SIMULATION OF THE OXIDATION KINETICS OF NO$_x$ IN A GAS DISCHARGE

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We investigate the mechanisms of the oxidation of NO in a gas discharge. We consider the influence of admixed water on the efficiency of removal of nitrogen oxides. Power expenditures are evaluated and optimal values for the temperature of a mixture and lifetime of particles in a reactor are found.

Ventings of sulfur and nitrogen compounds into the atmosphere on combustion of fuel at power electric stations and in diesel engines represent a very substantial factor in the pollution of the environment. Apart from physicochemical techniques, which are used traditionally for decomposing harmful admixtures and which have a number of drawbacks [1-3], currently new nontraditional methods are being developed, which make use of nonequilibrium plasma. Moreover, attention is especially being paid to reactors on the basis of corona or barrier discharges as the most promising for purifying industrial gas effluents [1-5]. It is known that the main special feature of such discharges is that in an initially neutral gaseous mixture, high-energy electrons with mean energy values of the order of 10 eV or higher are formed which effectively excite, ionize, and dissociate heavy particles. In such a medium the processes of decomposition of harmful compounds occur most intensely. We investigated the possibilities of applying a gaseous discharge, such as a corona or a barrier discharge, for removing NO$_x$ from the exhaust gases of power plants.

The process of purification of exhaust gases is subdivided into three stages. At the first stage NO is reoxidized up to higher oxides. The second stage consists in converting higher oxides of nitrogen into nitric acid by way of reactions with OH radicals [3, 4]. The removal of nitric acid from a gas flow occurs at the third stage of the process of purification. Depending on whether nitric acid is present in a liquid or a gas phase, its removal is achieved either by condensation or by adding ammonium with subsequent precipitation in the form of ammonium salts. Of the three stages, the first one, i.e., oxidation of NO, is the most difficult to effectuate. This is because a nitrogen oxide molecule is extremely stable and virtually does not enter into reactions with other molecules. Therefore, the execution of the first stage within the framework of traditional technologies is associated with considerable time and energy expenditures. At the same time, oxidation of NO can be easily carried out in a low-temperature plasma. Below, we will analyze the prospects of conducting the first stage of freeing exhaust gases from NO$_x$ in a gas discharge.

NO oxidation can be effected in a number of ways, for example, by reaction with oxygen molecules [4]:

$$NO + NO + O_2 \rightarrow 2\,NO_2.$$ (1)

The role of reaction (1) is great only in the wake of exhaust gases in the absence of intense mixing with air. This is a very slow process with the characteristic time of occurrence in the atmospheric air equal to $2 \cdot 10^3$ sec if the rate constant of reaction (1) is taken to be equal to $k = 1.4 \cdot 10^{-38}$ cm^6/sec [4]. At the same time, in a corona or a barrier discharge a considerable portion of the energy of electrons is spent for the dissociation of O$_2$ molecules by shocking electrons. In such a medium, along with oxygen molecules there are many radicals, i.e., O atoms. In this case, the formation of NO$_2$ can also occur by means of direct reaction with oxygen atoms:

$$NO + O + M = NO_2 + M \tag{2}$$

with the rate constant $k = 6.5 \cdot 10^{-32}$ cm^6/sec at $T = 350$ K [5]. However, in the presence of water in a mixture, the process with participation of OH radicals is more efficient:

$$NO + OH + M = HNO_2 + M, \tag{3}$$

whose rate constant is $k = 5 \cdot 10^{-31}$ cm^6/sec at $T = 350$ K [5]. The OH radicals are produced by reactions of water molecules with oxygen atoms:

$$H_2O + O = OH + OH. \tag{4}$$

The rate constant of this reaction is not large and at $T = 350$ K it is equal to $k = 3.2 \cdot 10^{-22}$ cm^3/sec [5]. However, in the process of the dissociation of oxygen molecules by shocking electrons, electron-excited oxygen atoms may appear in addition to O atoms:

$$e + O_2 = e + O + O \, (^1D). \tag{5}$$

The energy threshold of this process is 8.4 eV. At the same time, for the process of the dissociation of O_2 molecules, in which two oxygen atoms are formed in the ground state, an energy of 6.1 eV is needed. Therefore, reaction (5) proceeds efficiently only in strong electric fields, which are achieved in corona and barrier discharges. For example, in a barrier discharge in pure oxygen, the relationship between the formed electron-excited and unexcited oxygen atoms at $E/N = 150$ Td may reach 1:100 by the time 10^{-8} sec [6]. Thus, there exists still another channel for the formation of OH radicals in reactions of water molecules with electronically excited oxygen atoms:

$$H_2O + O \, (^1D) = OH + OH. \tag{6}$$

The rate constant of this reaction is independent of temperature and is rather large $(2.3 \cdot 10^{-10}$ cm^3/sec), placing this mechanism in the forefront at low temperatures. The role of the direct reaction of NO molecules with O(^{1}D) atoms is not clear at present.

