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CLASSIFICATION OF METHODS FOR SANITARY PURIFICATION OF GASES FROM NITROGEN OXIDES

Nitrogen oxides are among the most common and dangerous air pollutants. Their main amount is formed during high-temperature combustion of organic fuels in thermal power plants. Sources of nitrogen oxide emissions into the atmosphere differ in the amount of exhaust gases, the content of nitrogen compounds and other impurities, as well as the degree of oxidation of nitrogen oxide (II) (NO)*, temperature and pressure. In order to systematize the developed methods and conduct targeted research in this area, a classification of methods for sanitary purification of gases from nitrogen oxides was carried out. This classification is based on the ability of nitrogen oxides to oxidize, reduce, sorb and form substances that are easily regenerated under various conditions. The processes of* NO *oxidation using liquid, solid and gaseous oxidants were studied. Kinetic equations were obtained that describe the rate of this process depending on the concentration of solutions, temperature and pH of the medium. A high-temperature method has been developed in which thermal decomposition of nitrogen oxides occurs in the temperature range from 500 °C to 5000 °C using an arc plasmatron with a tungsten cathode and a copper anode. The catalytic properties of natural and artificial materials for increasing the rate of* NO *oxidation have been studied. It has been established that the reaction of heterogeneous catalytic oxidation of* NO *has a positive temperature coefficient. Catalysts capable of increasing the reaction rate by 1.5–2.5 times have been proposed. The considered purification methods can be used in the nitric acid industry during the operation of large units to achieve the maximum permissible concentration (MPC) standards in the surface layer of the atmosphere.*

Key words: *sanitary gas purification, nitrogen oxides.*

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КЛАСИФІКАЦІЯ МЕТОДІВ САНІТАРНОГО ОЧИЩЕННЯ ГАЗІВ ВІД ОКСИДІВ НІТРОГЕНУ

Оксиди нітрогену належать до найпоширеніших і найнебезпечніших забруднювачів повітря. Основна їх кількість утворюється під час високотемпературного спалювання органічного палива в теплоенергетичних установках. Джерела викидів оксидів нітрогену в атмосферу різняться за кількістю відхідних газів, вмістом сполук нітрогену та інших домішок, а також за ступенем окиснюваності оксиду нітрогену (II) (NO), *температурою і тиском. З метою систематизації розроблених методів і цілеспрямованого проведення досліджень у цій галузі було здійснено класифікацію методів санітарного очищення газів від оксидів нітрогену. Ця класифікація базується на здатності оксидів нітрогену окиснюватися, відновлюватися, сорбуватися та утворювати речовини, які легко регенеруються за різних умов. Досліджено процеси окиснення* NO *за допомогою рідких, твердих і газоподібних окиснювачів. Отримано кінетичні рівняння, які описують швидкість цього процесу залежно від концентрації розчинів, температури та pH середовища. Розроблено високотемпературний метод, у якому термічний розклад оксидів нітрогену відбувається в діапазоні температур від 500 °С до 5000 °С із використанням дугового плазмотрона з вольфрамовим катодом і мідним анодом. Досліджено каталітичні властивості природних і штучних матеріалів для підвищення швидкості окиснення NO. Встановлено, що реакція гетерогенного каталітичного окиснення* NO *має позитивний температурний коефіцієнт. Запропоновано каталізатори, здатні збільшувати швидкість реакції в 1,5–2,5 рази. Розглянуті методи очищення можуть застосовуватися в азотно-кислотній промисловості під час експлуатації великих агрегатів для досягнення норм гранично допустимої концентрації (ГДК) у приземному шарі атмосфери.*

