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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Nitrous Oxide: Properties, Producing, Grounds of Manipulations, and Fields of Application

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Abstract—-Published in different sources and obtained experimentally and by calculation data on the physicochemical characteristics, existing methods of producing, principles of manipulation and possible fields of application of nitrous oxide as chemical product are considered.

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Nitrous oxide was for the first time obtained more than 200 years ago (in 1793) by English scientific Joseph Priestley. However, in spite of well studied physicochemical properties, it for long time did not find practical application. Only 50 years later after discovery, because of the anesthesiological properties, it began to use in medicine.

In the period of the rapid development of rocket and space technology it was paid attention to the high-energy characteristics of nitrous oxide, its ability to exhibit strong oxidizing properties and to decomposition into nitrogen and oxygen in 2 : 1 ratio, which was close to the air composition. Owing to these properties nitrous oxide could be recommended as a rocket propellant (RP), and on this basis were developed single-component and two-component low trust rocket engines for the operation system of cosmic apparatuses (CA), and also the gas generators used for providing the vital activity of man in a locked space and for obtaining high-energy nitrogen in the laser installations. Recently nitrous oxide attracts attention of technologists as highly effective oxidizer for different chemical processes. Below are presented the physicochemical properties of nitrous oxide characterizing it as a promising chemical compound, which successfully can be used in the chemical industry and in the new technology.

PROPERTIES OF NITROUS OXIDE

Physical Properties

Under the normal conditions the nitrous oxide (nitrogen hemioxide) is a colorless gas with specific pleasant weak smell and sweet taste. It is liquefied, and in the cylinders is stored in the liquid state under the pressure. Formula N_2O; molecular weight 44.01; molecular volume at 0°C and 0.1 MPa 22.25 l.

Previously it was considered that the molecule of nitrous oxide had symmetrical structure. At present is accepted that it slightly polar ($\mu = 0.17$) and has linear asymmetric structure: $N{\equiv}N{=}O$. Bond lengths in the molecule: N–N 1.125 Å; NO 1.186 Å.

Electronic configurations of molecule N_2O correspond to the resonance of structures:

$$:\underset{\cdot\cdot}{\overset{-}{N}}=\overset{+}{N}=\underset{\cdot\cdot}{O} \leftrightarrow :N=\overset{+}{N}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$$

Ionization potential of N_2O is 12.6 eV. The power constants of valence bond are equal to 18.2 ($N{\equiv}N$) and 12.0 ($N{=}O$).

In free state the nitrous oxide is the constant component of air (0.00005 vol %).

The properties of nitrous oxide are sufficiently well studied and published in different sources [1–8]. Below are represented some of its physicochemical constants which in the different sources differ somewhat from each other.

Thermophysical properties:
– boiling point –88.7°C (184.7 K);
– melting point (freezing) –90.7°C (182.3 K).
Critical parameters:
– temperature 36.6°C (309.6 K);

– pressure 7.25 MPa;
– density 454 kg m^{-3};
– volume 0.0973 dm^3 mol^{-1} (2.21 l/kg).

Parameters of the triple point:
– pressure 87.9 kPa (658.9 mm Hg);
– temperature –90.6 °C (182.4 K).

Heat of formation of gas phase in the standard state (enthalpy):
at –273°C (0 K) 85.029 kJ mol^{-1};
at 16.18°C (289.18 K) 81.6 kJ mol^{-1};

heat of decomposition (standard) at 298°C 81.5 kJ mol^{-1};
heat of melting 6.54 kJ mol^{-1};
heat of evaporation 16.55 kJ mol^{-1};
heat of liquid nitrous oxide evaporation on the line of saturation at different temperatures: at T = –13°C (260 K) 11.58 kJ mol^{-1}; at T = 22°C (295 K) 7.30 kJ mol^{-1}; at T = 32°C (305 K) 4.75 kJ mol^{-1}.

Entropy at 25°C (298 K) in the standard state 219.90 J mo l^{-1} K^{-1}.
Heat capacity at T = 0°C (273 K) and P = 0.1 MPa:
– liquid 111.3 J mo l^{-1} K^{-1};
– gaseous 37.4 J mo l^{-1} K^{-1};
– at 25°C (298 K) in the standard state 8.63 J mo l^{-1} K^{-1}.

Coefficient of the thermal conductivity of liquid (λ_{liquid}, W m^{-1} K^{-1}) and gaseous (λ_{gas}, W m^{-1} K^{-1}) nitrous oxide on the line of saturation at different temperatures:

at T = –13 °C (260 K) $\lambda_{liquid} = 0.1200$; $\lambda_{gas} = 0.0176$;
at T = 22 °C (295 K) $\lambda_{liquid} = 0.1276$; $\lambda_{gas} = 0.0230$;
at T = 32 °C (305 K) $\lambda_{liquid} = 0.2341$; $\lambda_{gas} = 0.0290$.

Density and viscosity of nitrous oxide.
Density: – gaseous at T = 0°C (273 K) and P = 0.1 MPa 1.977 kg/m^3;
liquid:
– at T = –20°C (253 K) 1000 kg m^{-3};
– at T = 20°C (293 K) 784 kg m^{-3};
on the dissolution line of gaz–liquid at 25°C:
– for the gas 180 kg m^{-3};
– for the liquid 750 kg m^{-3}.

Coefficients of dynamic viscosity liquid ($\eta_{liquid} \times 10^{-4}$ Pa s) and gas ($\eta_{gas} \times 10^{-4}$ Pa s) phases and kinematic viscosity for the liquid ($\nu_{liquid} \cdot 10^{-6}$ m^2/s) phase on the line of saturation at different temperatures:

T = –3 °C (260 K), $\eta_{liquid} = 0.8565$; $\eta_{gas} = 0.1472$; $\nu_{liquid} = 0.0875$;

T = 22 °C (295 K), $\eta_{liquid} = 0.4985$; $\eta_{gas} = 0.2043$; $\nu_{liquid} = 0.0639$;
T = 32 °C (305 K), $\eta_{liquid} = 0.3812$; $\eta_{gas} = 0.2554$; $\nu_{liquid} = 0.0569$. Vapor elasticity of N_2O at T = 17°C (290 K) 4.71 MPa.

Vapor pressure over liquid N_2O:
at T = 0°C 3.03 MPa; at 18°C 4.95[MPa];
at T = 35.4°C 7.5 MPa.

It is established that elevating temperature of nitrous oxide even in a narrow range from 2 to 32°C, the pressure of its saturated vapor and the density of vapor phase sharply grow, and the density of liquid nitrous oxide on the line of saturation sharply decreases. The density of nitrous oxide with an increase in the temperature from 27 to 727°C in the range of pressures from 0.1 to 20 MPa decreases; moreover with an increase in the pressure this occurs faster.

Refractive index:
– of liquid N_2O at T = –90°C (183 K) 1.330;
– of gaseous N_2O at T = 0°C (273 K) and P = 0.1 MPa 558.

