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Decomposition of Nitric Oxide on Platinum

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The catalytic decomposition of NO on platinum has been studied in a flow reactor. When O_2 was added to the feed an oxidized surface was attained and all rate data on supported and unsupported catalysts gave a single Arrhenius line between 600 and 1050°C. By contrast, when O_2 was not added to the feed, a pre-reduced platinum foil gave higher rates than those found on an oxidized surface. The higher rates decayed slowly to the lower rates after addition of oxygen to the feed. The less active oxidized surface contains two oxygen atoms per platinum atom and is produced by a slow rearrangement of the unoxidized surface in the presence of a sufficient amount of oxygen at high temperatures.

INTRODUCTION

A summary of previous NO decomposition studies on platinum catalysts is shown in Table 1. The first wave of studies between 1923 and 1934 dealt with pure NO decomposing on platinum wires at very high temperatures in a static system (*1–3*). Later the catalytic decomposition of NO on supported platinum catalysts in flow reactors was studied at temperatures below 800°C (*4–6*). Most of the authors have given indications of an inverse dependence of the rate of decomposition upon the pressure of O_2 (*1–4,6*). Among these, we were able to demonstrate the O_2 inhibition quantitatively in a narrow temperature range (*6*). We reported earlier in Fig. 4 of Ref. (*6*) that the NO decomposition rate of Bachman and Taylor (*2*) extrapolated to our standard conditions of 48 Torr NO and 0% O_2 concentration lay above the Arrhenius line describing our data. We ascribed the high activity of platinum at 1210°C, found by Bachman and Taylor (*2*), to the absence of the surface oxide covering the metal at low temperatures. This suggestion was based on the findings of Lang *et al.* (*7*) who reported that heating a clean stepped platinum surface to 800°C in 10^{-6} Torr O_2 caused disordering of the stepped surface after 900 s and a more disordered surface after longer times. The disordering was attributed to the formation of PtO_2 at the surface. Heating the crystal above 900°C in vacuum restored the original structure of the platinum.

The main purpose of the present work was to study the rearrangement of platinum surfaces by O_2 and to explain the discrepancy in the rates of NO decomposition obtained by Bachman and Taylor (*2*) and ourselves (*6*). We studied the NO decomposition at high temperatures on platinum foils with and without adding O_2 to the feed. Also, we determined the composition of the surface platinum oxide by chemisorption measurements.

EXPERIMENTAL METHODS

The flow reactor, the total pressure, the standard gas mixtures, the Pt/Al_2O_3 catalyst and the experimental procedures were the same as those described in Ref. (*6*) with few exceptions discussed in the following sections. A platinum foil, 57 μm in thickness, was purchased from Engelhard Industries. It was reported to be

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TABLE 1
SUMMARY OF SOME PREVIOUS NO DECOMPOSITION ON PLATINUM CATALYSTS

Authors	Catalyst	Reactor	Gas mixture	Temp range (°C)	Pressure (Torr)	Reaction order with respect to NO	Ref.
Green and Hinshelwood (*1*)	Pt-wire	Batch	100% NO	882–1450	200–500	1	(*1*)
Bachman and Taylor (2)	Pt-wire	Batch	100% NO	1210	201–479	2	(2)
Zawadski and Perlinsky (*3*)	Pt-Rh wire	Batch	100% NO	860–1060	100	1	(*3*)
Sakaida *et al.* (*4*)	Supported Pt-Ni	Flow	0.404 and 0.432% NO in N_2	427–537	1–15 atm	2	(*4*)
Shelef *et al.* (5)	Supported	Flow	4–100% NO		760		(5)
	Pt-I		in He	386–532		~1	
	Pt-II			393-761		0.3–0.45	

99.9% pure, carbon being the main impurity (~400 ppm). The platinum foil was washed in benzene, etched in aqua regia and washed in distilled water. Quartz particles (60/100 mesh) were washed in 20% hydrofluoric acid then boiled in concentrated nitric acid to remove impurities and mixed with the catalyst by shaking in the reactor until the catalyst particles appeared to be uniformly distributed in the diluent.

The platinum surface of the supported platinum catalyst was measured by the method of Benson and Boudart (*8*). The dispersion of the metal was 3.7%. The surface area of the platinum foil was taken to be its geometric area. In support of this, the surface area of a platinum foil sample similar to ours was determined according to the Kr BET method and found to be equal to its geometric area (*9*).