Ключові слова: *санітарне очищення газів, оксиди азоту.*

Problem statement

Pollution of the Earth’s atmosphere or pollution air occurs when harmful or excessive amounts of substances, including gases (such as carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen oxides, methane, and chlorofluorocarbons) enter the Earth’s atmosphere [1]. On the basis of this, the limit-permissible concentrations (LPC) for a number of the most common pollutants are established [2, 3]. Visual evidence of the influence of atmospheric air pollution on human health is provided by statistical data on mass diseases of the population in large industrial cities and cases of catastrophic consequences caused by atmospheric pollution [4]. Nitrogen oxides are among the most widespread and dangerous air pollutants on our planet [5]. There are seven oxides of nitrogen that may be found in the ambient air. However, nitric oxide (NO) and nitrogen dioxide (NO_2) are the two principal nitrogen oxides associated with combustion sources. Ambient concentrations of these two gases vary widely according to local sources and sinks, but can exceed a total concentration ($NO + NO_2$) of 500 mg/m^3 in dense urban areas [6]. Exhaust gases, which include nitrogen oxides, are formed in a number of chemical industries, in oil refining processes, when burning different types of fuel at high temperatures.

Much attention is paid to the problem of cleaning waste gases from harmful substances, but the pace of scientific research in this area lags behind the pace of industrial development [7]. This problem needs to be solved in a short period of time. I have developed effective methods and equipment for cleaning waste gases.

Analysis of the latest research and publications

Analyzing the methods of sanitary cleaning of gases from nitrogen oxides, it can be said that the variety of sources of nitrogen oxide emissions into the atmosphere differ in many parameters [8, 9, 10]. For example, the amount of exhaust gases, the content of nitrogen oxides and other impurities in them, the degree of oxidation of NO, temperature, pressure.

Nitrogen monoxide (NO) is a non-salt-forming, indifferent compound and hardly reacts with most of the known absorbers. In this regard, the preliminary oxidation of NO into NO_2 and N_2O_3 is necessary for more complete extraction of nitrogen oxides from gas mixtures. In industry, the method of homogeneous oxidation of NO in the gas phase using oxygen is used [11]. However, as practice shows, at low concentrations of NO, the rate of homogeneous oxidation of nitrogen oxides is extremely low. From the kinetic equation

$$\frac{d\mathrm{NO}_2}{d\tau} = KP_{\mathrm{NO}}^2 \cdot P_{\mathrm{O}_2}$$

it can be seen that with a decrease in the concentration of NO, for example, from 1.0 % to 0.1 %, i. e. by 10 times, the rate of the oxidation reaction decreases by 100 times. This leads to the necessity of installing bulky and expensive oxidation structures. Sometimes, to intensify the process, oxygen is added to the nitrous gas, increasing its content to 8–10 %. Such a method is not effective due to the extremely small increase in the degree of purification and the low degree of use of dosed oxygen (not more than 0.1–0.5 %). To reduce the concentration of nitrogen oxides in exhaust gases from 0.3 % to 0.15 %, it is necessary to increase the oxygen content in the gas from 3–5 % to 8–10 %, i. e. add about 5000 m^3/h of oxygen. Moreover, only 25–30 m^3/h of oxygen reacts with NO, and the remaining 4870 m^3/h are released into the atmosphere. Developed more effective methods of increasing the rate of oxidation of NO, it is possible to achieve a high degree of purification of gases from nitrogen oxides.

It should be noted that at atmospheric pressure, even highly oxidized nitrous gas, which has a degree of NO oxidation of more than 50 %, cannot be completely extracted from gas mixtures by absorption methods. The final content of nitrogen oxides in exhaust gases is, as a rule, 0.02–0.05 %. Therefore, the sanitary norm of cleaning gases from nitrogen oxides during the oxidation of NO by oxygen in the gas phase can be provided for systems that emit no more than 30–50 thousand m^3 of gas per time. Further intensification of the process of oxidation and absorption of nitrogen oxides is possible with an increase in the rate of oxidation of NO in the liquid phase, or in the presence of catalysts.

The purpose of the work are systematization and classification of existing and new methods of cleaning atmospheric air from nitrogen oxides.

The classification is based on the following physical and chemical properties of nitrogen oxides:

- the ability of nitrogen oxides to be oxidized under the action of liquid, solid and gaseous oxidants;
- the ability of nitrogen oxides to be reduced to molecular nitrogen under the influence of high temperatures, as well as in the presence of liquid, solid and gaseous reducing agents and catalysts;
- the ability of nitrogen oxides to enter into chemical reactions with various groups of substances with the formation of salts and complex compounds that can be regenerated.

