

The Production of Nitrogen Oxides on Platinum and Nickel from Atomic Nitrogen and Molecular Oxygen

M. E. Ryskin and S. V. Syromiatnikov

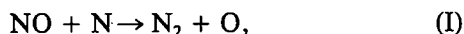
N. N. Semenov Institute of Chemical Physics, Acad. Sci. Russia, Kosygina 4, 117334 Moscow, Russia

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The reactions of N-atoms with molecular oxygen and N₂O catalyzed by Pt and Ni were studied by spectroscopic and mass-spectrometer methods in a discharge flow system. The products of this reaction were NO and/or NO₂ and N₂O which were produced in the temperature range from 100 to 400°C. © 1994 Academic Press, Inc.

INTRODUCTION

Heterogeneous catalytic reactions of nitrogen atoms have been studied in few works. Reeves, Mannella, and Hartek (1) have revealed that the recombination of N + O on nickel, cobalt, and other materials leads to the formation of the electronically excited molecules NO and N₂. Later Halpern, Murphy, and Fenn (2) attempted to detect vibrationally excited NO molecules which could be produced by the reaction of nitrogen atoms and oxygen on platinum. However, the only product of the reaction that they found by FTIR emission spectroscopy was N₂O. According to Ref. (2), the rate of N₂O production was approximately 10% of the recombination rate. Kisliuk, Baculeva, and Tretiakov have also studied this reaction in UHV conditions and have shown (3) that both NO and N₂O occur in the reaction of N-atoms with oxygen preadsorbed on Pt. As it was noted by authors of Ref. (2), one of the possible reasons for their failure to observe NO produced by the catalytic reaction was the destruction of these molecules by the fast gas-phase process (4)



and so the direct detection of NO under these conditions is very difficult. However, the production of NO molecules in such conditions may be tested by the detection of O-atoms, which are produced by reaction (I). O-atoms have a greater lifetime than NO molecules under the same conditions and so they could be readily detected by spectroscopic methods.

In the present work we have utilized the above method

to investigate the catalytic reaction of N and O₂ on Pt and Ni surfaces.

EXPERIMENTAL

The experiments were carried out in a conventional type discharge-flow system (Fig. 1). Nitrogen atoms were generated by passing high purity nitrogen (the main impurities were: CO₂, 3 × 10⁻⁴%; CO, 2 × 10⁻⁴%; CH₄, 5 × 10⁻⁴%) additionally purified in a liquid-nitrogen trap before the microwave discharge cavity. Under a typical pressure of 3 Torr the flow velocity was ≈ 10 m/s.

The reactor was placed downstream of the discharge and included a special glass valve which could switch the flow from one tube (path C) to another (path EH). The first of them, the reaction tube (path C), contained the catalyst (Pt or Ni wire 0.05 cm diameter, 20 cm long coiled into a spiral), while the second, the comparison tube (path EH), contained a tungsten wire coated with fused silica. Both wires could be heated by electric current to a desired temperature which was monitored by resistance measurements. Path EH served to heat up the gas to the same temperature as in path C, where the catalyst was placed. The presence of two paths with the same gas temperature permits us to estimate correctly the yield of O-atoms due to the gas-phase reactions of nitrogen atoms with oxygen, and thus to measure the net yield due to the catalytic reaction.

Oxygen (99.999% purity), N₂O (medical purity), and other gases were mixed with the nitrogen flow through a variable calibrated leak at the entrance of the reactor.

To study the influence of N-atom concentration on the catalytic reaction rate, a special system (regulator) was used. It was placed between the source of nitrogen atoms and the reactor.

The operation of the regulator (5) is based on passing of the part of active nitrogen through a lateral line which contained a hot platinum wire. It is known that platinum effectively removes N-atoms by a recombination, and so the regulator is able to vary the concentration of N-atoms.