The platinum foil was cut into 4 × 4 mm pieces which were mixed with the quartz diluent and put into the reactor. The initial standard pretreatment of the platinum foil consisted of heating at 1050°C in flowing 10.5% O_2 in He for 8 hr; the reactor was then flushed with a flow of He at 1050°C for 0.5 hr. The catalyst was next left in contact with a flow of H_2 at 600°C for 4 hr. The reactor was then flushed with He at 600°C for 0.5–1 hr to remove H_2 before introducing the reactants. The temperature of the reactor was then increased to the desired value. This pretreatment was designed to remove surface carbon. Following a series of runs the activity of the catalyst was checked by returning to a flow condition used in an earlier run and found to stay constant within experimental error. Thus, all steady-state kinetic data were taken during a period of constant activity.

In some of the runs in which O_2 was not added into the feed, two types of standard pretreatment were given for each run: one consisted of flushing the catalyst with He at reaction temperature for 0.5–1 hr and the other consisted of first flushing the sample with H_2 at 600°C for at least 1 hr then leaving it in contact with a flow of He at reaction temperature for at least 0.5 hr.

Auger electron spectroscopy (AES) was employed to check whether the platinum foil surface after treatment with O_2 was clean (not covered with carbon). The experimental set up and procedures are given in Ref. (10). It was found that approximately 0.5 hr treatment of platinum foil with O_2 at 10^{-5} Torr and 700°C removed carbon from the surface. It should be noted that the platinum foil before examination by AES had already been given the standard pretreatment in our flow reactor. Thus, AES indicated that NO decomposition on platinum foils was carried out on a surface free from carbon.

In our differential flow reactor, the rate of reaction r for the reaction with stoichiometric equation,

$$NO = 1/2\ N_2 + 1/2\ O_2, \qquad (1)$$

is obtained directly, as for a well-stirred reactor, by the relation:

$$r = \frac{\mathrm{N}}{A} 2\bar{n}(x_f - x_i), \qquad (2)$$

where r is expressed in $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$, A is the surface area of the catalyst (cm^2), N is Avogadro's number, $\bar{n}$ is the total molar flow rate ($\mathrm{mol\ s}^{-1}$) and x_f and x_i are the mole fractions of either N_2 or O_2 at exit and at inlet of the reactor, respectively (*6*).

The contribution of quartz diluent, reactor walls and gas phase decomposition at 1050°C to the catalytic decomposition of NO was found to be negligible.

The work reported for NO decomposition with no O_2 added to the feed is based upon an integral reactor operated at constant pressure and temperature, and at steady state. Longitudinal mixing by diffusion, radial gradients of concentration and velocity and rate limitations due to external diffusion were judged to be negligible (*10*). A material balance per unit time for NO in a surface area element according to the stoichiometric Eq. (1) becomes (*11*):

$$d\bar{n}_{\mathrm{NO}} = \frac{1}{\mathrm{N}} A_l(dL)r, \qquad (3)$$

where A_l is the surface area of the catalyst per unit length of the reactor (cm), L is the reaction zone length (cm), $A_l(dL) = dA$ and $\bar{n}_{\mathrm{NO}}$ is the molar flow rate of NO ($\mathrm{mol\ s}^{-1}$). But the fractional conversion f is defined by the relation:

$$f = \frac{\bar{n}^0_{\mathrm{NO}} - \bar{n}_{\mathrm{NO}}}{\bar{n}^0_{\mathrm{NO}}}, \qquad (4)$$

where $\bar{n}^0_{\mathrm{NO}}$ is the number of moles of NO entering the reactor per unit time ($\mathrm{mol\ s}^{-1}$) (*11*). Equation (4) was substituted into Eq. (3) and the latter was integrated:

$$\frac{A(\mathrm{NO})^0}{\bar{n}^0_{\mathrm{NO}}} = \mathrm{N}(\mathrm{NO})^0 \int_0^{f_l} \frac{df}{r}, \qquad (5)$$

where $(\mathrm{NO})^0$ is the molar concentration of NO at inlet of the reactor ($\mathrm{mol\ cm}^{-3}$) and f_l is the fractional conversion at exit of the reactor. The reason for introducing $(\mathrm{NO})^0$ will become apparent later. Values of f_l vs $B = A(\mathrm{NO})^0/\bar{n}^0_{\mathrm{NO}}$ were obtained experimentally and plotted on Cartesian coordinates. The curves were graphically differentiated to obtain the rate at zero contact time by the expression

$$(r)_{\tau=0} = \mathrm{N}(\mathrm{NO})^0\left(\frac{df_l}{dB}\right)_{B=0}, \qquad (6)$$

where τ is defined as:

$$\tau = \frac{n_s}{\bar{n}^0_{\mathrm{NO}}} = \frac{1.19 \times 10^{15}}{\mathrm{N}} \frac{A}{\bar{n}^0_{\mathrm{NO}}}, \qquad (7)$$

where $n_s = 1.19 \times 10^{15}/\mathrm{N}$ is the total number of moles of surface platinum (mol) and 1.19×10^{15} is the number of sites per cm^2 of platinum surface (8.4 $\mathrm{Å}^2$/site).