According to the proposed classification (Fig. 1), the considered methods of cleaning gases from nitrogen oxides are divided into four classes: oxidative, reducing, sorption, and other methods. Each class is divided into four groups. Each group combines a number of similar cleaning methods. Both existing and new methods of sanitary purification of gases from nitrogen oxides fit into the scheme of the proposed classification.

Oxidative methods of sanitary purification of gases from nitrogen oxides are based on preliminary oxidation of NO with subsequent absorption of NO_2 and N_2O_3 by various absorbers. Conducting numerous experiments on absorption by various absorbers, it was noted that the degree of absorption usually exceeded the theoretically possible. With alkaline absorption of nitrous gas containing 1 % of nitrogen oxides with a degree of oxidation of 30 %, the theoretically possible degree of absorption should be 60 %. It was established by calculation that in the process of absorption, an additional homogeneous oxidation of NO in the gas phase takes place by another 5 %. Consequently, the total possible degree of absorption should be 65 %. In fact, it was possible to obtain an absorption rate of 80–90 % or more in the experiments.

It is possible to conclude that in the process of absorption, the oxidation of nitrogen oxide occurs not only in the gas phase, but also in the liquid phase [12, 13]. This important fact formed the basis of further research conducted under conditions favorable to the process of oxidation of nitrogen oxides in the liquid phase. This gives great advantages, since the amount of the liquid phase in the exchange process is hundreds and thousands of times less than the gas phase. Due to this, technological operations with liquid can be carried out in significantly smaller reaction volumes. Oxidative processes occurring in parallel in liquid and gas media have different speeds. In a liquid environment, the speed is lower than in a gaseous environment. The amount of NO oxidized in the liquid is approximately 50 %. It has been established that for