Coefficient of isobaric volume expansion of N_2O:
at T = 0°C (273 K) and P = 0.1 MPa $\alpha = 3.761 \times 10^{-3}$ K^{-1};
at T = 200°C (473 K) and P = 0.1MPa $\alpha = 3.669 \times 10^{-3}$ K^{-1}.

Isothermal compressibility of N_2O at T = 0°C (273 K) and P = 0.1 MPa $\beta_T = 1.33 \times 10^{-3}$ K^{-1}.

Speed of sound in the vapor phase of nitrous oxide at T = 0 °C (273 K) 263 m s^{-1}.

Nitrous oxide is a dielectric. Specific voluminous electrical resistance of the liquid nitrous oxide in the range of temperatures from –40 °C to 25 °C is (2.5–3.5) × 10^{14} Ohm m.

Dielectric constant of gaseous nitrous oxide at the temperature 25°C (298 K), pressure 1 MPa and frequency 10^6 Hz 1.00103.

Chemical Properties

Under ambient conditions N_2O is inert chemical compound. In the temperature range from –50 to +50°C it is stable and it is comparatively nonreactive. Nitrous oxide does not react with water, solutions of acids and alkali. At the same time N_2O can be dissolved in the water under pressure. Its solubility in water at 5°C is 1.048, and at 20°C 0.629 of volumes of gas in one volume of water

[8]. To its solution in water formally corresponds the unstable hyponitrous acid H_2N_2O, which is decomposed easily into water and nitrous oxide:

$$2H_2N_2O = 2N_2O + H_2O \quad (1)$$

Under a pressure, N_2O is dissolved in organic solvents such as acetone, acetic acid, methyl and ethyl alcohols, aniline, amyl acetate, chloroform, benzene and other, and also in the solutions of some inorganic salts (chlorides, sulfides, nitrites). Nitrous oxide is not oxidized by such strong oxidizers as $KMnO_4$, Cl_2O and others. Nitrous oxide also does not react with oxygen under the normal conditions and practically it is not oxidized to 500°C. At heating above 500 °C in oxygen N_2O ignites and is oxidized:

$$2N_2O + 3O_2 = 4NO_2 + 26.6 \text{ kJ mol}^{-1} \quad (2)$$

The oxidation of nitrous oxide by ozone is possible. Reaction proceeds to the formation of nitrogen dioxide, therewith the equilibrium concentration of hemioxide at the temperature up to 150°C can reach 1×10^{-9} % (by volume). Charcoal being heated in the nitrous oxide can burn:

$$2N_2O + C = CO_2 + 2N_2 + 393.5 \text{ kJ mol}^{-1} \quad (3)$$

Nitrous oxide is capable of entering into reaction with alkaline and alkaline earth metals and with some transition metals (Fe, Co, Cr and other) [9, 10]:

$$N_2O + Mg = MgO + N_2 + 682.1 \text{ kJ mol}^{-1} \quad (4)$$

$$N_2O + Fe = FeO + N_2 + 345.6 \text{ kJ mol}^{-1} \quad (5)$$

Nitrous oxide reacts with hydrogen, ammonia, carbon oxide and hydrocarbons with the significant heat liberation [11–14]:

$$N_2O + H_2 = N_2 + H_2O + 329.5 \text{ kJ mol}^{-1} \quad (6)$$

$$3N_2O + 2NH_3 = 4N_2 + 3H_2O + 879.2 \text{ kJ mol}^{-1} \quad (7)$$

$$4N_2O + CH_4 = CO_2 + 4N_2 + 2H_2O + 1028.9 \text{ kJ mol}^{-1} \quad (8)$$

$$N_2O + CO = CO_2 + N_2 + 374.7 \text{ kJ mol}^{-1} \quad (9)$$

However, it is difficult to initiate combustion. At the temperatures above 600°C nitrous oxide acts as strong oxidizer due to the liberation at its decomposition of active oxygen and additional heat. The combustible substances possessing electron affinity burn in nitrous oxide more intensively than in oxygen, with the liberation of a significant amount of heat (especially at the combustion of methane and ammonia). Comparative data on the oxidation of methane in the presence N_2O and oxygen are given in [13].

At the manipulating with nitrous oxide it is necessary to keep in mind that under some conditions and ratio the above-mentioned substances in the mixture with the nitrous oxide can explode at heating. So the mixture of equal volumes of N_2O and H_2 at the contact with flame gives energetic flash. A mixture of N_2O and NH_3 can explode with the large force at the ignition. Study of the ignition of N_2O mixtures with CO in the temperature range from 627 to 1627 °C showed that additives of H_2 and H_2O accelerate reaction, while hydrocarbons and NO inhibit it [11]. The process of reaction of nitrous oxide with hydrogen, ammonia and hydrocarbon is noticeably accelerated at the passing the mixtures above the catalyst surface. So the oxidation of hydrogen on the copper catalyst with the noticeable speed begins already at 150°C and proceeds intensively in the temperature range from 200 to 300°C [12].

Study of the reaction of reduction of nitrous oxide by hydrogen, carbon oxide, ammonia and methane on the supported cobalt catalysts made it possible to establish a number of the activity of these reducing agents [15]:

$$H_2 > CO > NH_3 > CH_4 > C_2H_6$$

Thermal Stability

Pure nitrous oxide is thermally stable at the atmospheric pressure to the temperature of 500 °C. However, being endothermic compound, it is prone to decomposition by several ways: thermal, catalytic, photochemical and in the electrical discharge [16–18]. In general form, the decomposition of N_2O can be represented by the equation, from which follows that amount of the liberated heat (hence, the temperature of decomposition products) depends strongly on the degree of its decomposition:

$$N_2O \rightarrow (1-x)N_2O + 0.5xO_2 + xN_2 + xQ, \quad (10)$$

where x is degree of the nitrous oxide decomposition. So at the degree of decomposition 0.2 the calculated temperature of decomposition products is ~300°C, and at 100% decomposition ~1600°C. Therefore at the use N_2O

as the rocket propellant should be expected a change in the specific impulse of the engine depending on the degree of its decomposition. It is established [19, 20], that the noticeable homogeneous thermal decomposition of N_2O begins at 590°C. At 900°C nitrous oxide is decomposed completely with the liberation of much heat:

$$N_2O = 2N_2 + O_2 + 163.3\ \text{kJ mol}^{-1}. \qquad (11)$$

Activation energy of the thermal decomposition of nitrous oxide sufficiently high being equal to 246.8 kJ mol^{-1}. This means that for its decomposition it is necessary to spend a large quantity of heat. The standard heat of the decomposition of nitrous oxide at 25°C is 91.5 kJ mol^{-1}. At the study of thermal decomposition of N_2O was revealed the influence of different factors on the decomposition rate constant [16–18, 21]; the relative effects of different gas-diluents (including water vapors) on the decomposition rate at low and high pressures over a wide range of temperatures are obtained [22, 23].