The stable products of catalytic reaction such as N₂O

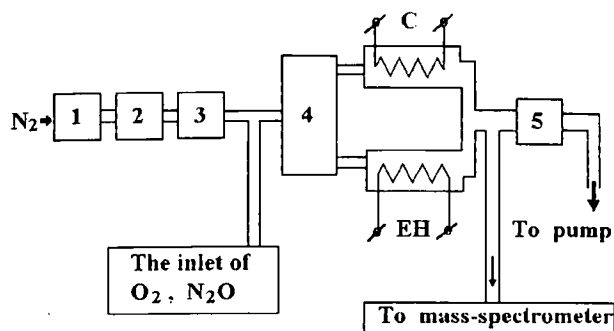


FIG. 1. Schematic drawing of an experimental setup: (1) liquid nitrogen trap, (2) microwave discharge cavity, (3) regulator of [N], (4) switching out of flow, and (5) detection zone of glow; (C) catalyst and (EH) the electrical heating.

could be detected by a monopolar mass-spectrometric (MMS) analysis. For this analysis a gas flow was passed through a trap cooled by liquid nitrogen, where the N_2O molecules were condensed; after the trap was heated, they could be measured by MMS.

Unstable products of the catalytic reaction, NO or/and NO_2 , were detected by an indirect method using a measurement of O-atom concentration (see below).

Before placement in the reactor, the catalyst was cleaned electrochemically and then annealed in the reactor in an atmosphere of oxygen, hydrogen, and their mixture. The catalyst was believed to be clean if the catalytic oxidation of hydrogen on its surface occurred actively.

Measurements of the Atom Concentration

At the reactor exit, the concentration of the nitrogen atoms was measured by recording the glow of the first positive band of N_2 . The intensity of this glow over the range from 480 to 670 nm is known to be proportional to $[N]^2$ (6),

$$I_1 = A [N]^2, \quad [1]$$

where the luminescence constant, A , was determined in special experiments by simultaneous measurements of I_1 and N-atom concentration by an NO-titration method (7).

The O-atom concentration was measured by a detection of emission of $NO(B^2\Pi)$ molecules at 379.5 nm which occurs as a result of the recombination of O- and N-atoms in the gas phase:



The intensity of this glow, I , is proportional to N- and O-atom concentrations (6):

$$I = B [N] [O]. \quad [2]$$

The luminescence constant B depends on the composition and pressure of a gas. For small amounts of O_2 or N_2O

added to nitrogen, the value of B was found (5) to be equal to

$$B = B_0(1 + \alpha_Q[Q])^{-1}, \quad [3]$$

where Q is O_2 or N_2O and

$$\alpha_{O_2} = (1.2 \pm 0.3) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}$$

$$\alpha_{N_2O} = (2.6 \pm 0.65) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}.$$

Using [1] and [2], one can find

$$[O] = \frac{I}{B \cdot [N]} = \frac{\sqrt{A}}{B_0} \cdot (1 + \alpha_Q[Q]) \cdot \frac{I}{\sqrt{I_1}}. \quad [4]$$

Thus, by measuring the magnitudes of I_1 and I simultaneously, we can calculate the O-atom concentration. The value of \sqrt{A}/B_0 , needed for the calculations, was found in special experiments where the value of the O-atom concentration was known. To make such a known concentration, we added oxygen to the active nitrogen. Oxygen atoms were produced by the reaction



and their concentration was equal to

$$[O] \approx 2K_3 \cdot [N] \cdot [O_2] \cdot t, \quad [5]$$

where $t = 26 \pm 3$ ms is the time of flight of the flow from the inlet of O_2 to the detection zone. $K_3 = 9.8 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}$ is the rate constant of reaction (III), which was measured in (4, 8).

In order to the procedure of monitoring the NO/ NO_2 concentration by following the O-atom concentration be correct two main conditions should be fulfilled:

1. the conversion of oxygen bound in NO/ NO_2 molecules to O-atoms should be complete;
2. the measurements of the O-atom concentration should be quite accurate.

The detailed analysis of the O-atom concentration measurements shows that this procedure is based on Eq. [4] derived from well-grounded relations [1]–[3], and that the main source of errors in the measurements is the procedure of calibration using reaction (III) and Eq. [5]. Due to some uncertainties in K_3 values obtained by various authors (4, 8) ($\Delta K_3/K_3 \approx 30\%$) and the errors in values of $[N]$, I , I_1 , and $\alpha_Q[Q]$ the total error in O-atom concentration is of the order of 50%.

Note here that the relative values of O-atom concentrations may be found more precisely than the absolute concentrations because the former do not require the calibration procedure.