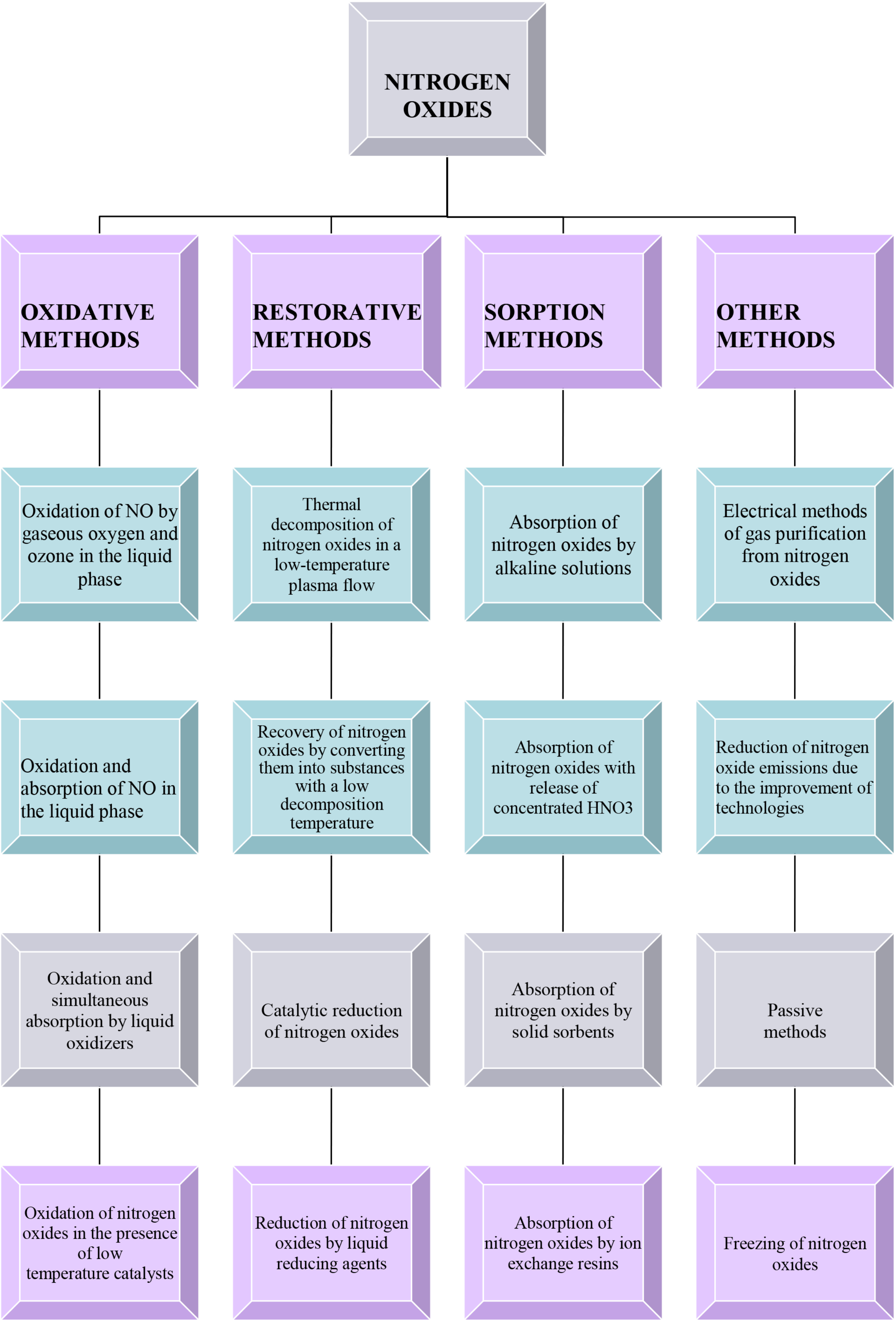

Fig. 1. Classification of methods of sanitary cleaning of gases from nitrogen oxides

the intensification of the oxidation process during the absorption of nitrogen oxides from low-concentration and low-oxidized gases into the gas phase, it is expedient to dose oxygen, bringing its concentration to 6–7 %. A further increase in the concentration of O_2 in nitrous gas is ineffective. Intensification of the process of absorption of nitrogen oxides is possible only by simultaneously increasing the share of NO oxidized in the liquid phase, which is achieved by saturating the working solution with oxygen in the remote reactor.

Absorption methods are a process of selective gas absorption by a liquid. Two phases are involved in absorption processes – liquid and gas. At the same time, the transition of the substance from the gas phase to the liquid phase (during absorption) or, conversely, from the liquid phase to the gas phase (during desorption) occurs. Thus, absorption processes are one of the types of mass transfer. Absorption occurs only if the partial pressure of the absorbed component in the gas phase is greater than the equilibrium partial pressure of the same component above the given solution. The greater the difference between these pressures, the greater the driving force of the process and the faster absorption occurs. The limit state of the system is the achievement of equilibrium, i. e., when only reversible processes are possible.

Physical absorption and chemisorption are distinguished. During physical absorption, the gas is held in the liquid only due to mechanical (physical) bonds and it is not accompanied by a chemical reaction, while during chemisorption, a chemical reaction occurs between the components.

Processes of sanitary purification of gases from nitrogen oxides are based on preliminary oxidation of nitrogen oxide (II) with subsequent absorption of nitrogen oxides (IV) and (III) (NO_2 and N_2O_3) by various absorbers [14]. The limiting stage of the process is the rate of oxidation of nitrogen oxide (II) to nitrogen oxide (IV). Since this reaction takes place in the gas phase, the absorption apparatus must have a sufficiently large free volume, so the absorption process is carried out in multistage packing or plate columns. In experiments on the absorption of nitrogen oxides by various liquid absorbers, the degree of absorption is 80–90 %. In the process of absorption, nitrogen oxides are oxidized not only in a gaseous but also in a liquid medium. The parameters aimed at the intensification of the oxidation process of nitrogen oxide (II) in the liquid phase were investigated, and the rates of NO oxidation in the gas and liquid phases were also compared.

In industry, the method of homogeneous oxidation of NO in the gas phase with the help of oxygen is used. However, as practice shows, at low concentrations of NO, the rate of homogeneous oxidation of nitrogen oxides is extremely low.