RESULTS

The platinum foil catalyst was tested at 900 and 1000°C for effects of external film diffusion by varying the linear velocity by a factor of approximately 9 at a fixed contact time and constant total pressure and partial pressures of the reactants. The fractional conversion was independent of the linear velocities for both temperatures [Fig. 4 and similar figures in Ref. (*10*)]. These runs ruled out the importance of external mass transfer for the NO decomposition. The importance of these findings, for the runs in which O_2 was not added into the feed, becomes apparent below.

Kinetics with Addition of O_2 to the Feed

In order to study the decomposition on the platinum foil the treatment of the data

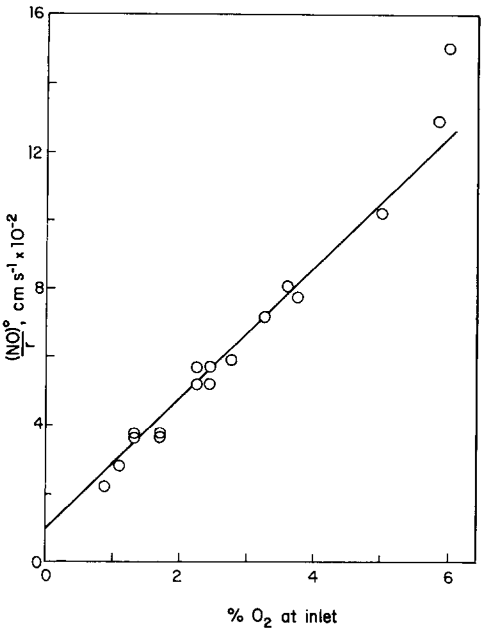

FIG. 1. Effect of O_2 on the $(NO)^0/r$ ratio at 1000°C for Pt-foil. Percentage of NO at inlet = 1.9 to 9.1.

described in Ref. (*6*) was changed; both NO and O_2 concentrations at the inlet of the reactor were varied. The dependence of the reaction rate upon the partial pressures of NO and O_2 was determined at a total pressure of 765 Torr and temperatures from 700 to 1050°C. The amounts of NO and O_2 in the feed were varied from 1.9 to 9.1% and from 0.8 to 7.1%, respectively. The results indicated a linear dependence of the $(NO)^0/r$ ratio on O_2 pressure. A plot of data in this form at 1000°C is shown in Fig. 1. However, plots of the $(NO)^0/r$ ratio vs $(O_2)^{1/2}$ or $(O_2)/(NO)$ or $(O_2)^{1/2}/(NO)$ did not fit the data.

After inspection of Fig. 1 and similar plots which are shown elsewhere (*10*), it was concluded that the rate could be adequately represented by an expression identical to that of the NO decomposition on metal oxides and supported platinum (*6*):

$$r = N\frac{k(NO)}{1+\alpha K(O_2)}, \qquad (8)$$

where r is the NO decomposition rate from Eq. (2) ($cm^{-2}\ s^{-1}$), (NO) and (O_2) are the molar concentrations of (NO) and (O_2) (mol cm^{-3}), k is a constant (cm s^{-1}), K is a constant ($Torr^{-1}$), and α is a conversion factor (Torr mol^{-1} cm^3). Kinetic considerations given below indicate that k and K are a rate constant and an adsorption equilibrium constant, respectively.

The values of k and K obtained from Fig. 1 and similar figures at the other temperatures together with the values for Pt/Al_2O_3 ($D = 0.037$, 0.34) obtained earlier by us (*6*) are given in Table 2. The values of k and K for platinum foil are listed at and above 700°C, as we could not determine the fractional conversion below 700°C due to the very small surface area of platinum foil.