Consider in more details the process of conversion of bound oxygen to free oxygen atoms. The gas-phase reactions important for the examined system are given in Table I together with their rate constants. The values of yields

TABLE 1
The Conversion of NO/NO₂ Mixture in Active Nitrogen

Reaction	Rate constant (4) at 300 K (cm ³ sec ⁻¹) ^a	Yield of O atoms per 1 molecule of nitrogen oxide
(I) N + NO → N ₂ + O	K ₁ = 3.1 × 10 ⁻¹¹	1
(IV) N + NO ₂ → 2O + N ₂	K ₄ = 9.1 × 10 ⁻¹³	0.9
(V) N + NO ₂ → O + N ₂ O	K ₅ = 3.0 × 10 ⁻¹²	
(VI) N + NO ₂ → O ₂ + N ₂	K ₆ = 7.0 × 10 ⁻¹³	
(VII) N + NO ₂ → 2NO	K ₇ = 2.3 × 10 ⁻¹²	
(VIII) O + NO ₂ → NO + O ₂	K ₈ = 9.1 × 10 ⁻¹²	

^a [N] = 1.5 × 10¹³ cm⁻³, t = 26 ms.

^b [O] = 8.0 × 10¹¹ cm⁻³.

of O-atoms per 1 molecule of oxide given in the table are calculated for typical experimental conditions by integrating corresponding kinetic equations.

During the calculations we supposed that N-atom concentration is not changed by the reaction. This assumption is based on the experimental results (see below) which show that the concentration of N atoms after catalysis is approximately 20 times greater than that of NO/NO₂ molecules.

As can be seen from Table 1, if the mixture NO/NO₂ does not contain NO₂, then reaction (I) converts all NO molecules to free atoms. In the opposite case when the mixture contains NO₂ molecules only their conversion in active nitrogen proceeds through several paths. Reactions (VII) and (VIII) generate NO-molecules which then are rapidly converted to O-atoms by reaction (I). Reactions (IV) and (V) produce O-atoms directly. There are also relatively more stable products of the reactions O₂ and N₂O which react with N-atoms slowly. The numerical estimations of the yield of O-atoms based on known values of rate constants and measured values of the concentration of N- and O-atoms show that the overall conversion of NO₂ under typical experimental conditions is approximately 95%, and the yield of O-atoms per 1 molecule of NO₂ under the same conditions is 0.9. So we may conclude that both oxides, NO and NO₂, are rapidly converted to O-atoms and the yield is close to unity, and so the measurement of O-atom concentration permits one to evaluate the concentration of NO/NO₂ molecules, but does not permit one to distinguish between these two oxides.

RESULTS AND DISCUSSION

Platinum

Figure 2 represents the dependencies of the yield of O-atoms on the temperature for both lines of gas flow: for

Pt-containing-path C and for comparison path, path EH. Both dependencies are essentially different. In the case of path EH, a monotonous increase of [O] is observed, but in the case of path C the dependence of [O] on T has a peak at the temperature of 315–320°C. The increase of [O], which is observed for the path EH in temperature range from 30 to 500°C, in our opinion is due to the increase of the rate of process (III) in the gas phase. The activation energy of this process according to (4, 8) is equal nearly to 7 kcal/mol. Our data give approximately the same value, though it should be noted that quantitative comparison of these results with that of the works (4, 8) is not a simple problem, because of the necessity to take into account the profiles of temperature and N-atom concentration in the reactor. However, we may assert that the rate of formation of oxygen atoms in the gas phase in the Pt-containing line is smaller than that in the case without the Pt-catalyst. This difference is due to the low

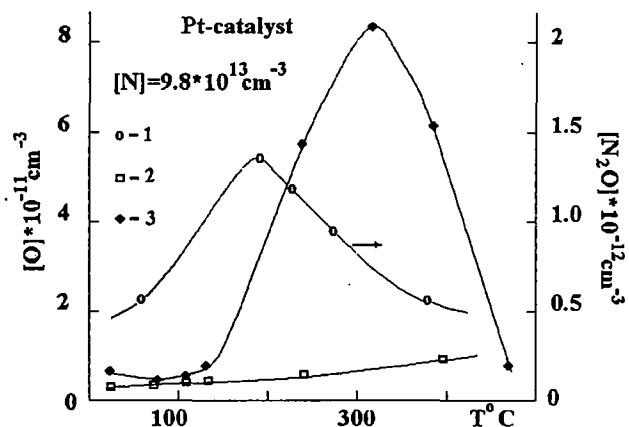


FIG. 2. The yield of O-atoms vs temperature, T°C for both lines of gas flow: for Pt-containing path (3) and for comparison path (2), and the N₂O-production yield against the temperature of platinum (1), at [O₂] = 3.3 × 10¹⁴ cm⁻³.