A significant number of works is devoted to the study of the thermal decomposition of nitrous oxide in the shock waves in the range of temperatures 1154–1954°C in the atmosphere of Ar, He, N_2, and CO; the schemes of decay are proposed and results of calculations of constant and activation energy are published [16, 24, 25].

On the basis the analysis of available published data it is possible to conclude that thermal decomposition of gaseous nitrous oxide proceeds by two consecutive reactions: the bimolecular reaction of activation of the nitrous oxide molecule and monomolecular reaction of decay of the excited molecule. At a low pressure the first reaction is limiting, at the high pressures (more than 10 MPa) the limiting step is the second process.

CATALYTIC DECOMPOSITION; THE CATALYSTS OF DECOMPOSITION

A significant number of works is devoted to the study of catalytic decomposition of N_2O on different chemical compounds. Primary attention in them is paid to the study of mechanism and kinetics of the process of decomposition, since this reaction often was used as the model.

Mechanism of Decomposition

The kinetics of the catalytic decomposition of nitrous oxide on the platinum metals is studied in detail [26–34]. In one of the early works [27] has been proposed the reaction mechanism which includes the adsorptive equilibrium of oxygen on the catalyst and an equation describing the process in which the rate of N_2O decomposition is unlimitedly impeded by oxygen at the increase in the pressure of the latter:

$$W = K_1 P_{N_2O}/(1+ \sqrt{b}_{O_2} P_{O_2}) \qquad (12)$$

where K is the reaction rate constant; P is partial pressure of O_2 and N_2O; b is the mole fraction of O_2 in the reaction products.

However, this equation does not agree with the data of the work [28], in which is shown existence of the limit of the reaction deceleration by oxygen: it occurs at the reaching of a certain P_{O_2} value. At reaching this pressure (which depends on temperature) the reaction rate becomes depending on it. Proceeding from the assumption that the adsorption of oxygen is not reversible, a mechanism of N_2O decomposition is proposed which includes two directions of the reaction. Although in both directions of the reaction of N_2O with adsorbed oxygen are formed identical final reaction products (O_2 and N_2), the sources of adsorbed oxygen are different. At proceeding reactions in the first direction the particles (O) are formed upon N_2O decay, in the second at the adsorption of O_2. At the low P_{O2} the advantage has the first direction, which is described by first order equation on N_2O:

$$W_1 = [\, K_1\, K_2/(\, K_1 + K_2)]\, P_{N_2O} \qquad (13)$$

where K_1 and K_2 are the rate constants of the reactions. At a high P_{O2} value the reaction predominantly proceeds by the second direction and is also described by the first order equation, but of another form, and the physical sense of the rate constant is other, than in equation (13)

$$W_2 = (\, K_2/2)\, P_{N_2O} \qquad (14)$$

where K is the reaction rate constant, P_{N_2O} is partial pressure of vapors N_2O in the mixture.

It is established [29, 30], that the process of decomposition of gaseous nitrous oxide on Pt, Pt–Ir, Ir, Rh and Pd on aluminum oxide is also described by first order equation on N_2O. The obtained values of E and k_0 for each catalyst depend on temperature. The catalysts contacted with the N_2O decomposition products at high temperatures increase their activity. The authors explain this fact by penetration at high temperatures of the formed oxygen to the crystal lattice of metal and make more labile the surface oxygen which participates in the reaction. The obtained values of the activation energy on the platinum catalyst (~130 kJ mol^{-1}), palladium and iridium (149 and 166 kJ mol^{-1}, respectively) agree with published data [28, 31, 32].

A study of the kinetics of N_2O decomposition on rhodium applied to the oxide aluminum carrier showed [33, 34] that the process of N_2O decomposition can be described by different equations depending on the conditions of its conducting. Thus, at the initial moment when decomposition reaction is not impeded by the formed oxygen, the process is described by the equation:

$$W_1 = K_1 P_{N_2O} \qquad (15).$$

At increase in the temperature, when formed oxygen renders braking effect the process can be described by one of the following equations:

$$W_2 = K_2 C_{N_2O}/C_{O_2}^{0.25} \qquad (16)$$

or

$$W_3 = K_3 C_{N_2O}/C_{O_2}^{0.5} \qquad (17)$$

From these equations is evident that the order of reaction on N_2O in the investigated temperature (520–600 K) and concentrations range is equal to one, and the order on oxygen is fractional, and is varied from zero to –0.5 depending on the conditions. The calculated activation energy does not depend on the form of kinetic equation and equals (149 ± 15) kJ mol^{-1}. At the same time pre-exponential factor depends on the form of equation (K_1 = 2.269; K_2 = 0.272; K_3 = 0.035). This can mean that on the rhodium catalyst the decomposition of N_2O proceeds at the same centers in entire investigated temperature range. The decrease of pre-exponent with an increase in the order of reaction on oxygen can testify about strengthening of the braking effect of oxygen. As showed the thermo-desorption studies of this catalyst after the determination of activity, at the linear rise in temperature to 600°C from the catalyst surface area is desorbed a small quantity of oxygen [35]. Further heating of catalyst at 800°C leads to intensive oxygen evolution. The presence of two maxima on the desorption curve testifies about two forms of the adsorbed O_2 differing by the binding energy with the catalyst. It must be noted that the thermodesorption curve of the O_2 evolution from the initial catalyst has only one peak at ~870°C, appearing also at the heating of the oxidized catalyst. Therefore one can assume that the peak at ~870°C is caused by the decomposition of rhodium oxide. That is, the process of poisoning the rhodium catalyst by oxygen must be reversible. A significant number of works is devoted to the study of the mechanism of N_2O decomposition on the oxide systems [33–42]. However, in spite of simplicity of the reaction, there is no unequivocal and clear idea on this topic up to now. Hauffe [36] suggests that the decomposition reaction of N_2O on the hole-type semiconductor (*p*-type) is the donor reaction (i.e. the passage accomplishes hole). According to the proposed mechanism, the limiting stage is the desorption of oxygen which depends on the interaction of (O^-) with the free positive holes.

According to [37], the limiting stage of reaction is somewhat different, but also is connected with the participation of the free holes of the semiconductor: at high temperature (abive 400°C) the N_2O decomposition can occur without participation of conductivity of electrons and holes, that is, by another mechanism, e.g., by exchanging oxygen between the surface and the gas phase. This assumption is made on the basis of the data on the isotopic exchange at high temperatures which show that the oxygen adsorbed by the catalyst surface is not distinguishable from the oxygen of surface layer [38, 39].

The analogous point of view belongs to Winter [40] who proposed a hypothesis about the geometric structure of adsorption complex of N_2O on the oxides. He assumes that in the first stage nitrous oxide is connected with the F-centers (single oxygen vacancy on the surface), then it joins electron and forms surface compound. Therewith the formed in the complex N_2O molecule is not linear (in contrast to the molecule in the gas phase). Observed change of catalytic properties is due to a change in the crystal structure of catalyst but not with the type of the semiconductor properties of oxide, as proposed in [36].