Arrhenius and van't Hoff plots, shown in Fig. 2, were prepared from the values of k and K for Pt/Al_2O_3 at 600, 650 and 700°C and for the platinum foil at 700, 800, 900, 1000 and 1050°C. We obtained the values of the preexponential factor of the rate constant A (cm s—1), the activation energy E (kcal mol^{-1}), the standard entropy of adsorption ΔS^0 (cal mol^{-1} K^{-1}), and the standard enthalpy of adsorption ΔH^0 (kcal mol^{-1}) from the plots of Fig. 2

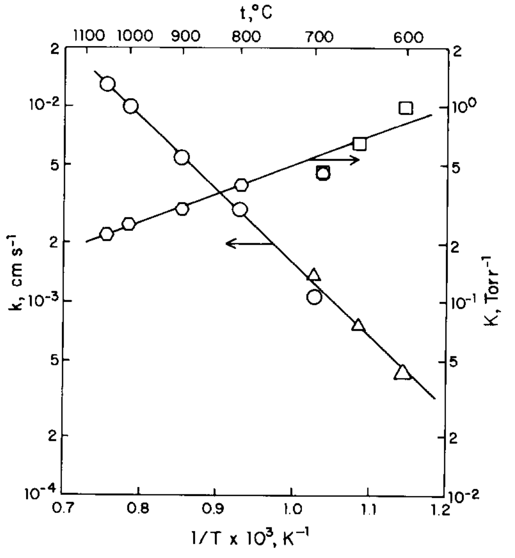

FIG. 2. Temperature dependence of rate and adsorption parameters. (□△) Amirnazmi *et al.* (*6*); (○○) Pt-foil.

TABLE 2

RATE AND ADSORPTION EQUILIBRIUM CONSTANTS k AND K ON OXIDIZED PLATINUM SURFACES

Catalyst	% NO in feed		k					K				
		(°C):	600	650	700			600	650	700		
Pt/Al_2O_3	1.3		4.3×10^{-4}		1.5×10^{-3}			1.00		0.47		
	2.5		4.3		1.5			1.00		0.47		
(D = 0.037)	5.0		4.4	7.8×10^{-4}	1.4			1.00	0.64	0.46		
	7.5		4.4	7.7	1.5			1.01	0.65	0.49		
Pt/Al_2O_3 (D = 0.39)	5.2		4.1×10^{-4}					1.21				
		(°C):	700	800	900	1000	1050	700	800	900	1000	1050
Pt-foil	1.9–9.1		1.1×10^{-3}	2.9×10^{-3}	5.5×10^{-3}	1.0×10^{-2}	1.3×10^{-2}	0.46	0.40	0.30	0.25	0.22

TABLE 3
PARAMETERS OF RATE AND ADSORPTION EQUILIBRIUM CONSTANTS ON OXIDIZED PLATINUM SURFACES

Catalyst	A (cm s^{-1})	E (kcal mol^{-1})	$-\Delta H°$ (kcal mol^{-1})	$-\Delta S°$ (cal mol^{-1} K^{-1})	$E - \Delta H°$ (kcal mol^{-1})
Pt/Al_2O_3–Pt-foil (I)	8.1	17.1	6.6	8.0	23.7
Pt/Al_2O_3(II)	19	18.4	14.0	16	32.4
Pt/Al_2O_3[a]		20.1			

[a] Shelef *et al.* (*5*).

and the results in Table 2. These values together with the apparent activation energy for supported platinum reported by Shelef *et al.* (*5*) are listed in Table 3. The plot of ln K vs reciprocal temperature showed a possible break between 700 and 800°C; therefore, two sets of values for ΔH^0 and ΔS^0 are listed: the first set was obtained by considering a straight line passed through the points at 650, 800, 900, 1000 and 1050°C (I in Table 3), and the second set was obtained by passing another straight line through the points at 600, 650 and 700°C (II in Table 3).

Direct evidence for a marked change in the surface of platinum depending on its pretreatment can be extracted from the titration data given in Table 4. The catalyst was Pt/Al_2O_3 treated in flowing O_2 at 720°C for 12 hr and later used for NO decomposition in the presence of O_2 at 700°C. The apparatus and procedure are described elsewhere (*8,12*).

In a first pretreatment, a sample of the catalyst was outgassed in vacuum for 0.5 hr at room temperature and 3 hr at 150°C; H_2 at 40 μmol s^{-1} was then flowed through the sample and the temperature was raised to 425°C. Reduction was carried out for 2 hr at this temperature, following which the sample was outgassed at 425°C for 1 hr and cooled to room temperature. Oxygen was admitted to the sample at room temperature and 760 Torr and allowed to contact the sample for 1 hr. After pumping out the O_2 for 1 hr, the H_2 uptake was measured. In a second pretreatment, another sample of the same oxidized catalyst was not reduced but merely outgassed at 120°C for 2 hr and then titrated with hydrogen at room temperature. Following this titration, the same sample was outgassed at 425°C for 2 hr and then the uptake of H_2 at room temperature was measured (sample 3). From consideration of H_2 uptakes which are in the ratio 3:5:1 (Table 4), we propose the following stoichiometric equations:

TABLE 4
CHEMISORPTION OF H_2 AT 25°C ON 0.6% Pt/Al_2O_3[a]

Pretreatment	H_2 uptake (μmol g^{-1})	O/Pt_s	Ratio of uptakes
1. 2 hr reduction by H_2 at 425°C followed by 2 hr evacuation at 425°C and then exposure to O_2 at room temperature	1.72	1.0	3
2. 2 hr evacuation at 120°C	2.86	2.0	5
3. 2 hr evacuation at 120°C, titration by H_2 at room temperature, followed by 2 hr evacuation at 425°C	0.56		1

[a] After 12 hr oxidation at 720°C.