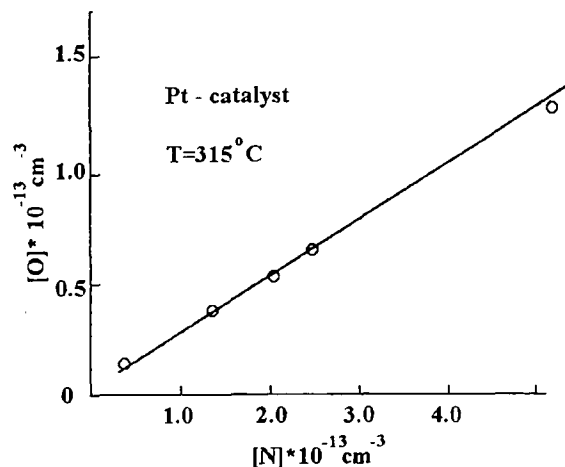


FIG. 3. The yield of O-atoms vs N-atom concentration for Pt-catalyst. $[O_2] = 3.3 \times 10^{14} \text{ cm}^{-3}$.

value of N-atom concentration in the Pt-containing line. So we may conclude that the platinum catalyzes a reaction resulting in the appearance in the gas phase of O-atoms. The rate of this heterogeneous reaction exceeds by tenfold the rates of gas phase reactions ((I) and (III)) in the temperature range from 200 to 400°C. We suppose that this reaction is the Pt-catalyzed production of NO and/or NO₂ from N-atoms and molecular oxygen. The fact that this reaction is the reaction of N-atoms and O₂ but not a process due to any excited particles generated by the MW-discharge is asserted by the results of kinetic measurements. Figures 3 and 4 represent the dependence of the yield of O-atom on N-atom concentration (Fig. 3) and on O₂ concentration (Fig. 4). As can be seen from Fig. 3, the yield of O-atoms due to Pt-catalyzed reaction is proportional to the N-atom concentration. In Fig. 4, the curve obtained for the Pt-containing line contains two linear

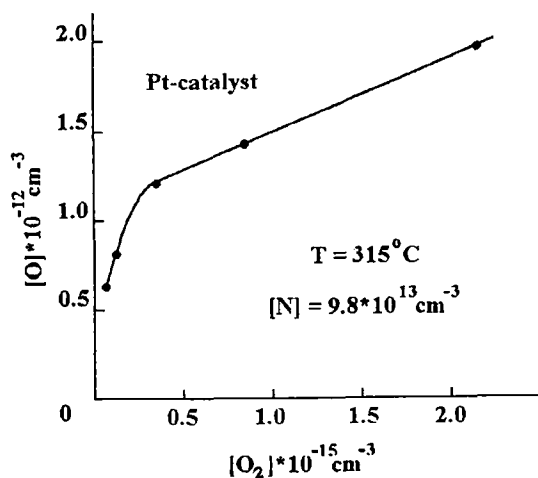


FIG. 4. The yield of O-atoms vs O₂ concentration for Pt-catalyst.

parts. The comparison of this dependence with the appropriate one obtained for path EH (which is linear for all O₂-concentration) allows one to conclude that the curve shown in Fig. 4 is the sum of two terms. The first term (at high [O₂]) describes a contribution of gas-phase reaction (III), but the second term (at low [O₂]) describes that of a heterogeneous reaction. Thus, the represented data testify, in our opinion, that the surface of hot platinum catalyzes production of NO and/or NO₂ from N and O₂. The temperature at which the rate of the production of NO and/or NO₂ is maximum is nearly 315°C. This temperature is above the temperature of the maximum of the TDS-peak of NO measured in (3, 9), which is equal to 90–180°C for desorption of the nondissociative form of NO (9), and is greater than the temperatures of impact production of NO in the reaction of N + O_{ads} (120°C) (3) and the temperature of recombination of adsorbed atoms N_{ads} + O_{ads} (230°C) (3). Although the direct comparison of temperatures of the maximum of TDS-peaks and the maximum of reaction rate is not quite correct, and more rigorous analysis of the kinetics is necessary, we may conclude that the desorption of NO is not the limiting step of the reaction studied.