It should be noted that an excess of atomic oxygen can decrease the efficiency of NO oxidation and lead to the recovery of nitrogen oxide in reactions with NO_2 molecules:

$$NO_2 + O + M = NO + O_2 + M. \tag{7}$$

The rate constant of this reaction is $7 \cdot 10^{-32}$ cm^6/sec at $T = 350$ K [5].

An increase in the local intensity of the electric field is capable of stimulating not only the processes of the dissociation of oxygen molecules by shocking electrons with the formation of electron-excited atoms O(^{1}D), but also the additional processes of the formation of nitrogen atoms, and then nitrogen oxides on dissociation of N_2 molecules by electron shock. For example, the relationship between the rate constants of the processes of dissociation of oxygen molecules (5) and nitrogen molecules is 10:1 at $E/N = 80$ Td; it decreases with a further increase in the electric-field strength [7]. An additional formation of NO may occur by means of reactions of nitrogen atoms with radicals, such as OH and O, as well as with O_2 molecules. The greatest contribution to the formation of nitrogen oxide is made by the reaction

$$N + OH = NO + H, \tag{8}$$

whose rate constant is equal to $5.3 \cdot 10^{-12}$ cm^3/sec at $T = 350$ K; it decreases with an increase in temperature following the law $T^{-0.5}$ [5]. Reaction (8) does not exert a noticeable effect on the process of NO oxidation until the ratio NO:N does not exceed 100:1. It is satisfied under the conditions considered in electric fields smaller than $E/N = 100$ Td.

At the second stage of purification, nitric acid is formed as a result of the reaction of NO_2 molecules with OH radicals [3, 4]:

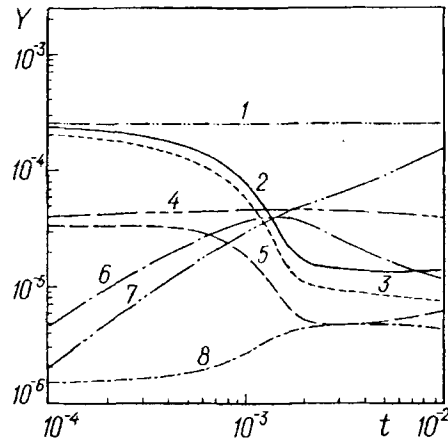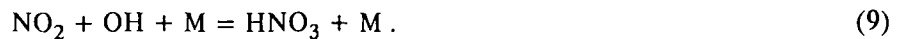Fig. 1. Time evolution of the basic components of the mixture at $T = 350$ K, $A = 10$ sec^{-1}: 1) initial concentration of NO; 2) NO$_x$; 3) NO; 4) O; 5) NO$_2$; 6) HNO$_2$; 7) HNO$_3$; 8) OH. t, sec; Y, molar fractions.

TABLE 1. Initial Gas Mixture

Component	Molar fractions
N$_2$	0.7
O$_2$	0.15
CO$_2$	0.09
H$_2$O	0.06
NO	0.00023
NO2	0.00003

$$NO_2 + OH + M = HNO_3 + M .$$ (9)

The rate constant of this reaction is equal to $1.5 \cdot 10^{-30}$ cm^6/sec at $T = 350$ K; it decreases with an increase in temperature following the law $T^{-3.2}$ [5]. Reaction (7) may complete with this process, decreasing the efficiency of purification. However, if the relationship OH:O $\geq$ 1:100 is satisfied, the process of the formation of nitric acid (9) becomes dominating. As seen from Fig. 1, this relationship is valid under the conditions considered.