One of the methods of intensification of the process of absorption of nitrogen oxides is the oxidation of nitrogen monoxide by oxidants stronger than oxygen, for example, ozone or an ozone-oxygen mixture. The use of ozone is inappropriate due to the low efficiency and high cost of ozone. Studies with the introduction of ozone into the liquid phase showed that in this case ozone acts not only as an oxidizer, but also as a catalyst, which increases the degree of oxidation of nitrogen oxide (II) and the relative rate of absorption by one and a half times. When nitrogen oxides are absorbed by nitric acid, regardless of its initial concentration, the introduction of a small amount of ozone into the liquid phase increases the speed of the absorption process and the degree of oxidation (Table 1).

Table 1

Effect of ozone in the liquid phase on the oxidation of nitrogen oxide (II)

	The maximum concentration of obtained HNO_3, %	Relative rate of absorption
Ozone-free	53	1.0
With ozone in the liquid phase (0.16 %)	60	1.5

Intensification of the process of homogeneous oxidation of nitrogen oxides in the liquid phase by gaseous oxidants (oxygen or ozone) is associated with the diffusion of oxidants into the liquid phase. Diffusion of oxygen into the solution is the slowest stage of homogeneous oxidation of nitrogen oxides in the liquid phase, and therefore it controls the entire process.

The rate of diffusion of gaseous oxidizers in the liquid phase depends on many factors: temperature, pressure, concentration of components, turbulence of flows. To increase the rate of homogeneous oxidation of NO in the liquid phase, it is necessary to influence the system by changing one or more of the listed parameters.

The rate of the NO oxidation reaction can be increased if it is carried out in the liquid phase with the help of liquid oxidizers. In this case, the oxidants are in a liquid state, and the reaction rate will not depend on the diffusion rate of the oxidants in the solution. Thus, the slowest stage of the process is eliminated.

A number of liquid oxidizing agents are known, which are superior in their activity to oxygen. These include aqueous solutions of H_2O_2, $KMnO_4$, $KBrO_3$, $K_2Cr_2O_7$, $(NH_4)_2Cr_2O_7$, Na_2CrO_4, $KClO_4$, $NaClO_2$, $K_2S_2O_3$, $(NH_4)_2S_2O_8$, NH_4ClO_4, $K_2Cl_2O_7$, $K_2S_2O_7$, HNO_3. Some of these oxidizers are of theoretical and practical interest for the process of oxidation of nitrogen oxide (II) for the purpose of sanitary gas purification. To study the NO oxidation process, the following liquid oxidants were taken: H_2O_2, $KMnO_4$, $KBrO_3$, $K_2Cr_2O_7$, Na_2CrO_4, $(NH_4)_2Cr_2O_7$, NaOCl, HNO_3 and royal jelly vodka. To find out the principle possibility of interaction of nitrogen oxides with the listed liquid oxidants, thermodynamic parameters were calculated [15].

Analysis of the results of thermodynamic calculations ΔH° indicates the principle possibility of the process of oxidation of nitrogen oxides by liquid oxidants. The greater the numerical value of the equilibrium constant and the decrease in enthalpy, the more complete the reaction can proceed in the forward direction. Large values of equilibrium constants allow us to conclude that these reactions proceed almost to the end.

Experimental determination of the rate of oxidation and absorption of nitrogen oxides was carried out on a mechanized experimental setup [16]. In contrast to oxidation in the gas phase, the rate of oxidation by liquid oxidizers also increases with increasing temperature. The positive temperature coefficient of the reaction is explained by the fact that during the oxidation of NO in the liquid phase, the intermediate reaction of formation of dimer N_2O_2 does not occur, which with increasing temperature shifts to the left, towards the decomposition of N_2O_2 and controls the overall process of oxidation of NO.

An important role is played by the fact that the rate of decomposition of liquid oxidants increases with increasing temperature, with the release of atomic oxygen and active oxygen-containing ions or radicals, which oxidize nitrogen oxide at a high rate. The high oxidizing power of atomic oxygen, oxygen-containing radicals and ions is observed only at the time of release, after which they lose their activity. Here it should be taken into account that some oxidation reactions with liquid oxidants proceed quite quickly even at room temperature. An increase in temperature in this case leads to rapid decomposition of the oxidizer. The released atomic oxygen and other active compounds do not have time to react with nitrogen oxide in the liquid phase, and, passing into the gas phase, lose their activity.