Hence one can conclude that there is no commonly accepted opinion about the mechanism of the nitrous oxide decomposition.

On the basis of the published data on the kinetics and mechanism of N_2O decomposition, in [26] is made the following conclusion:

– the reaction rate is proportional to pressure P_{N_2O};

– in many instances the process of decomposition is decelerated by O_2;

– nitrous oxide can be adsorbed by catalyst without decomposition, the attainable degree of filling surface is small, up to 1%, the heat of adsorption activation is small, not higher than 10 kcal mol^{-1};

– the catalytic activity of oxides decreases with an increase in the oxygen–catalyst binding energy.

Catalysts of the Nitrous Oxide Decomposition

The analysis of published data shows that the study of kinetics and mechanism of N_2O decomposition was carried out with the use as catalysts of the wide circle of chemical compounds including metals and their alloys, oxides, spinels, carbides, zeolites and other.

Metallic catalysts were tested both in the compact form (foil, powder, wire, single crystals) and being applied to different carriers. As the compact metallic catalysts most often were used Pt [28–34, 43–46], Pd [29–34, 44–48], Ag [32, 42, 47, 49], Ir [29, 30, 33, 34, 40, 50–55] and Rh [29, 33, 34, 40, 41, 50–64], less often Ru [65, 66], Ni [33, 34, 51] and Cr [33, 34]. The investigations with the use of these metals mostly are devoted to the study of the mechanism of nitrous oxide decomposition they were carried out at the varied conditions, and the values of the activation energy obtained by different authors on one and the same metal and on the different metals are essentially distinguished: Pt (71–252) kJ mol^{-1} [28], (81–180) kJ mol^{-1} [45], 155 kJ mol^{-1} [44], 130–272 kJ mol^{-1} [30]; Pd 96 kJ mol^{-1} [44], (81–180) kJ mol^{-1} [48], 126 kJ mol^{-1} [31, 32], (68–179) kJ mol^{-1} [30]; Ir 167 kJ mol^{-1} [31, 32], 128 kJ mol^{-1} [40], (114–254) kJ mol^{-1} [30], (70–105) kJ mol^{-1} [33, 34]; Rh (85–161) kJ mol^{-1} [30], (52–151) kJ mol^{-1} [33, 34]; Ag 88 kJ mol^{-1} [48], (197–117) kJ mol^{-1} [32], 204 kJ mol^{-1} [33, 34].

Therefore it is difficult to compose a series of the activity of metals in the N_2O decomposition reaction. At the same time in a number of publications are given comparative data on the activity. In [33, 34] are presented the comparative data on the activity of a series of metallic catalysts prepared from wire and briquettes of the "metal–rubber" type. It is established that by the minimum temperature of the reaction beginning they are ranged in the series:

Ni (510°C) > Ag (~530°C) >> Pt, Pt–Rh (10),
Pt–Ir (10) (~550°C) > Pt–Rh (20) (~560°C) > Pd (~580°C)
>> Mo (650°C) > Ni–Cr (Kh20 N80), W–Re (710 °C).

The degree of N_2O decomposition at 800 °C on these catalysts was: for Ni 0.34; for Pt and its alloys with Rh and Ir 0.26, for nichrome 0.03. The inspection of catalysts after tests showed that the nickel samples are changed most strongly: they become of green color and increase in weight by ~4.5%. This testifies about the essential oxidation of wire. Therefore the relatively high activity of nickel metallic catalysts can be explained by the formation of nickel oxide which shows noticeable activity in the N_2O decomposition reaction.

In the same publications [33, 34] are presented the comparative data on the activity of the substituted metallic catalysts with the metals of platinum group as the active constituent (13–15% of active component on Al_2O_3). Placing these data in the ascending order of the temperature values at which the degree of N_2O decomposition reaches 0.05 and 0.2 enables establishment the following series of activity: Rh (255°C) > Ru (320°C) > Ir (330°C) >>Pt (430°C) > Pd (490°C).

Rhodium is the most reactive, and starts to decompose N_2O already at 250°C, and at 320°C the degree of decomposition reaches value 0.05 (1st experiment), at 350°C the degree of N_2O decomposition reaches 20%. In the repeated experiment with the same sample the N_2O decomposition starts at 200°C, and the degrees of decomposition 0.05 and 0.2 are reached respectively at 260 and 305°C. As it was noted above, this is connected with the gradual oxidation of the surface of rhodium catalyst.

The high activity of rhodium catalyst ($T_{\min}$ 250–300°C) and its change in the process of N_2O decomposition is noted also in [40, 51]. Data of [51] show that initial temperature of N_2O decomposition on rhodium is 250°C and rhodium is more active than iridium ($T_{\min}$ 400–450°C).

The least active among the metals of Pt group is Pd. The reaction of N_2O decomposition on it (single measurement) starts at 360°C, and the degree of decomposition 0.05 is reached at 455°C. At the repeated test the initial temperature of decomposition is reduced by 50°C, and the degree of decomposition 0.05 is reached at 420°C, which is caused by the oxidation of the surface of metal [33–35], i.e., the activity of the oxides of the Pt group metals in the reaction of decomposition is higher than that of metals themselves.

Oxide and mixed catalysts. Considerably more works are devoted to the study of N_2O decomposition on the oxide catalysts, mostly the oxides of transition metals. The studies were carried out both with individual oxides and with those applied to different carriers. Among the published data should be noted the works [33, 34, 40–42, 51, 67]. In [40] by the static method are examined 19 transition metal oxides which by their specific catalytic activity form the following series (decrease in activity): Rh_2O_3 > IrO_2 > CaO > CuO > SrO > HfO_2 >> Fe_2O_3 > NiO > ThO_2 > ThO_2 > SnO_2 > CeO_2 >> MgO > Cr_2O_3 > ZnO > Ga_2O_3 > BeO > Al_2O_3 >>TiO_2.

It is evident that rhodium and iridium oxides show the highest activity. However, at the construction of this series the author did not consider difference in the catalyst surface area since at the preparation they underwent heat treatment at different temperatures and for different time. Possibly, this fact explains the observed inconsistence at the comparison of these results with the data of other publications.

Determined by flow method at the atmospheric pressure the comparative data on the activity of 21 oxides are presented in [41]. According to the data of the temperature of beginning of N_2O decomposition the investigated oxides are arranged in the following series: Co_3O_4 > NiO > CuO > ThO_2 > Al_2O_3 > CdO >> CeO_2, ZrO_2 > SnO_2 > Fe_2O_3 > Cr_2O_3, ZnO >> Nd_2O_3 > MgO > CaO > Sb_2O_4 > WO_3 >> U_3O_8, BeO > SiO_2 > GeO_2. It is evident that the oxides of cobalt and nickel are the most active; the minimum temperatures of the beginning of decomposition are 280 and 294°C, respectively. The activity of the oxides which follow in the series after them is considerably lower, so for the copper oxide $T_{\min}$= 400 °C.