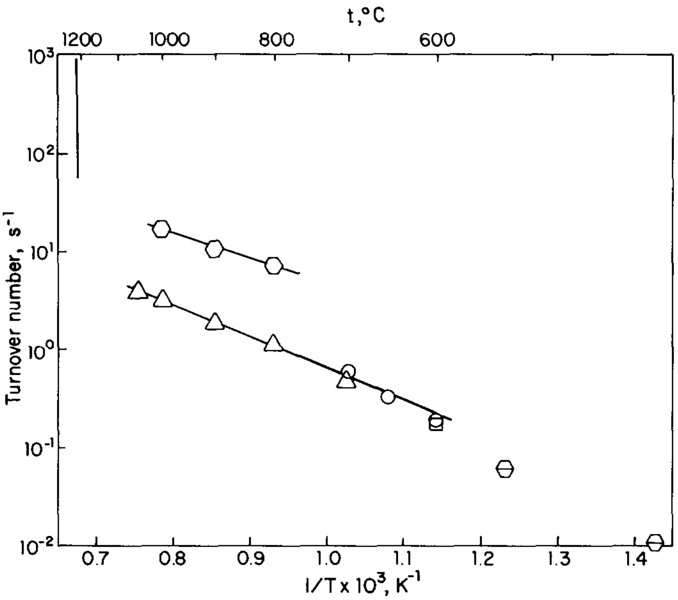

FIG. 3. Activity of Pt catalysts. O_2 was added: (○) D = 0.037 (6); (□) D = 0.39 (6); (△) Pt-foil. O_2 was not added: (○) Pt-foil; (⊖) Sakaida *et al.* (4); (|) Bachman and Taylor (2).

$$Pt_sO + \frac{3}{2} H_2 \rightarrow Pt_sH + H_2O, \quad (9)$$

$$Pt_sO_2 + \frac{5}{2} H_2 \rightarrow Pt_sH + 2H_2O, \quad (10)$$

$$Pt_s + \frac{1}{2} H_2 \rightarrow Pt_sH, \quad (11)$$

for the first, second and third pretreatments respectively, and conclude that the sample oxidized at 720°C has two oxygen atoms per surface platinum atom.

Figure 3 is a plot of the logarithm of turnover number N (molecules reacting per second per surface site) extrapolated to zero oxygen pressure vs $1/T$ at approximately 5% initial NO concentration. In the calculation of N, for the foil it was assumed that there were 1.19×10^{15} sites/cm^2 of platinum geometric surface (8.4 Å^2/site). In this plot we have also included the extrapolated NO decomposition rates reported by Bachman and Taylor (2), and Sakaida *et al.* (4), and us (6).

Kinetics Without Addition of O_2 to the Feed

Since the extrapolated result of Bachman and Taylor (2) lies above the Arrhenius line describing our data as shown in Fig. 3, it seemed necessary to study the NO decomposition without adding O_2 to the feed. These experiments were undertaken on the basis of the hypothesis that the inhibiting effect of small quantities of O_2 formed from NO decomposition might have been different from the case when large quantities of O_2 were added to the feed. Consequently, the dependence of the fractional conversion upon the parameter B was determined for the platinum foil catalyst at a total pressure of 764 to 1530 Torr and temperatures from 800 to 1000°C by varying either the molar flow rate of NO or the amount of catalyst in the reactor. The composition of the feed gas was varied from 2.0 to 10.12% NO in He. The catalyst bed volume was kept approximately constant when the amount of the platinum foil in the reactor was varied.

Values of f_l were plotted as a function of B at various temperatures. Figure 4 is a plot of data at 900°C from runs with 0.90, 3.57 and 3.76 g of catalyst corresponding to approximately 19.4, 72.4 and 81.0 cm^2 of surface area, respectively.

