

## NITROGEN HEMIOXIDE: PROPERTIES AND NEUTRALIZATION METHODS

S. A. Kulyukhin,<sup>1</sup> O. A. Ustinov,<sup>2</sup> A. Yu. Shadrin,<sup>2</sup>  
and Yu. A. Voskresenskaya<sup>2</sup>

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*The physical and chemical properties of  $N_2O$  and methods for its trapping and decomposition are examined. It is found that organic solvents, water, hydrazine hydrate, and a solution of potassium bichromate in sulfuric acid dissolve  $N_2O$  but its stabilization by this method is unreliable. Catalytic decomposition upon heating is acknowledged to be an effective method of neutralizing  $N_2O$ . Different composite materials, including those containing d and f elements, were studied as catalysts. It was found that suitable composites for catalytic decomposition of  $N_2O$  are  $SiO_2-Cu$ ,  $Al_2O_3-Ni$  at  $150^\circ C$  and  $Al_2O_3-Cu$ ,  $Al_2O_3-Fe$ ,  $Al_2O_3-Ni$ , and  $SiO_2-Cu$  at  $250^\circ C$ . It was shown that the passage of ethanol vapors above the composites at the indicated temperature increases the degree of decomposition of  $N_2O$  by a factor of 10. The results obtained were used to develop a gas-purification system in the technology for reprocessing spent nitride fuel.*

Nitrogen hemioxide (nitrous oxide, dinitrogen oxide)  $N_2O$  is of interest from the standpoint of environmental protection. Its destructive action on the ground layer of the atmosphere and in the greenhouse effect is obvious.  $N_2O$  emission into the atmosphere reaches  $\sim 12.7 \cdot 10^6$  tons, of which about 35% is of anthropogenic origin (thermal power plants, automobiles, some chemical production, agriculture) [1]. In nuclear power,  $N_2O$  is formed when nitride fuel dissolves in nitric acid in the process of hydrometallurgical processing or in denitration processes; in the first instance its amount reaches 1 mole/mole of uranium nitride [2–4].

**Physicochemical Properties.** Nitrogen hemioxide is a colorless gas; the melting point is  $-91^\circ C$  and the boiling point  $-88.5^\circ C$  [5]. Its room temperature activity is very low. The most complete presentation of the basic chemical properties of  $N_2O$  is given in [6].

$N_2O$  reacts with nitric acid vapor with ammonium nitrate being formed. Nitrous acid interacts with dinitrogen oxide; NO is formed in the process. In the liquid phase at  $25^\circ C$ , tin chloride, titanium chloride, and sodium sulfate reduce  $N_2O$  to ammonia, hydroxylamine, and nitrogen, respectively. Nitrogen hemioxide reacts with metals. Magnesium powder in contact with water and  $N_2O$  reacts and hydrogen is released; zinc filings react similarly – hydrogen and nitrogen are released together with a small amount of ammonia. At room temperature, iron in a moist medium reduces  $N_2O$  reacts and nitrogen and hydrogen are formed. Zinc, cadmium, manganese, tin, and lead are slowly oxidized by  $N_2O$  at temperatures  $550-650^\circ C$ , cobalt and nickel at  $230^\circ C$ , and iron at  $<170^\circ C$ . Sodium and potassium form with  $N_2O$  upon heating the corresponding metal peroxide and nitrite. At  $200^\circ C$ ,  $N_2O$  reacts with sodium oxide with sodium nitrate and nitrogen being formed. A similar reaction occurs at the following temperatures ( $^\circ C$ ): with barium dioxide  $500-600$ , manganese oxide  $350$ , tungsten dioxide  $450$ , molybdenum monoxide  $<500$ , tin oxide  $400$ , copper monoxide  $350$ , lead dioxide  $200$ , and uranium dioxide  $450$ .

Upon heating,  $N_2O$  starts to decompose at  $520^\circ C$  and decomposes completely at  $900^\circ C$ . The final products of decomposition are nitrogen and oxygen, but a secondary reaction with formation of NO also occurs. In the presence of

<sup>1</sup> Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences (IFKhE RAN), Moscow, Russia.