On the basis of studies conducted under standard conditions, a range of activity of six liquid oxidizers has been established, which decreases in the following sequence:

$$KBrO_3 > KMnO_4 > H_2O_2 > Na_2CrO_4 > (NH_4)_2Cr_2O_7 > K_2Cr_2O_7.$$

The reaction rate coefficients for aqueous solutions with a mass fraction of oxidizing agents of 3 % respectively have the following values, mol/(dm^3 · s):

$$620 \cdot 10^{-6} > 365 \cdot 10^{-6} > 338 \cdot 10^{-6} > 204 \cdot 10^{-6} > 60 \cdot 10^{-6} > 30 \cdot 10^{-6}.$$

The oxidizing power of oxidizers differs significantly. An aqueous solution of potassium bromate ($KBrO_3$) turned out to be the most active of the tested oxidants in relation to NO.The effect of the concentration, temperature, and pH of the medium on the rate of oxidation by liquid oxidizing agents of nitrogen oxide (II) was studied. Research was conducted by the method of a full factorial experiment.

As a result of the processing of experimental data, equations describing the rate of oxidation of NO by liquid oxidizers depending on the concentration of solutions, temperature, and pH of the medium were obtained. These equations have the form:

– for potassium bromate $KBrO_3$

$$U_{KBrO_3} = -\left[432{,}65 + 76{,}25C_{KBrO_3} - 4{,}437t + 4{,}17\,pH\right]\cdot 10^{-6}\ \text{mol/(dm}^3\cdot\text{s)};$$

– for potassium permanganate $KMnO_4$

$$U_{KMnO_4} = \left[137{,}5 + 64{,}75C_{KMnO_4} + 1{,}137t + 2{,}833\,pH\right]\cdot 10^{-6}\ \text{mol/(dm}^3\cdot\text{s)}$$

– for hydrogen peroxide H_2O_2

$$U_{H_2O_2} = \left[29{,}99 + 176{,}25C_{H_2O_2} + 183{,}75t + 69{,}99\,pH\right]\cdot 10^{-6}\ \text{mol/(dm}^3\cdot\text{s)}$$

Thermal methods. One of the effective methods of neutralizing nitrous gases is the decomposition of nitrogen oxides. The difficulty of implementing this reaction lies in the necessity of heating the gas mixture. Theoretical studies and technical and economic calculations were carried out for low-power systems with a high content of nitrogen oxides in the exhaust gases. Using thermal methods, nitrogen oxides can be decomposed into harmless substances N_2 and O_2. This method is characterized by simplicity, compactness, insignificant capital and operating costs.

Oxygen compounds of nitrogen can exist in the form of the following oxides: nitrogen oxide (I) N_2O, nitrogen oxide (II) NO, nitrogen oxide (IV) NO_2, nitrogen oxide (III) N_2O_3, nitrogen oxide dimer (IV) N_2O_4, nitrogen oxide (V) N_2O_5. There are also unstable compounds – nitrosylazide N_4O, trinitramide $N(NO_2)_3$ and nitrate radical NO_3^-. Depending on the valence of nitrogen, its oxygen compounds have different compositions and, accordingly, different physical and chemical properties. So, for example, the dimer of nitrogen oxide (IV) is an active substance that reacts with almost all organic and inorganic compounds, while nitrogen oxide (II) is a weakly active substance. The degree of oxidation of nitrogen in the above-mentioned compounds is largely determined by temperature. Depending on the temperature, different nitrogen oxides can exist. In the presence of an oxidizer (oxygen or ozone) and a low temperature, the oxidation reaction of nitrogen oxide (II) proceeds spontaneously and irreversibly in the following direction: $NO + NO_2 \rightarrow N_2O_4 \rightarrow N_2O_5$.

Nitrogen oxide (V) can exist in a solid state even at low temperatures. Solid N_2O_5 in its stable form is nitronium nitrate (NO_2NO_3). When heated in gaseous form, it decomposes into NO_2^+ and NO_3^-. NO_3^- – is easily oxidized, giving off an oxygen atom. Nitric oxide (IV) easily dimerizes by the reversible reaction: $2NO_2 \rightleftarrows N_2O_4$.