The series of the activity (by the $T_{\min}$) of the transition metal oxides applied to the aluminum oxide carrier is represented in the publications [33, 34]: Co_3O_4 (415 °C) > NiO (425 °C) >> MnO_2 (430 °C) > CuO (440 °C) >> Cr_2O_3 (445 °C) > Fe_2O_3 (465 °C). It is evident that among the investigated oxides most active are also the oxides of cobalt and nickel.

The data for more than 50 different oxide catalysts (both separate and applied to different carriers) are presented in [51]. According to the data of the author the catalysts on the basis of nickel oxide (applied to the zirconium oxide), iridium oxide and rhodium oxide (applied to γ-Al_2O_3) are the most promising of the investigated oxides. However, in the work the fundamental physicochemical characteristics of catalyst (total and specific surface area, porous structure), are not given that does not allow to compare the data for the different oxides and with the data of other works.

Comparison of the represented series of activity evidences that in essence they coincide, although were obtained by the different methods: the oxides of rhodium, iridium, cobalt and nickel are the most active. However, there are contradictory results on the activity of some oxides. According to [19], N_2O decomposition on NiO begins at 350°C; at the same time in [40] is indicated that the reaction starts at 294°C, and according to the data of [51] decomposition is absent at 300°C; according to the data of [33, 34] reaction begins at 425 °C.

It is established that the activity of individual oxides can be changed by the introduction of the additives of other oxides. Adding Li_2O and Ga_2O_3 to ZnO, and Al_2O_3 and WO_3 to TiO_2 decreases the catalytic activity of ZnO and TiO_2 [36]. At the same time the introduction into NiO of Li_2O increases, and of In_2O_3 decreases its catalytic activity [36], although Li_2O accelerates chemical adsorption of O_2 (electron acceptor) by ZnO and NiO [68, 69].

A significant number of studies of N_2O decomposition was carried out with the use as catalysts of complex oxide systems of the type of solid solutions and spinel:

– the dual oxides of CoO or Fe_2O_3 with MgO [37]; NiO–MgO [70]; Fe_2O_3–MgO [71]; CuO–ZnO, CoO, CuO, ZnO [52]; CaO–MgO [59];

– chromites $CuCr_2O_4$, $NiCr_2O_4$ [72, 73, 74, 79].

Activity of the more complex systems in the N_2O decomposition reaction was determined such as aluminates, manganites and lanthanides [74–78]. The comparison of activities of such systems showed that cobalt aluminates are more active (T_{init} of decomposition 470°C), than Cu and Ni aluminates, Ni and Zn chromites, Na, Ca, and Ba stannates. At the same time aluminates of non-transition metals (Mg, Zn and Li), Mg, Co, Ca chromites and Mg ferrites are of low activity. It must be noted, that the data on the activity of these compounds from the different sources are essentially different. Of interest are the data on the activity of the dual oxides with varied ratio [41]. It is shown [80] that doping the solid solutions of the systems MgO–Cr_2O_3 with Cr^{3+} ions contributes to their catalytic activity (in the region of 400–500°C) calculated on one chromium atom. Analogous dependence is observed for the solid solutions NiO–MgO (300–400°C) [81].

For the developing a catalyst of N_2O decomposition are important the studies of the activity of oxides or mixtures of the oxides which can be the most promising carriers of the catalysts [33, 34]: ZrO_2 > Al_2O_3–CaO > Al_2O_3–ZrO_2 >> Al_2O_3–AlN > (γ + θ + β)-Al_2O_3 >>

Al_2O_3–SiO_2 > SiO_2 (from the quartz glass) > α-Al_2O_3.

It is evident that the most promising oxides for developing the carriers appear the oxides of zirconium and aluminum.

Practical interest can present the data on the activity of zeolites [82–87]. Zeolite ZSM-5 was used as a catalyst and as a carrier for Rh [58] and Cu (T_{min}=300°C) [58] (T_{min} = 375–450 °C) [86].

Thus, from published data follows that activity in the nitrous oxide decomposition reaction was investigated for a large number of chemical compounds: metals and their oxides, complex systems on the basis of these oxides, and also zeolites (natural and synthetic), chromates and chromites, aluminates and other compounds. However, the obtained results not always agree between themselves and therefore are of somewhat contradictory nature that does not make it possible to comprise a general series of activity and to select the most promising catalyst.

THE METHODS OF PRODUCING NITROUS OXIDE

Nitrous oxide is obtained by the reaction of nitric or nitrous acid with different reducing agents (hydrogen sulfide, sulfurous acid and other). In industry one of the most common and old methods of producing nitrous oxide is the method of the thermal decomposition of nitric acid salts, in particular ammonium nitrate, at the temperature 170–260 °C [8]. The process corresponds to the following equation:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O + 36.8\ \text{kJ mol}^{-1}. \qquad (18)$$

The N_2O decomposition proceeds with an acceleration and is accompanied by the liberation of a large amount of heat [1, 8] therefore special caution at its conducting is required since the explosion is possible at the rapid heating. By this technology in joint stock company “Cherepovets Nitrogen” is produced N_2O for pharmacopoeia under the name “Medical nitrous oxide” (FS-42-2926-99). Company “Klim” LLC by purification of this product produces the nitrous oxide of high purity (TU 2114-00723102861 -2002) which is stored in the cylinders in the liquid state. According to the valid normative documentation the commodity products must satisfy the following technical requirements (vol %):

Quality characteristic	pharmacopoeial	high purity
Basic material not less	96.0	99.9960
Noncondensing gases, not more	3.0	–
Narbon oxide not more	15 ppm	–
Narbon dioxide, not more	25 ppm	0.0010 ppm
Halogens	absence of the opalescence	–
Nitrogen oxide, not more	2 mg/dm^3	0.0005
Acidity or alkalinity	neutral	–
Vapors of water, is not more	2 mg/dm^3	0.0004
Volume fraction of oxygen, not more	–	0.0002
Volume fraction of nitrogen, is not more	–	0.0002
Volume fraction of sulfur dioxide	–	0.0005

A number of proposals was published on the improvement of the process of producing N_2O with the purpose of decrease in the temperature of conducting the reaction and increase purity of basic product [88–90]. In connection with the development of a number of the new industrial technological processes where N_2O is used as the oxidizer and is expended in a large amount, the method of thermal decomposition is unacceptable. For these purposes recently was proposed a number of the methods of its obtaining among which noteworthy the method of catalytic reduction of NO by carbon monooxide or hydrogen in the presence of homogeneous or heterogeneous catalysts. As the catalysts are recommended the metals of the platinum group [91, 92]. However, the most promising is the thermocatalytic method of the direct oxidation of ammonia by oxygen where as the catalysts are recommended platinum–rhodium alloy, oxides of manganese, bismuth, cobalt and others [93–97]:

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O. \qquad (19)$$

However the catalysts proposed are insufficient by activity and selectivity on the basic product (less than 84%), produce in high yield NO and are of low mechanical strength, therefore impossible to develop the industrial technology of production N_2O by this method.