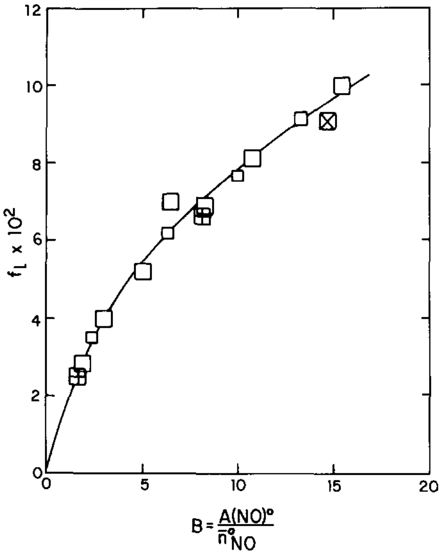

FIG. 4. Fractional conversion versus $B = A(NO)^0/\bar{n}^0_{NO}$ at 900°C for Pt-foil. (⊞) $A = 19.4$ cm^2; (□) $A = 72.4$ cm^2; (⊠) $A = 81.0$ cm^2; (□) % NO at inlet = 3; (□) % NO at inlet = 4.8; (□) % NO at inlet = 6.5; (□) % NO at inlet = 10.12.

Rate expressions (8), and

$$r = N\frac{k_0(NO)^2}{(O_2)}, \qquad (12)$$

reported by Bachman and Taylor (*2*) where k_0 is the overall reaction rate constant (cm s^{-1}), and

$$r = N^2\frac{k'(NO)^2}{[1 + \alpha^{1/2}K^{1/2}(O_2)^{1/2}]^2}, \qquad (13)$$

proposed by Sakaida *et al.* (*4*) where k' is a reaction rate constant (cm^4 s^{-1}) and the following equation:

$$r = N\frac{k(NO)}{1 + K(O_2)^n/(NO)}, \qquad (14)$$

with $n = 0.5$ and 1 were examined for the data at 900 and 1000°C. These equations were substituted into Eq. (5) and the latter was integrated. Equations (12) and (13) did not fit the data and were eliminated. It was possible to decide which one of the rate expressions (8) or (14) fitted all the data better. To show this let us integrate Eqs. (8) and (14) with the results:

$$\ln(1-f_l) + \frac{K}{2}(NO)^0[f_l + \ln(1-f_l)] = -\frac{kA(NO)^0}{\bar{n}^0_{NO}} = -kB, \qquad (15)$$

$$\ln(1-f_l) - \frac{K}{2}\left[\ln(1-f_l) + \frac{f_l}{1-f_l}\right] = -\frac{kA(NO)^0}{\bar{n}^0_{NO}} = -kB, \qquad (16)$$

where Eqs. (15) and (16) correspond to Eqs. (8) and (14) with $n = 1$, respectively. The left side of Eq. (15) is a function of f_l and $(NO)^0$; hence, when the latter is varied a plot of f_l vs B should not give a smooth curve. In contrast, the left side of Eq. (16) is independent of $(NO)^0$; hence, all data points in a plot of f_l vs B should pass through a smooth curve and this indeed is the case at 900 and 1000°C [Fig. 4 and similar figures in Ref. (*10*)]. Since the concentration of O_2 in the reactor was small, Eq. (14) with $n = 0.5$ or $n = 1$ could not be distinguished. Equation (14) with either $n = 0.5$ or $n = 1$ appears to fit all of the data at 900 and 1000°C. On the basis of the preceding arguments, B is a useful and natural parameter. The value of K in Eq. (14) could not be determined accurately.

The values of k obtained in Fig. 4 and figures in Ref. (*10*) are given in Table 5. An Arrhenius plot was prepared from the values of k at 800, 900 and 1000°C, and from this plot the values of A and E were obtained. These values together with the values of the activation energies reported by Green and Hinshelwood (*1*), Sakaida *et al.* (*4*) and also the apparent activation energies reported by Bachman and Taylor

TABLE 5

RATE CONSTANT k ON PLATINUM METAL

	k	
800°C	900°C	1000°C
1.9×10^{-2}	3.2×10^{-2}	5.0×10^{-2}

TABLE 6
PARAMETERS OF RATE CONSTANT ON PLATINUM METAL

Catalyst	A (cm s^{-1})	E (kcal mol^{-1})
Pt-foil	9.4	13.3
Pt-wire[a]		14.3
Pt-Rh-wire[b]		24.6–26.9
Pt-wire[c]		22.0–25.0
Pt/Al_2O_3[d]		3.1

[a] Green and Hinshelwood (*1*).
[b] Bachman and Taylor (*2*).
[c] Zawadski and Perlinsky (*3*).
[d] Sakaida *et al.* (*4*).

(*2*), and Zawadski and Perlinsky (*3*) are listed in Table 6.