The outgoing exhaust gases of power plants consist of a complex mixture of nitrogen, oxygen, carbon dioxide, water vapor, and admixtures of NO and other components. Generally speaking, their composition depends on both the type of starting material and the regime of combustion. As a starting material we adopted a typical mixture whose composition is presented in Table 1. This gaseous mixture is equilibrium (except for nitrogen oxides). It results from combustion of diesel fuel in air in the ratio 1:10 and passage through an outlet collector. Nitrogen oxides are formed in the process of combustion at high temperatures [8], their concentrations are "frozen," and they are higher than the corresponding equilibrium concentrations for a temperature of 450 K. On the other hand, these values are two times higher than the maximum permissible doses of the content of NO$_x$ in air established by EC standards in 1997 [3]. In the present work, we posed the problem of determining the regimes of operation of a plasmachemical reactor under which the amount of NO in a mixture can be reduced by 50% or more.

To calculate the kinetics of oxidation of NO in a gas discharge, we solved the system of equations of chemical kinetics

$$v \frac{\partial n_i}{\partial z} = \sum_{i,j} v_{i,j} R_{i,j} ,$$ (10)

TABLE 2. Fundamental Reactions Used in Calculations

No. of reaction	Reaction	k, cm^3/sec
1	$O(^1D) + H_2O = OH + OH$	$k_1 = 2.3 \cdot 10^{10}$
2	$O + H_2O = OH + OH$	$k_2 = 7.6 \cdot 10^{-15} T^{-1.3} \exp(-8605/T)$
3	$NO + O + O_2 = NO_2 + O_2$	$k_3 = 2.4 \cdot 10^{-27} T^{-1.8}$
4	$NO + O + N_2 = NO_2 + N_2$	$k_4 = 9.1 \cdot 10^{-28} T^{-1.6}$
5	$N + NO_2 = N_2O + O$	$k_5 = 1.4 \cdot 10^{-12}$
6	$O + NO_3 = O_2 + NO_2$	$k_6 = 1.0 \cdot 10^{-11}$
7	$NO + O_3 = NO_2 + O_2$	$k_7 = 2.0 \cdot 10^{-12} \exp(-1400/T)$
8	$NO_2 + O_3 = NO_3 + O_2$	$k_8 = 1.2 \cdot 10^{-13} \exp(-2450/T)$
9	$O + NO_2 + M = NO_3 + M$	$k_9 = 8.1 \cdot 10^{-27} T^{-2.0}$
10	$N_2 + O = NO + N$	$k_{10} = 8.3 \cdot 10^{-11} \exp(37,944/T)$
11	$NO + NO_3 = 2NO_2$	$k_{11} = 1.9 \cdot 10^{-11}$
12	$NO + O_3 = NO_2 + O_2$	$k_{12} = 2.0 \cdot 10^{-12} \exp(-1400/T)$
13	$N + O + M = NO + M$	$k_{13} = 5.5 \cdot 10^{-13} \exp(155/T)$
14	$NO_2 + H = 2NO$	$k_{14} = 3.0 \cdot 10^{-12}$
15	$N + OH = NO + H$	$k_{15} = 2.2 \cdot 10^{-11} \cdot T^{-0.25}$
16	$NO + O = N + O_2$	$k_{16} = 6.3 \cdot 10^{-15} \cdot T^{-1.0} \exp(-20,820/T)$
17	$OH + NO + M = HNO_2 + M$	$k_{17} = 6.4 \cdot 10^{-25} \cdot T^{-2.4}$
18	$OH + NO_2 + M = HNO_3 + M$	$k_{18} = 2.1 \cdot 10^{-22} \cdot T^{-3.2}$
19	$OH + HNO_3 = H_2O + NO_3$	$k_{19} = 1.5 \cdot 10^{-13}$
20	$O + NO_3 = O_2 + NO_2$	$k_{20} = 1.0 \cdot 10^{-11}$
21	$HO_2 + NO = NO_2 + OH$	$k_{21} = 3.7 \cdot 10^{-12} \exp(240/T)$

where n_i is the concentration of the ith component of the mixture; z is the direction along the discharge tube of the reactor; v is the gas flow velocity along the discharge tube; v_{ij} are the stoichiometric coefficients of the jth reaction; R_{ij} is the reaction rate. The source term, which reflects the specificity of chemical-kinetics stimulation in a gas discharge, was written as $A[O_2]$, where $[O_2]$ is the concentration of oxygen molecules in the mixture, A is the parameter defined as

$$A = k_d n_e. \tag{11}$$

Here k_d is the effective rate constant of dissociation of O_2 molecules by shocking electrons, which depends on the electric-field strength; n_e is the concentration of electrons. The parameter A has the dimension [sec^{-1}] and, consequently, represents an effective frequency of dissociation averaged over the volume of a plasmachemical reactor. For the numerical solution of the equations of chemical kinetics, we used the Gear method intended for rigid systems of differential equations.