<sup>2</sup> Bochvar All-Russia Research Institute for Inorganic Materials (VNIINM), Moscow, Russia.

TABLE 1. N<sub>2</sub>O Solubility in Some Liquid Media at 25°C [6]

Medium	Solubility, mole/liter
H <sub>2</sub> O	0.02–0.03
HNO <sub>3</sub> , HCl, H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub>	0.025
Ethanol	0.12
Acetone	0.25

TABLE 2. N<sub>2</sub>O Absorption in Water Solutions at 20–25°C (linear velocity of the gas flow 0.5 cm/sec, gas–liquid contact time 10 sec, [N<sub>2</sub>O]<sub>ini</sub> 1.5–2.1 mM [7])

Water solution, mole/liter	Absorption	
	Volume per volume of liquid	mole/liter
H <sub>2</sub> O	0.24	0.01
12 HNO <sub>3</sub>	0.096	0.004
7.2 HNO <sub>3</sub>	0.0072	0.0003
24 NH <sub>4</sub> OH	0.12	0.005
1.0 NaOH	0.144	0.006
1.0 N <sub>2</sub> H <sub>4</sub> ·nH <sub>2</sub> O	0.24	0.01
0.5 (NH <sub>2</sub> ) <sub>2</sub> CO	0.151	0.0063
0.1 n KMnO <sub>4</sub>	0.055	0.0023
0.1 n KMnO <sub>4</sub> + 12 HNO <sub>3</sub>	0.065	0.00273
0.2 UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0.0072	0.0003
0.1 n K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.401	0.0167
Saturated K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in concentrated H <sub>2</sub> SO <sub>4</sub>	0.497	0.0207

platinum-group metals, hydrogen and ammonia reduce N<sub>2</sub>O at 150–200°C to elemental nitrogen. Carbon monoxide and hydrocarbons act similarly. Ammonia and its derivatives (carbamide, melamine, cyanuric acid, and others) can reduce nitrogen oxide in oxygen (selectively).

As one can see from Tables 1 and 2, organic solvents, water, hydrazine hydrate, and a solution of potassium bichromate in sulfuric acid absorb N<sub>2</sub>O well.

Nitrogen hemioxide is absorbed by various sorbents. The maximum Langmuir capacity of some sorbents is (cm<sup>3</sup>/g): biocarbon VS-286 54.7 ± 0.8, activated carbon AS-775 72.7 ± 2.1, Al<sub>2</sub>O<sub>3</sub> (S<sub>sp</sub> = 175 m<sup>2</sup>/g) 12 ± 0.9, SiO<sub>2</sub> (S<sub>sp</sub> = 205 m<sup>2</sup>/g) 8.5 ± 0.4 [8].

Analysis made it possible to draw the following conclusions.

The solubility of N<sub>2</sub>O in some liquid organic and inorganic media is high, but as a result of the passage of a gas flow containing radioactive substances a large volume of liquid radioactive wastes, including flammable and explosive wastes, can form. In addition, reliable stabilization of N<sub>2</sub>O is not guaranteed. Treatment of N<sub>2</sub>O with liquid reducing reagents results in the formation of nitrogen, hydroxylamine, or ammonia. The kinetic parameters of the processes are unknown, but it is obvious that the neutralization of N<sub>2</sub>O from gas flows containing radioactive substances by such methods also leads to the formation of large volumes of wastes and the appearance of secondary gaseous emissions. The reduction of N<sub>2</sub>O by metals and its interaction with metal oxides upon heating are promising as real solutions to the problems of neutralization, but they entail

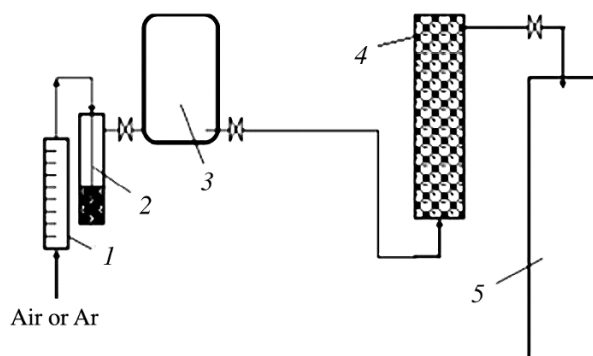


Fig. 1. Schematic diagram of a laboratory setup for studying the catalytic decomposition of  $N_2O$ : 1) rotameter; 2) hydraulic seal with glycerin; 3) reaction chamber with  $N_2O$ ; 4) reactor with catalyst; 5) accumulation tank for collecting the final gaseous products.