By the Institute of Catalysis of Russian Academy of Science on the basis of the created highly active substituted alumo–manganese–bismuth catalyst (MnO_2–Bi_2O_3/α-Al_2O_3) is developed a technology of producing N_2O by the direct selective oxidation of ammonia [98]. The catalyst was examined in this reaction on a pilot plant at the NH_3–O_2 molar ratio ~1 : 1 and pressure in the reactor 0.2 MPa. It is shown that this catalyst can be successfully used in the reactors both with the fluidized and fixed bed ensuring at a temperature of synthesis (340–380)°C the yield of end product not less than 88%. In this case the catalyst showed not only high activity, but also stability: no decrease in its activity was observed in the entire period of work.

At present on the basis of the results of the tests on the pilot plant and the mathematical simulation is proposed a technological scheme of producing concentrated N_2O by the selective oxidation of ammonia on the developed catalyst [99]. Large-capacity industrial production with a power of up to 100 thousand tons N_2O per year is projected which will ensure the demand of chemical industry for the nitrous oxide [100].

PRINCIPLES OF MANIPULATION WITH NITROUS OXIDE

Toxicity

Nitrous oxide is low toxic compound, which is quite significant for its application. Maximum permissible concentration in air of working zone is 500 mg/m^3 [101, 102].

At inhalation of gaseous N_2O in the mouth is perceived sweet taste. At its inhalation in the mixture with air (volume fraction of N_2O up to 20%) it excites nervous system causing intoxication weakening pains and the assault of laughter. Therefore N_2O was called "laughing gas". In the small concentrations with oxygen, N_2O is used in medicine as the narcotic anaesthetizing means, but during the inhalation in the high concentrations is caused suffocation, as a result of the displacement of oxygen from the lungs.

Liquid nitrous oxide can cause freezings of skin and of the eye mucous membrane since at the expiration from a vessel in a large amount it is converted into the snow-like mass with the temperature –90°C. Therefore workers must be provided with special clothing.

At the poisoning by nitrous oxide the patient must be immediately removed from the gassed room to fresh air, placed in the horizontal position and is transmitted to doctors.

Fire Hazard

Nitrous oxide relates to the class of oxidizers; therefore it is a fire hazard liquefied gas since it can intensively react with some flammable materials. Minimum energy of gas ignition at a pressure 0.5–3.0 MPa and initial temperature 18.3°C is $10\rho^{-2.27}$ J [103, 104].

As noted above, gaseous nitrous oxide forms dangerously explosive mixtures with the hydrocarbon vapors (methane, ethylene, acetylene, oil, kerosene and other), with ammonia, hydrogen, carbon monoxide and carbon disulfide. Below are represented the concentration limits of explosiveness of some gas mixture (volume fraction of N_2O in the vapor mixture) at a pressure 0.1 MPa:

Substance	Explosiveness limit, %
Hydrogen	5.2–80.0
Ammonia	2.2–72.0
Methane	4.3–22.9
Butane	1.8–21.0
Cyclopropane	1.0–30
Methyl chloride	5.0–absence
Ethylene	2.0–40.0
Propane	2.0–26.0
Propylene	1.4–29.0
Carbon disulfide	1.0–52.0
Chloromethane	2.0–33.0
Carbon oxide	4.5–90.0

Liquid and gaseous nitrous oxide at the ambient conditions does not detonate. At the same time gaseous nitrous oxide at the elevated pressure (above 0.5 MPa) is dangerously explosive. This is explainable by the fact that it is the endothermic compound, capable at the initiation by an external source of ignition to spontaneous decomposition, which proceeds with the liberation of a large quantity of heat (81.5 kJ mol^{-1}) with a sharp growth of pressure in the closed volume, which can lead to the damage of the vessel. The potential initiators of the explosive decomposition of nitrous oxide can be electrical discharge, shock wave, hot wire, and at a pressure above 6.5 MPa a discharge of static electricity and a spark at the friction.

At normal temperature and pressure below 0.5 MPa and in the absence of organic impurities and other combustible additives, nitrous oxide is thermally stable and not explosive compound. However, at the presence of vapors of above-mentioned chemical compounds its sensitivity to the explosion grows. Introduction of the retarding gases (nitrogen, air, carbon dioxide) decreases the capability of nitrous oxide to explosion. To the decrease the probability of explosive decomposition contributes decrease in temperature and, correspondingly, in the partial pressure of the saturated vapors.

For the extinguishing of the fire from the nitrous oxide in the working space are used conventional means.

Requirements to the Equipment at the Work with N_2O

Nitrous oxide at the normal conditions is a chemically stable compound; therefore it does not possess corrosiveness with respect to many structural metallic materials in the range of temperatures from –50 to +50°C. This means that for preparing the equipment intended for the work with the nitrous oxide it is possible to use practically all materials used in the chemical industry (chromium–nickel and carbon steels, and a number of copper, aluminum and nickel alloys).

As the interlaying materials one should use polyfluoroethylene resin and pyrographite. The traditionally used in the chemical industry rubber materials at the contact with the liquid or gaseous nitrous oxide lose the strength properties. In this case one should consider that the lower limit of the use of construction materials is determined by the boiling point of nitrous oxide (–88°C).

For the safe and stable work of the installations operating with nitrous oxide, the finishing of the internal surfaces of equipment (cylinders, pipes, reactors, controlling and measuring equipment, etc.) contacting with the nitrous oxide is the necessary condition. Especially dangerous is the slag, which catalyzes the N_2O decomposition. Therefore before the beginning of work all the equipment must be appropriately prepared with the subsequent inspection of the finishing the internal surface of vessels and pipes. As the lubricants one should use materials on the basis of fluoric and perfluoride polymers.

Storage and the Transportation

Since nitrous oxide under the pressure is easily liquefied, it is stored and transported in the liquid form in the cylinders with a capacity of up to 10 liters. The cylinders are filled by weght. Space factor of cylinders is 0.62 kg/l. In cylinders the nitrous oxide is contained simultaneously in liquid (below) and gaseous (above) forms, which makes it possible to obtain if necessary either the gaseous or liquid nitrous oxide. Pressure in the filled cylinder is about 5.7 MPa and it will remain constant till the total expense of liquid part, after which storage pressure will begin to fall. At the pressure below 1 MPa is forbidden to take nitrous oxide from the cylinder.

Cylinders with nitrous oxide can be transported by any form of transport, but as a hazardous cargo. Cylinders with the nitrous oxide should be stored in the aired warehouse rooms or in open air under the shed at a temperature not higher than 30 °C and separately from the combustible gases.