Generally speaking, the parameter A defined by formula (11) depends on many conditions; it is different for different types of gas discharges. According to our estimates, its characteristic values for stationary low-pressure
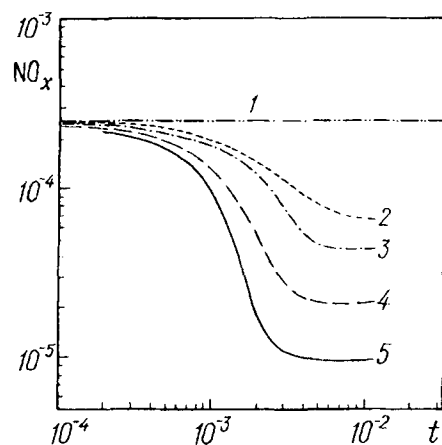
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Fig. 2. Decrease in nitrogen oxide with time at $A = 10 \text{ sec}^{-1}$ and different temperatures of the mixture: 1) initial concentration of NO (molar fractions); 2) $T = 550$ K; 3) 500; 4) 450; 5) 400. t, sec; NO_x, molar fractions.

discharges, such as a glowing discharge, are equal to $0.1-0.5 \text{ sec}^{-1}$ in pure nitrogen [9] and to $\sim1-3 \text{ sec}^{-1}$ in oxygen [10]. For a modified glowing discharge in air sustained at pressures of the order of atmospheric pressure and at $E/N = 80-100$ Td, the value of the parameter A increases up to $30-50 \text{ sec}^{-1}$ [11]. In the case of a stationary corona in air in the region near a corona-forming electrode, the characteristic values of the parameter A change within the limits $10-500 \text{ sec}^{-1}$ [5, 12]; in a barrier discharge in oxygen they can be equal to about 10^2 sec^{-1} [6]. The parameter A attains the maximum value ($\sim10^4-10^5 \text{ sec}^{-1}$) in the head of a nanosecond corona discharge streamer in air [3, 13, 14]. However, the characteristic times of the occurrence of chemical reactions considerably exceed the time of the streamer development. Thus, having evaluated the parameter A in solving the equations of chemical kinetics, we can make recommendations on the type of discharge that should be preferred in purification.

We considered a kinetic scheme consisting of 83 gas-phase reactions for 32 chemical components. Reaction-rate constants were calculated on the basis of [4, 5]. The fundamental reactions used in calculations are listed in Table 2.

For estimating energy expenditures on purification, the characteristic value for current density in a stationary corona discharge was assumed to be equal to $j = 10 \text{ mA/cm}^2$ [15]. The power input was evaluated by the formula

$$W = jE/N ,\tag{12}$$

where E/N is the value of the reduced electric field, Td.

The corresponding value of energy contribution per NO molecule removed was determined from the formula

$$W_m = 897 \frac{W}{\Delta n \cdot 10^6} ,\tag{13}$$

where Δn is the difference between the initial and final concentrations of NO_x; W is the power input, $\text{W} \cdot \text{h/m}^3$.

The evolution of the main components of the mixture with time for a temperature of 350 K is shown in Fig. 1. The active O and OH particles react with the NO molecules (reactions (2) and (3)) and convert them into NO_2 and HNO_2 in a time of the order of 10^{-4} sec. As is known, HNO_2 molecules are unstable at temperatures above 100°C and decompose into NO and NO_2 [3]. The nitrogen dioxide NO_2 react with the OH radicals with the formation of HNO_3 (reaction (9)). The characteristic time of this process is 10^{-2} sec at a given temperature. Thereafter the concentration of NO increases, which can be explained by the competition between the processes of NO oxidation and the nitrogen oxide formation reactions when active components interact with the N atoms and NO_2 molecules (reactions (7) and (8)). As the temperature increases, the efficiency of NO_x oxidation drops, as is evident from Fig. 2, since the rate constants of reactions (3) and (5) decrease with an increase in temperature
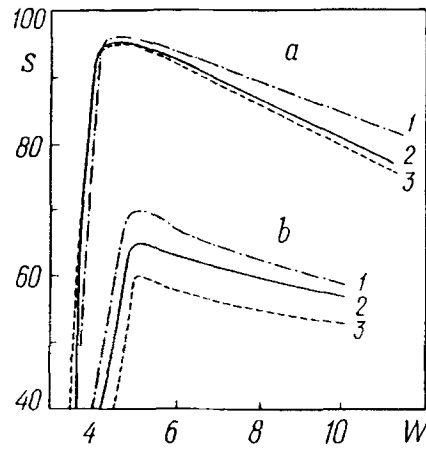
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Fig. 3. Degree of conversion (%) of nitrogen oxides depending on the power input at a temperature of 350 K (a) and 500 K (b) at different initial concentrations of H_2): 1) 3%; 2) 6; 3) 10. S, %; W, W·h/m^3.