TABLE 3. Decomposed  $N_2O$  Amount per 1  $cm^3$  of Composite and Degree of Decomposition at 250 and 150°C

Composite	Layer height, cm	Decomposed amount, $10^2$ mmol	Degree of decomposition, %
250 °C			
$Al_2O_3$	5	$7.3 \cdot 10^{-2}$	1.2
$Al_2O_3-Ni$	7.2	2.6	16.2
$Al_2O_3-Cu$	4.3	2.2	8.9
$Al_2O_3-Fe$	4.4	2.2	9.1
$SiO_2-Ni$	5.6	3.2	16.3
$SiO_2-NiFe$	5.5	1.8	8.9
$SiO_2-Co$	5.8	2.8	14.9
$SiO_2-Mn$	6	1.5	8.4
150 °C			
$Al_2O_3-Ni$	7.2	0.8	11
$SiO_2-Cu$	6	3.3	16.1

continuous consumption of reagents, which under the conditions of radiochemical production processes gives rise to technological difficulties. The use of reducing gases (hydrogen, ammonia, carbon monoxide, hydrocarbons) in the presence of catalysts makes it possible to neutralize  $N_2O$  at  $\sim 400^\circ C$ , but the problem of fire and explosion safety remains unsolved. The use of conventional carbon-containing sorbents does not solve the problem of the strong stabilization of  $N_2O$ . In addition, their use does not eliminate the problems associated with fire safety. The decomposition of  $N_2O$  upon heating does not require reagents, but the process temperature is high ( $900^\circ C$  and higher) and high electricity consumption is required. The use of catalysts greatly lowers the decomposition temperature of the  $N_2O$  and is probably the optimal variant for its neutralization.

Analysis [9] attests that pure and mixed oxides of different metals, metal-containing composite materials, for example,  $Ni/\alpha-Al_2O_3$ ,  $Au/Co_3O_4$ ,  $Rh/ZrO_2-Al_2O_3$ ,  $Ag-Pd/Al_2O_3$ ,  $Ru/Al_2O_3$ , and others, zeolites, pure metals, and others, as catalysts suitable for decomposition of  $N_2O$  have now been studied in detail. The composites  $CuAl_2O_4/Al_2O_3$ ,  $Ag/Al_2O_3$ ,  $CoO-NiO/ZrO_2$ ,  $Co_2AlO_4/CeO_2$ ,  $CuO/Al_2O_3$ ,  $La_{0.8}Ce_{0.2}CoO_3$ , and  $FeZSM-5$  alloyed with yttrium, zirconium, perovskites, hexaaluminates, and some other materials are used for technological processes. These catalysts have manifested high catalytic activity in gas flows with low content of oxygen and water vapor at temperatures above  $375^\circ C$ .

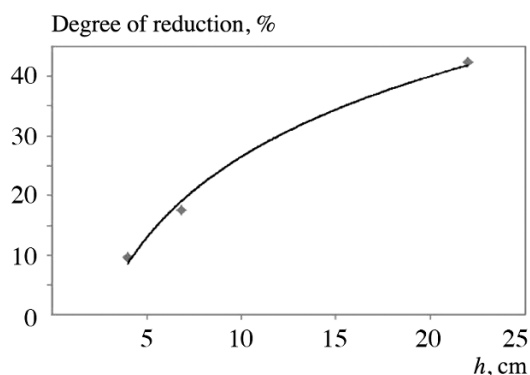


Fig. 2. Degree of decomposition of  $N_2O$  at  $250^\circ C$  as a function of the height  $h$  of the layer.