Action on the Environment

In a number of publications the nitrous oxide is represented as “hot-house” gas [105]. Its concentration in the atmosphere is about 0.3 ppm and increases by ~0.2 % yearly [106]. At the same time the number of researchers considers that N_2O does not contribute directly to the decrease of ozone layer, since at room temperatures it is not reactive and at reaching the stratosphere N_2O is converted under the action of ultraviolet irradiation into nitrogen and oxygen. However, insignificant part can be converted into the nitrogen oxide:

$$N_2O \rightarrow NO + 0.5N_2;\ H^\circ = 4833\ \text{kJ mol}^{-1} \qquad (20)$$

By this route can be formed up to 1.2 mln ton of NO_x, i.e., N_2O can affect environment [68].

FIELDS OF APPLICATION A NITROUS OXIDE

Chemical Industry and Medicine

Owing to its narcotic properties, N_2O found wide application in medicine at surgical operations. Since recently nitrous oxide is recommended to use in the food and cosmetic industry as a disperser at producing different creams. It is established that its introduction into the combustion chamber of internal combustion engine leads to an increase in its power. As excellent refrigerant, nitrous oxide can find application in the refrigeratory industry [107], while as strong oxidizer – in the chemical industry [108–123].

However, until recently nitrous oxide practically was not used in the industry. Now in the press are published the works, in which N_2O is proposed for application in the liquid-phase oxidizing catalytic processes as a strong oxidizer, which makes it possible to carry out catalytic synthesis more effectively than oxygen [108–114]. This is new direction in the chemical technology. It is found that replacement of molecular oxygen by the nitrous oxide leads to an increase in the selectivity of the reaction of methane and other hydrocarbons transformation into different chemical products [115, 116]. Application of catalysts contributes to intensification of the oxidation process. Thus, iron ions catalyze activly the gas-phase reaction of oxidation of ethane [117]:

$$C_2H_6 + 2N_2O \rightarrow CH_3CHO + H_2O + 2N_2 \qquad (21)$$

Metals of IVth period direct the reaction of CH_4 oxidation with nitrous oxide to the formation of methanol [118]:

$$CH_4 + N_2O \rightarrow CH_3OH + N_2, \qquad (22)$$

Most strongly the oxidizing properties of N_2O are manifested in such a specific reaction as the oxidation of benzene into phenol. For the first time this reaction was carried out in the presence of catalysts on the basis of vanadium, molybdenum and tungsten oxides at 500–600°C (selectivity on phenol ~71%) [111]. Later it was established that on zeolites the oxidation of benzene can be carried out at lower temperatures (300–400°C) with the higher (~100%) yield of phenol [119, 120]. The most effective catalyst in this reaction proved to be zeolite with the structure ZSM-5 of the alumosilicate composition [119]. In the reaction of oxidation of benzene with use of N_2O also proved to be zeolites containing iron, the ferrosilicate analogs of ZSM-5 [121]. Furthermore, it was found that with N_2O can be performed oxidative hydroxylation also of other aromatic compounds [122, 123].

The above-indicated reactions have fundamental value for industrial producing of a number of chemical substances, which could not be obtained in a satisfactory yield without the use of nitrous oxide.

Survival Systems

Decomposition of nitrous oxide results in formation of nitrogen and oxygen in 2 : 1 ratio, that is the excellent respiratory mixture, close by composition to air (36.3% of O_2 and 63.7% of N_2), i.e., N_2O can be a source of oxygen. This property makes it possible to recommend N_2O as the source of oxygen for the human life supporting in the extraordinary situations, including under-water, underground, or in the cosmic space. The investigations carried out in the State Institute of Applied Chemistry for these purposes resulted in the development of highly effective catalyst (K-252, oxide copper–chromium–alminum) and is proposed a construction of a gas generator based on the catalytic decomposition of N_2O [124].

Laser Technology

Since at the N_2O decomposition is formed a high-temperature gas mixture (near 1600°C) it can serve as source for obtaining high-energy nitrogen in the laser installations. On the other hand the formation of atomic oxygen and large energy release at the CO and O_2 recombination make it possible to consider the system $CO–N_2O$ as the effective source of the excited CO_2 molecules for the of CO_2 laser [125].

Rocket and Space Technology

Nitrous oxide is a high-energy chemical compound which at the same time is nontoxic, stable in the region from –34 to 60°C, fire- and -explosion safe, corrosion inactive and inexpensive. Therefore nitrous oxide satisfies the requirements to the rocket propellants [1, 3]. For a long time it was not of interest for the specialists of rocket engineering. Gradual improvement of the aggregates of space technology, in part, the creation of low-trust engines, and requirements on the use of ecologically pure chemical rocket propellants forced of the specialists of this branch to focus attention on nitrous oxide as a promising “green” fuel [51, 126–131].

Nitrous oxide has one additional advantage over other rocket propellants: it can be stored on the board of the automatic spacecraft in liquified state and converted to gas at the feeding into the combustion chamber. This makes it possible to exclude substitution mode of feeding and to develop engines with the force of gram level which is especially important for the micro–satellites. Some calculated energy characteristics of generator gas formed at the decomposition of liquid and gaseous nitrous oxide at a pressure 40–60 MPa are represented below.

Characteristics	Liquid phase	Gas phase
Temperature of the product of decomposition in the reactor, K	1775 (1502)	1900 (16270)
R, J kg^{-1} K^{-1}	283	283
Characteristic speed, m s^{-1}	1065	1105

As is evident, at the complete decomposition of gaseous N_2O the products temperature can reach 1900 K (1627°C), and characteristic speed 1105 m s^{-1}. For the comparison, the calculated theoretical values at the use of hydrazine (at $X = 0.25$) are 1450 and 1340, respectively. Theoretical specific impulse at the use of N_2O also is sufficiently high, 206 s. At the completeness of decomposition 0.8 the adiabatic temperature is equal 1325°C, and specific impulse is 1762 m s^{-1}. For the comparison for hydrazine and hydrogen peroxide, the single-component fuels which at present successfully are used in rocket engineering, the specific impulse is respectively 245 and 179 s.

For the first time N_2O was used in the rocket engineering as oxidizer in Germany and England during World War II. However, after that the interest in N_2O as rocket propellant was lost. And only in the early 80th of the past century was renewed the work with nitrous oxide. On its basis in the firm SSTL (England) are developed the micromotors for correction of trajectory of cosmic units, where N_2O is used as the source of “cold gas”, in particular, for the orbit correction of the micro-satellite UOSAT-12 [131].

For successful application of nitrous oxide in the rocket-space technology (as in the laser and the survival systems) is necessary a highly effective catalyst of its decomposition. However, in spite of the significant number of works on the catalytic N_2O decomposition, the catalyst capable of repeated application to the decomposing with the large effectiveness it is not developed up to now. This is connected, first, with the fact that nitrous oxide is a stable chemical compound, and a significant quantity of energy should be released for the initiation of the process of its decomposition. Therefore for the purpose of the saving energy on the board of a cosmic apparatus the catalyst must initiate decomposition reaction N_2O at the lowest possible temperature. Second, into the process of N_2O decomposition is evolved much heat, and therefore the temperature in the catalyst layer can reach ~1600°C. Hence the catalyst must be thermally stable to this temperature. Third, at the N_2O decomposition one of the products formed is oxygen, moreover, it is evolved at the initial moment in the atomic form. Therefore catalyst must be chemically resistant (not to undergo essential phase transformations) in the products of N_2O decomposition.