The degree of polymerization also depends on the temperature. Already at a temperature of 21.15 °C, liquid N_2O_4 decomposes into NO_2 molecules. And at a temperature above 140 °C, the reaction completely shifts to the right and only NO_2 can exist in the gas phase. Upon further heating of nitrogen oxide (IV), it decomposes: $2NO_2 \rightleftarrows 2\,NO + O_2$. Complete decomposition of nitrogen oxide (IV) into nitrogen oxide (II) occurs at a temperature of 600 °C. Nitrogen oxide (II) is quite stable. However, at a temperature above 1000 °C, it decomposes: $2NO \rightleftarrows N_2 + O_2$.

The temperature range of the existence of various nitrogen oxides in the gas phase can be represented by the following diagram:

$$N_2O_4 \xrightarrow{21{,}5\text{–}140\,^{\circ}C} NO_2 \xrightarrow{150\text{–}600\,^{\circ}C} NO \xrightarrow{600\text{–}1000\,^{\circ}C} N_2 + O_2$$

Heating higher nitrogen oxides leads to their decomposition into lower ones. Ultimately, to molecular nitrogen and oxygen. This regularity is the basis of the developed method of thermal decomposition of nitrogen oxides. The reaction of formation and decomposition of nitrogen oxide (II) is reversible:

$$2N_2 + O_2 \rightleftarrows 2NO - 43140 \text{ cal } (179.9 \text{ J}).$$

From the point of view of the neutralization of nitrous gases, the final equilibrium concentration of nitrogen oxides, which is reached by simple thermal decomposition, is too high, and the time to establish the equilibrium concentration in the region of low temperatures is too large. By heating nitrous gas to a temperature of 2000 °C, it is possible to reduce the concentration of nitrogen oxides to 1.34 %. This process takes just 1 second. To reduce the concentration to 0.02 %, it will take time of $4 \cdot 10^5$ s, which is impossible in real conditions, because it will be connected with the installation of a reactor with a volume of about 1000 m^3 per 1 m^3 of nitrous gases. The rate of formation of nitrogen oxides is directly proportional to the content of oxygen in the mixture. If in the process of decomposition of nitrogen oxides, the formed oxygen is removed (bound) from the system, then the rate of formation of nitrogen oxides and the equilibrium concentration can be reduced. This property is used in the method of thermal decomposition of nitrogen oxides. Gaseous, liquid, and solid reducing agents can be used as components that bind oxygen. Such as: hydrogen, carbon monoxide, methane, ammonia, kerosene, gasoline, fuel oil, coke, coal, graphite. The same combustible components are used to heat the gas to the decomposition temperature. They studied the process of thermal decomposition of nitrogen oxides in the temperature range from 500 °C to 5000 °C [17]. To achieve such temperatures, an arc plasmatron with a power of 20 kW was used with a tungsten cathode and a copper anode, which were cooled by running water. Nitrogen oxides, the amount of which corresponded to the given concentration of NO in the gas mixture, were injected into the operating plasmatron. The mixture was heated to a temperature of 2000–4000 °C. At such a temperature, oxides decompose into nitrogen and oxygen molecules. The initial concentration of nitrogen oxides in these experiments ranged from 0.001 % to 10 %, and the average temperature in the reactor was 2000 ÷ 2100 °C. The temperature in the reactor was determined by calculation based on the heat balance of the plasmatron. As the concentration of nitrogen oxides increases, the degree of their decomposition increases. So, for example, with an initial concentration of nitrogen oxides N_xO_y the gas mixture of 5 %, the degree of decomposition was 52 %. When the initial concentration of nitrogen oxides increased from 5 % to 10 %, the degree of their decomposition increased to 77 %. At the same time, the concentration of N_xO_y the outlet remained at the level of 2.4 %.

