 700°C | | | | 600°C | 900°C |
|---|---|---|---|---|---|---|
| Author | $CuO$<br>$N \times 10^4$ | $NiO$<br>$N \times 10^5$ | $Fe_2O_3$<br>$N \times 10^5$ | $Al_2O_3$<br>$N \times 10^6$ | $Co_3O_4$<br>$N \times 10^3$ | $ZrO_2$<br>$N \times 10^4$ |
| This work | 6.6 | 2.2 | 1.5 | 5.5 | 1.9 | 3.5 |
| Yur'eva *et al.* (*4*) | 0.9 | 53 | 59 | | 48 | |
| Winter (*5*) | 15 | 700 | 6.5 | 170 | | |
| Shelef *et al.* (*4*) | | | | 0.5 | 2.9 | |
| Fraser and Daniels (*2*) | | | | 57 | | 2.0 |

shown in Fig. 4 as a line due to the uncertainties involved in the calculation. Their extrapolated result lies above the line predicted by our rate expression (6). Although their experimental setup and analysis of the results are somewhat questionable, all uncertainties should have resulted in obtaining smaller values of the reaction rate than predicted by us. Platinum metal in an atmosphere containing oxygen is normally covered by an oxide layer. At the high temperature of 1210°C, employed by Bachman and Taylor (*6*), this layer is thermodynamically unstable (*20*). Thus, it is tempting to ascribe the high activity of platinum at 1210°C to the absence of the surface oxide covering the metal at lower temperatures.

In the case of Shelef *et al.* (*4*), no comparison between their data on supported Pt and ours can be made because they do not give a value for the surface area of the metal after using the catalyst and because of the presence of an unknown amount of inhibiting oxygen in their reactor.

Sakaida *et al.* (*9*) studied the decomposition of NO in an integral reactor on a 0.1% Pt/$Al_2O_3$ catalyst containing also 3.0% Ni. Their initial rates at 1 atm, extrapolated to our experimental conditions by using the rate expression (6) and assuming a reasonable platinum dispersion of 50%, are shown in Fig. 4. The agreement with our results is good. Neglecting any contribution of nickel to the rate of decomposition of NO is justified since nickel oxide is much less active than platinum (Table 2).

## CONCLUSION

Not too much significance should be attached to some of the individual values of the apparent activation energies and reaction orders with respect to nitric oxide pressure reported in the literature. It must be remembered that reaction orders and activation energies frequently have been obscured by the inhibiting effect of oxygen and/or nonstationary state phenomena. The main result of this work was to demonstrate the oxygen inhibition quantitatively. The nature of the sites will be discussed in a future publication, together with the mechanism of the reaction, including the elementary steps which need not be considered in the two-step sequence required to describe the kinetics.

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