according to the laws $T^{-2.4}$ and $T^{-1.3}$. An increase in temperature also stimulates the processes of "demise" of active OH particles during the formation of hydrogen peroxide in the reaction

$$OH + OH + M = H_2O_2 + M .$$ (14)

The dependence of the efficiency of NO oxidation on the power applied at a temperature of 350 K and characteristic time 10^{-2} sec is shown in Fig. 3. With an increase in the input of energy, the influence of the processes leading to the recovery and additional formation of NO increases (reactions (7) and (8)), and this decreases the efficiency of oxidation. At small values of W the percentage of oxidized NO is small. We can select an optimal value of energy input corresponding to 5 W·h/m^3 at which up to 95% of NO_x can be removed. Such an energy input is realizable at an electric field magnitude of $E/N = 80$ Td under the given conditions. In this case, the parameter A is equal to 10 sec^{-1}, which is close to the values in a stationary corona discharge. The corresponding value $W_m = 18$ eV/(NO) is in good agreement with the experimental value obtained in [3].

As indicated above, intense oxidation of NO occurs in processes with participation of OH radicals; therefore, it is necessary to determine the influence of the initial concentration of water on the efficiency of the removal of nitrogen oxides. It is shown in Fig. 3 that as the concentration of H_2O decreases, a higher degree of conversion of NO is observed, since the processes of recovery, which play an important role with an increase in power input, require for their initiation a rather high concentration of OH radicals. An increase in the initial concentration of water above a certain limit (Fig. 3) does not influence the efficiency of NO oxidation.

Thus, in the present work, we showed theoretically the possibility of effective application of gas discharges for removing nitrogen oxides from a mixture of exhaust gases of a diesel engine. The results obtained allow the following conclusions to be drawn.

1. The addition of water vapor to a gas mixture substantially increases the efficiency of oxidation of NO molecules. The most intense oxidation of nitrogen oxides is observed at the ratio $O_2:H_2O = 3:1$. A further increase in the initial concentration of water leads to a decrease in the degree of conversion.

2. An increase in the temperature of a gas mixture stimulates the processes of the formation of nitrogen oxide; therefore, the optimum temperature is selected to be 350 K, at which up to 95% of the initial concentration of NO_x is removed.

3. The characteristic time of the NO oxidation process at $T = 350$ K, atmospheric pressure, and $A = 10$ sec^{-1} is equal to 10^{-2} sec. This value allows one to determine the length of a plasmachemical reactor.

4. The maximum degree of conversion of NO_x is attained at a power input of 5 W·h/m^3. The value of the parameter A in this case is equal to 10 sec^{-1}; consequently, a stationary corona discharge can be used for purification.

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NOTATION

T, temperature, K; t, lifetime of particles in a reactor; E/N, reduced electric field, Td ($1 \text{Td} = 10^{-17}$ $\text{W} \cdot \text{cm}^2$); E, electric field strength, W/cm; N, concentration of neutral particles, cm^{-3}; R, rate of reactions; k, chemical reaction rate constant, cm^3/sec for binary reactions and cm^6/sec for thermomolecular reactions; M, a neutral molecule participating in three-particle collisions; n, concentration of components; Y, molar fractions; S, degree of conversion; W, power input, $\text{W} \cdot \text{h}/\text{m}^3$; W_m, energy expenditures per NO molecule; z, direction along the discharge tube of a reactor; v, velocity of gas flow along the discharge tube; ν_{ij}, stoichiometric coefficients of the jth reaction with participation of the ith component. Subscripts: m, refers to a molecule; i, number of a gas-phase component; j, number of a chemical reaction; d, dissociation process; e, electronic process.

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