Oxidation of nitrogen oxides in the presence of low-temperature catalysts. It is known that the rate of oxidation of nitrogen oxide by gaseous oxygen increases in the presence of some solid catalysts. Catalysts prepared on the basis of precious metals show the greatest activity. The catalytic properties of natural and artificial materials were investigated with the aim of using them in industry to increase the rate of NO oxidation. Research was carried out at a facility consisting of two reactors: a reactor for the oxidation of NO and a reactor for the absorption of nitrogen oxides. Based on the amount of absorbed nitrogen oxide, it is possible to state the degree of oxidation of NO, assuming that the degree of absorption is directly proportional to the degree of oxidation of the gas. When studying the influence of catalysts on the oxidation of nitrogen oxides, it was revealed that the conditions of the process significantly affect the speed. The parameters were changed within the following limits: NO concentration ($C_{NO} = 1 \div 2.25$ %); concentration of O_2 ($C_{O_2} = 5 \div 20$ %); contact time ($\tau = 0.52 \div 1.26$ s); temperature t (26 ÷ 30 °C); the initial degree of oxidation of NO ($d_o = 25$ %).

As catalysts, large-porous and small-porous silica gel, vanadium catalyst, hopkalite on a ceramic carrier, manganese oxide (IV) MnO_2, aluminogel, carboaluminogel, catalysts NTK-4, GIAP-10, coke, charcoal from apricot pits and a number of catalysts obtained by impregnation of coke with catalytically active substances. It was found that some catalysts are able to increase the rate of the heterogeneous oxidation reaction by 1.5–2.5 times. The reaction of heterogeneous catalytic oxidation of nitrogen oxide has a positive temperature coefficient, which is due to the manifestation of increased catalytic activity of catalysts with increasing temperature. Of all the tested catalysts for NO oxidation, the most effective were: hopkalite, which increased the degree of absorption of nitrogen oxides by 2.51 times, carboaluminum gel by 1.91 times, silica gel by 1.46 times, coal (from apricot pits) by 1.31 times, and coke by 1.17 times [16].

With more complete studies of hopcalite, it was found that its significant catalytic activity is manifested already at a temperature of 50 °C. Increasing the temperature above 80–100 °C is impractical due to the large amount of heat required to heat the gas and its subsequent cooling before absorption. With the growth of gas volume velocity, the amount of oxidized NO decreases. This is due to a decrease in the residence time of NO in the catalysis zone. With an increase in the concentration of O_2 and NO, an increase in the rate of oxidation is observed.

Increasing the degree of oxidation of NO by adding nitrogen oxide (IV) gas. Nitrous oxide (III) obtained in this way can be absorbed by one of the known methods.

To increase the degree of oxidation of NO from α_1 to α_2, it is necessary to introduce nitrogen oxide (IV), the amount of which can be determined from the equation:

$$\Delta V_{\mathrm{NO_2}} = \frac{V_r \cdot C_r}{100}\left(\frac{\alpha_2 - \alpha_1}{1-\alpha_2}\right)\mathrm{m^3/h},$$

where V_r and C_r are, respectively, the quantity (m^3/h) and concentration of the initial gas mixture (%).

The concentration of gas after dosing NO_2 and depending on the required degree of oxidation of the gas will $C_r' = C_r\left(\frac{1-\alpha_1}{1-\alpha_2}\right)$. This method of NO_2 dosing is acceptable only for systems with a low initial gas concentration (0.1–0.5 %) and a low degree of NO oxidation. Economically, it is more favorable than the method of oxidation of NO to N_2O_3 in oxidizing devices.

Conclusions

The processes of oxidation of nitrogen oxide (II) by liquid, solid and gaseous oxidants were studied. The influence of various parameters on oxidation processes was investigated. It has been proven that an increase in temperature accelerates oxidation processes in the liquid phase in contrast to oxidation in the gas phase. It was established that by introducing gaseous reducing agents, the reaction of high-temperature decomposition of nitrogen oxides can be shifted to the side of their disintegration into simple harmless components. It is determined that the reaction of heterogeneous catalytic oxidation of nitrogen oxide has a positive temperature coefficient. Catalysts are proposed that can increase the reaction rate by 1.5–2.5 times.

A systematic classification of existing and new methods of sanitary purification of atmospheric air from nitrogen oxides has been developed. These cleaning methods can be used in the nitric acid industry, especially when operating large units, to achieve MPC standards in the surface layer of the atmosphere.

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