Furthermore the basic mode of operation of such catalysts is pulse, i.e., the short-term (from the less than one to tens of seconds) supply of fuel, and then a pause (from less than one second to several days) [132]. In accordance with the requirements for the rocket engines (RE) the catalyst must practically instantly (delay time not more than 0.1 s) initiate the process of decomposition at a minimum initial temperature and then after several tenths of second (not more than 0.5 s) to provide reaching the steady regime of the process. Due to the exothermic nature of this reaction the temperature of catalyst in this period sharply grows (up to 1600°C, depending on the degree of decomposition).

The catalyst must satisfy a number of the requirements, usually not the same as industrial catalysts, among them:

– high reproducibility of the indices of catalytic process in the reactor: dynamic characteristics (delay time and the time of output), consumption of fuel, temperature of the products of reaction, drop in pressure and the level of pulsation during entire resource and at each supply of the fuel, independently from the initial temperature of catalyst;

– steady working in the assigned range of temperatures, pressures and vibrations (acceleration to 12g at the given values of frequency and amplitude), under the conditions of different form of emissions in the cosmic space, climatic conditions and transport overcharge at the operation under the terrestrial conditions;

– the high degree of uniformity of the catalyst granules in the respect of activity, size, shape, strength and others.

Owing to the complexity of the task, up to now there is no catalyst which would completely satisfy the presented requirements, although the work on its creation in different scientific centers is carried out. Considerable achievements in this direction were obtained at the university of Surrey town (England) [51–55, 129–131], where was proposed not only catalyst, but also a construction of microrocket engine. Somewhat later on were initiated related investigations in France [133] and China [56–58, 134, 135]. In USSR the first work on the development of the catalyst for N_2O decomposition was initiated in the State Institute of Applied Chemistry in the middle the 70's of past century in connection with the creation of the micro-engines with the thrust from 1 to 10 N. As a result of these works were developed both the metallic catalyst of the type of "metal–rubber" on the basis of platinum, and a supported type catalyst on the basis of rhodium on the thermoresistant aluminum oxide carrier (K-251). These catalysts made it possible to study the process of decomposition in the model engines, which served as a basis for the developing the micro-rocket engine with the thrust of 1N [137].

Nitrous Oxide as the Oxidizer of Fuel

Nitrous oxide can be used and as oxidizer in the hybrid engines. In these engines one of the components is solid, the second is liquid or gas. As the fuel can be used polymethyl methacrylate, polyethylene or polybutadiene. These engines are simple, comparatively cheap, their operation does not lead to the environmental pollution. Therefore they are used for the correction of orbit of training and commercial cosmic units. American Rocket Company "AMROC" used as a fuel N_2O as oxidizer in the hybrid engines; it also intended to use it in combination with the solid (polypropylene, polybutadiene and other) and liquid (alcohols and other) propellants [128]. As the oxidizer the nitrous oxide was used in the hybrid sustainer engine on the American suborbital rocket vehicle Space Ship One [138]. The hybrid engines on the basis of N_2O are developed in the space university of Tuluza (France) [139].

It is planned to use in the engines a two-component system of N_2O with propane [128, 140]. The high specific parameters of fuel can be realized also at the combustion N_2O with ammonia or hydrazine: calculated specific impulse and the temperature of decomposition products at $\alpha = 1.0$ are respectively 3000 $m \cdot s^{-1}$ and 2720°C for ammonia and 3190 $m \cdot s^{-1}$ and 3020°C for hydrazine.

The fuel pair of special interest for the developers of rocket engines must be the pair nitrous oxide–methane which combustion produces much energy (1029 kJ mol^{-1}).

It is known that at the decomposition of nitrous oxide is liberated a significant amount of heat, which enhances temperature of the reaction products. This fact strongly hampers the selection of the construction materials, necessary for creating the combustion chambers. One way to simplify the technology of the creation of low-thrust engines and their operation is reduction the temperature of N_2O decomposition products by dilution of initial component with other chemical compounds, the so-called ballasting additives. Proceeding from chemical properties N_2O ad its ability of diffusion into other gases, as the ballasting additives can be used inert gases He, Ar, and also N_2 and CO_2, since they do not react with the nitrous oxide and therefore will not introduce additional heat into the camera of decomposition.

At the same time at the storage under pressure N_2O is liquefied; therefore can occur separation its mixture with He, N_2 or Ar into the components, and at the throttling from the cylinder this gas mixture will be of undetermined composition.

Of great interest as the ballasting component is carbon dioxide, which at 20°C and the pressure of 5.7 MPa is liquefied into a colorless liquid. At the throttling of the liquid mixture of these gases it is possible to obtain gas mixture of more uniform composition than with the inert gases.

The physicochemical properties of the possible ballasting mixtures have been published in a number of publications. In [141] are given the results of studying viscosity and diffusion coefficient of the binary systems of nitrous oxide with N_2, Ar and CO_2 in the range of temperatures from 25 to 200°C. It was established that the calculated values of the binary mixtures diffusion coefficients are consistent with the Law of corresponding states. In [142] are calculated the values of the thermal conductivity of two binary systems of nonpolar gases, N_2–N_2O and NO–N_2O, in the temperature range from 50 to 180°C. It was found that the presence of NO in N_2O effectively increases the rate of its catalytic decomposition on FeZSM-5 zeolite, and at the same time the nitrogen monooxide, carbon dioxide and water inhibit the process of N_2O decomposition [16, 53, 68, 143–145].

The carried out preliminary calculations showed that the temperature of the nitrous oxide decomposition products depends substantially on the quantity of introduced ballasting gas. Thus, introduction of 20% of He can decrease almost to a half the temperature of the N_2O decomposition products. Therefore this gas mixture merits attention for conducting the studies in connection with a good dissolution of helium in nitrous oxide. At the application of this gaseous mixture its stratification is excluded. However, the composition of the ballasting gas mixture must be determined for each introduced component individually.

CONCLUSION

Taking into account that nitrous oxide is not toxic, highly stable, not corrosive and compatabile with various construction materials, it is possible to conclude that it is one of the most promising oxidizers for developing new chemical processes, which failed at the attempted application of oxygen as an oxidizer. At the same time nitrous oxide is promising ecologically pure “green” rocket propellant, which can be used as “cold gas”; at catalytic decomposition it can be used as a high-energy working medium or as a source of oxygen for human survive in a locked space. Nitrous oxide can be used in rocket engineering as oxidizer in the bipropellant engine in combination with the solid or liquid propellants. Furthermore, it can be used in the CO_2 lasers.

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