Besides unstable products NO and/or NO₂, which disappear in the gas phase as a result of gas-phase reaction, the heterogeneous reaction of N + O₂ generates also the more stable nitrogen oxide N₂O which does not react in the gas phase with N-atoms and so may readily be detected by the mass-spectrometer. The dependence of the N₂O production yield against the temperature of platinum is shown in Fig. 2. It follows from Fig. 2 that the rate of N₂O production reaches the maximum at 210°C. This result is in accordance with (2) where it was shown that the maximum of the N₂O production rate of the reaction of N + O₂ on platinum is reached at a temperature of 200°C. Our result also is in accord with (3), in which the maximum of the TDS-peak of N₂O was found at 230°C. The maximum yield of N₂O at 210°C is approximately $1 \times 10^{12} \text{ cm}^{-3}$. This value is equal approximately to NO and/or NO₂ yield. The whole expense of nitrogen atoms in the production of nitrogen oxides does not exceed $2 \times 10^{12} \text{ cm}^{-3}$.

Thus, in the range of temperature from 210 to 350°C the fraction of nitrogen atoms that is expended in the catalytic reaction is approximately $2 \times 10^{12} \text{ cm}^{-3} / 4 \times 10^{13} \text{ cm}^{-3} = 5 \times 10^{-2}$ or 5%.

In conclusion of this section it will be noted that, unlike O₂ we did not detect any catalytic reaction of atomic nitrogen and N₂O on platinum.

Nickel

The data obtained from the reaction of N + O₂ on nickel catalyst are similar with the one for platinum. Figures 5–7

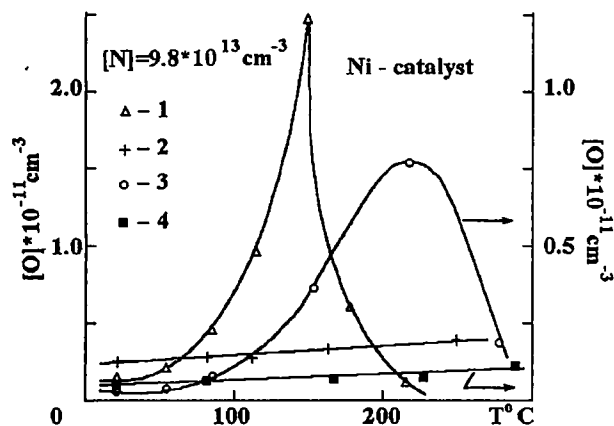


FIG. 5. The yield of O-atoms vs temperature for both lines of gas flow: for Ni-containing path (1), for comparison path (2), $[O_2] = 3.3 \times 10^{14} \text{ cm}^{-3}$; for Ni-containing path (3) and for comparison path (4), upon the addition of $[N_2O] = 4.6 \times 10^{14} \text{ cm}^{-3}$.

represent the yield of atomic oxygen versus temperature (Fig. 5), the atomic nitrogen concentration (Fig. 6), and the molecular oxygen concentration (Fig. 7). It should be noted that on nickel the catalytic reaction proceeds at a lower temperature than on platinum. The rate of the reaction on Ni reaches the maximum value at 170°C . At this temperature the difference between the rate of the catalytic reaction on nickel and the gas-phase reaction rate (Fig. 5) is more than that in the case of platinum. The maximal reaction rate on nickel is nearly to 2–3 times less than that on platinum. With increasing concentration of atomic nitrogen at the entrance in the reactor the rate of the reaction is proportionally increased (Fig. 5). The dependence of $[O]$ on molecular oxygen concentration (Fig. 6), as in the case of platinum, has more complicated