In Fig. 3 we have included the extrapolated initial NO decomposition rates at 800, 900 and 1000°C. These rates as N were calculated from the values of k in Table 5 and initial NO concentration of 5%.

Unsteady-State Condition of the Platinum Foil at High Temperatures

The inhibition by O_2 was a reversible phenomenon for all the platinum catalysts studied in this work. The attainment of the steady states corresponding to various partial pressures of O_2 in the reacting system was either instantaneous or relatively slow depending on whether partial pressures of O_2 were large or small. The platinum foil was investigated in detail at 1000°C and the results are shown in Fig. 5. The contact time τ, total pressure and % NO at inlet of the reactor were kept approximately constant. The broken lines represent the rates extrapolated to zero O_2 concentration (zero contact time). The rates at 20×10^{15} and 3.7×10^{15} cm^{-2} s^{-1} were calculated from a plot of f_i vs B at 1000°C (*10*) and Fig. 1, respectively. The solid lines represent the rates at short τ (low conversion). After the catalyst was given initial standard pretreatment, it was contacted with a flow of 5% NO in He. The rate of decomposition of NO was independent of time on stream. After 1 hr, 2.5% O_2 was added to the feed keeping the percentage of NO and τ approximately constant. The rate decreased *slowly* with time on stream and reached a new steady-state value corresponding to 2.5% O_2 in the system. After 3 hr, the O_2 content of the reaction mixture was increased to 5% and the rate dropped *rapidly* to a new steady state. The flow of O_2 was then discontinued and the flow rates of NO in He and He were adjusted in order to return to the original 5% NO in He conditions. At first the rate increased *rapidly* then *slowly* reached a value which was exactly in accordance with the original steady-state value.

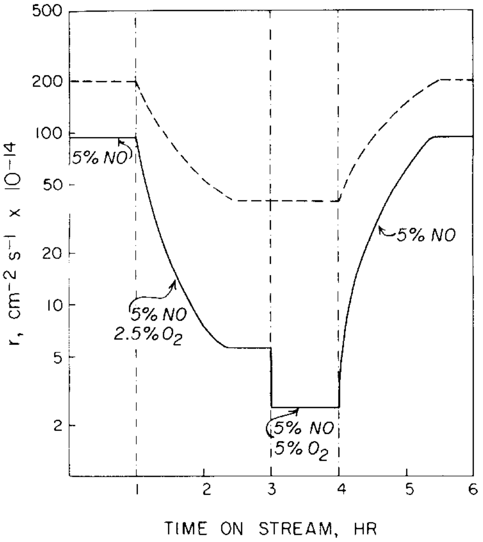

FIG. 5. Unsteady-state decomposition of NO on Pt-foil at 1000°C. (—) Rate r at short contact time ($\tau = 1.44 \times 10^{-2}$ s); (---) rate extrapolated to zero contact time.

We shall now discuss the data obtained in the present study. Then these data will be related to those of other investigators.

DISCUSSION

Rearrangement of Platinum Surface

As we look first at the information of Fig. 3 pertaining to the platinum foil and supported platinum catalysts, we recognize two sets of data passing through two straight lines. In the upper line we have values of N for the platinum foil catalyst. These are referred to as N for a catalyst of *high activity*. The second line gives values of N for supported and unsupported platinum catalysts. These N are referred to as those for catalysts of *low activity*. Our first concern is to explain the reason for the existence of the two sets of N.

The standard pretreatment given to the platinum foil before making runs was the same for both cases; therefore, it is clear that surface contamination was not responsible for the low values of N. It is also worth mentioning that we have already shown that our experimental results were obtained on clean platinum surfaces. A likely source of impurities is the diluent by which the contaminants can be added to the system. We have shown experimentally that the rates of NO decomposition on platinum with or without the diluent were the same; thus, it is clear that contaminants of this nature could not have been introduced to the platinum under our experimental conditions. The preceding facts certainly excluded the possibility that a carbon-covered platinum surface was responsible for high values of N (*13*).

Rather, it became clear that an *oxidized surface* was responsible for the low values of N while the high values of N appear to characterize the behavior of an *oxygen-free surface*. It should be noted that the low values of N were obtained by extrapolating the rates to zero O_2 concentration at inlet of the reactor. These values correspond to an already oxidized surface. The titration data showed that this oxidized platinum surface is in the form of Pt_sO_2. On the other hand, the high values of N were obtained by extrapolating the rates to true zero O_2 concentration in the system, and thus to a clean platinum surface on which no reaction has occurred.

We have established that O_2, whether formed from NO decomposition or introduced as a reactant, inhibits the catalytic sites reversibly and rapidly. By contrast the attainment of a new steady state after a step change in O_2 partial pressure is slow at all the temperatures, especially at the higher ones. Another interesting observation was that once the system had reached the steady state at 2.5% O_2 concentration, the induction period to reach the steady state at 5% O_2 was short.

To explain all observations we put forward the following hypothesis. In the decomposition of NO on platinum at high temperatures and short contact time, the amount of O_2 formed from the decomposition of NO is small and apparently not sufficient to rearrange a surface state believed to be Pt_sO_2. Hence, NO is decomposing on what seems to be platinum metal. On the other hand in the decomposition of NO on platinum in the presence of O_2 fed to the reactor, the oxidation of the surface platinum atoms takes place, after some time a rearranged surface is formed (Pt_sO_2), and at steady state NO is decomposing on this oxidized surface. The reason why the surface rearrangement is a slow process in both directions is not clear.

Kinetics of NO Decomposition on Oxidized Surface of Platinum

The kinetic data for platinum foils and supported platinum, when O_2 was added to the reactor, were found to obey Eq. (8) between 600 and 1050°C. This indicates that the same mechanism operates over that temperature range at least when the platinum surface has reached a steady-state coverage of oxygen. Rate Eq. (8) can be obtained by postulating only two elementary processes identical to those proposed for metal oxides (*6*):

$$\mathrm{NO} + * \xrightarrow{A} \mathrm{NO}*, \qquad \text{(I)}$$

$$\mathrm{O}_s + \mathrm{O}* \leftrightarrow \mathrm{O}_2 + *, \qquad \text{(II)}$$

with the assumptions that the adsorption of NO on 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. The mechanism of decomposition of NO on platinum metal and on oxidized surface of platinum will be discussed in detail in a separate paper, together with the nature of the sites and all of the elementary steps.

Comparison of Data

We shall now compare our data to those of others.[3] The rates are expressed as N (s^{-1}) at 48 Torr initial pressure of NO. Extrapolation of the available data to zero concentration of O_2 could not be done accurately for the work of some authors. Nevertheless, 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 NO decomposition rate of Bachman and Taylor (*2*) at 342 Torr and 1210°C, and the calculated rate then extrapolated to 48 Torr initial NO pressure by using their proposed rate expression. The initial rate was obtained by preparing a plot of their NO conversions vs time and then calculating the slope of the line tangent to the curve at zero time. Therefore, this rate presumably corresponds to a surface which is free of adsorbed oxygen. The result of this calculation is shown in Fig. 3 as a line due to the uncertainties involved in the calculation. The agreement with our result, obtained without adding oxygen into the feed, is not bad.

In the case of Shelef *et al.* (*5*), no comparison between their data on supported platinum 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 O_2 in their reactor.

Green and Hinshelwood (*1*) have reported that the initial rate of the decomposition of NO was first order with respect to NO and here again their rate expression agrees with ours at $(O_2) = 0$. Their extrapolated activation energy to almost zero time is in close agreement with our true activation energy (Table 6).

Sakaida *et al.* (*4*) studied the decomposition of NO in an integral reactor on a supported catalyst containing Pt and Ni, at very high space–times and their reported data according to their own suggestion was possibly diffusion limited. Not much significance should be attached to their rate expression due to the fact that they have not varied the NO concentration in the feed. It is important to note that under their experimental conditions, it is impossible to decide which rate expression fits the data best. Their initial rates at 1 atm were extrapolated to our experimental conditions by using the rate expression (8), assuming a reasonable platinum dispersion of 50%, and neglecting any contribution of nickel to the rate of decomposition of NO which is justified since nickel oxide is much less active than platinum (*6*). Agreement with our low activity results is not bad, as shown in Fig. 3.

CONCLUSION

Oxygen inhibits the decomposition of NO on platinum at high temperatures in two distinct ways. First, if the platinum surface is originally in contact with small partial pressures of oxygen, but is exposed to higher partial pressures of oxygen, the surface reaches slowly a new steady state which is catalytically less active than the

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[3] It is of interest to note that our high activity results are in good agreement with more recent work on the catalytic decomposition of pure NO on platinum wire at 400 to 2260 Torr between 900 and 1200°C in a static system (Pancharatnam, S., Lim, K. J., and Mason, D. M., *Chem. Eng. Sci.*, in press).

former one. Following our results and those of others (*7*), we ascribe the inactive state to a surface oxide Pt_8O_2. The second mode of inhibition of oxygen is that normally associated with competition for sites between inhibitor and reactant. It has already been reported by us in a previous publication (*6*).

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