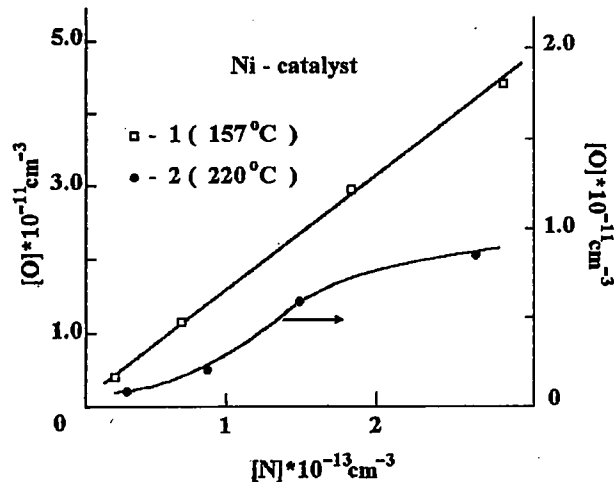


FIG. 6. The yield of O-atoms vs N-atom concentration for Ni-catalyst: (1) $[O_2] = 3.3 \times 10^{14} \text{ cm}^{-3}$ and (2) $[N_2O] = 4.6 \times 10^{14} \text{ cm}^{-3}$.

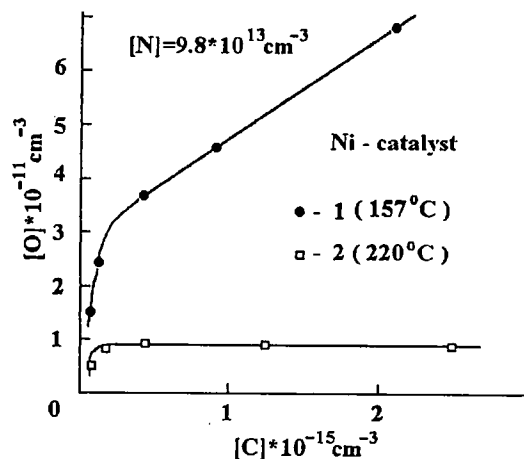


FIG. 7. The yield of O-atoms vs $[O_2]$ (1) and $[N_2O]$ (2) for Ni-catalyst. $[N] = 9.8 \times 10^{13} \text{ cm}^{-3}$.

character. Using the same arguments as in the case of platinum it may be concluded that the growth of the O-atom yield at high concentration of O_2 is due to the gas-phase reactions (I) and (III), but the steep part of curve (1) is concerned with the heterogeneous catalytic reaction.

The fraction of nitrogen atoms which is expended in production of NO and/or NO_2 at 170°C is nearly $2.5 \times 10^{11} \text{ cm}^{-3} / 2.3 \times 10^{13} \text{ cm}^{-3} \approx 0.01$ or 1%.

As distinct from platinum on the nickel catalyst it was found that the catalytic reaction between atomic nitrogen and N_2O takes place. Over the temperature range from 150 to 300°C (Fig. 5) we observed the growth of O-atoms concentration. It is known that the gas-phase reaction between N and N_2O is very slow (4). Consequently, it may be asserted that the increase of O-atoms yield in this case is related to the heterogeneous reaction between N and N_2O on nickel. The rate of this reaction approximately proportionally increases with the growth of N-atom concentration (Fig. 6) and with N_2O -concentration (Fig. 7). The reaction rate of $N + N_2O$ reaches a maximum value at $210\text{--}220^\circ\text{C}$. However, this value is two- to threefold less than that of $N + O_2$ (at 170°C).

It should be noted that, as distinct from platinum, N_2O was not produced, as verified by mass-spectrometer measurements. Perhaps the channel of N_2O production was blocked by the reaction of atomic nitrogen with N_2O on the nickel surface and so N_2O did not appear in the gas phase.

Thus, in the present work we have studied the heterogeneous catalytic reactions of nitrogen atoms with molecular oxygen or N_2O over the temperature range from 100 to 400°C on the surfaces of platinum and nickel catalysts and have shown that these reactions produce the nitrogen oxides. The behavior of these reactions on Pt- and Ni-catalysts has both common and different features. The

mechanisms of these reactions are under investigation at present.

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