It should be noted that catalysts for decomposing  $N_2O$  in a vapor-air flow at temperature below  $350^\circ C$  have not been found. In this connection the aim of this research was to find and develop catalysts for decomposing  $N_2O$  in a vapor-air flow at temperature below  $300^\circ C$ .

**Experimental Part.** Granulated composites based on  $Al_2O_3$  and  $SiO_2$ , which contain different  $d$  elements (Ni, Cu, Co, Fe, Mn, Ag) in oxide or metallic form were investigated in this work. The catalysts were obtained by using ammonia, hydrazine hydrate, or hydroxysilamine for treating matrices containing nitrate salts of metals followed by heating at  $300$ – $700^\circ C$ . Hydrogen reduction at high temperature was conducted in some cases.

The experiments on catalytic decomposition of  $N_2O$  were conducted using the apparatus shown in Fig. 1. The initial amount of  $N_2O$  was 2.9 mmol, the mass of the composite 10 g, lineal velocity of the gas flow 0.01 m/sec, temperature 150 and  $250^\circ C$ , their measurement error in the reactor  $\pm 3^\circ C$ , and  $N_2O$  content in the gas flow  $\sim 2$  mmol/liter.

In addition, experiments were performed on the catalytic decomposition of  $N_2O$  in the presence of ethanol vapors. For this, a bubbler with ethanol was placed in the setup shown in Fig. 1 between the reaction chamber with  $N_2O$  and the reactor with the catalyst. In addition, a bubbler with water, for the absorption of acetaldehyde formed during the reduction of ethanol in the presence of the experimental catalysts, and a column with  $SiO_2$  (for absorption of water vapor) was introduced additionally into the system after the reactor. The initial amount of  $N_2O$  was 1.1 mmol and the composite mass 15 g, linear velocity of the gas flow 0.02 m/sec,  $N_2O$  content in the gas flow  $\sim 0.8$  mmol/liter, and ethanol  $\sim 31.9$  mmol/liter.

The  $N_2O$  content in the gas phase was determined by means of IR spectrometry. The IR spectra were obtained by means of a Specord M80 spectrometer (Germany) using gas cells with KBr glass and working space length 100 mm. A quantitative determination of the  $N_2O$  content was made according to the  $\nu = 2244\text{ cm}^{-1}$  band ( $\epsilon = 0.2244\text{ mol}^{-1}\cdot\text{cm}^{-1}$ ) [10]. The measurement error was  $\pm 10\%$ .

**Results and Discussion.** It is evident in Table 3 that at  $250^\circ C$  the decomposition of  $N_2O$  on pure  $Al_2O_3$  occurs 20–40 times more slowly than on  $Al_2O_3$ -based composites coated with catalytic additives. The activity of  $Al_2O_3$ - and  $SiO_2$ -based composites is almost the same.  $Al_2O_3$ -Ni,  $SiO_2$ -Ni, and  $SiO_2$ -Co showed the highest catalytic activity. It was also determined that  $Al_2O_3$ -Ni and  $SiO_2$ -Cu show activity at  $150^\circ C$  also (see Table 3).

The dependence of the degree of decomposition of  $N_2O$  at  $250^\circ C$  on the height of the layer of catalyst was obtained for one of the experimental composites. As one can see in Fig. 2, the degree of decomposition of  $N_2O$  increases with increasing height of the catalyst layer, which is a consequence of the longer contact time between gas phase and the catalyst.

Therefore, the investigation of a large number of composites has revealed materials on which catalytic decomposition of  $N_2O$  at 150 and  $250^\circ C$  is possible and which can be used in the development of a technology for neutralizing the  $N_2O$  present in waste gases.

Additional research on catalytic reduction in the presence of gaseous reducers was directed at increasing the decomposition efficiency of  $N_2O$ . For this, by analogy with [11], where denitration and reduction of  $N_2O$  were conducted by means of methyl alcohol vapors, ethanol was chosen as the gaseous reducer. The decomposition was conducted at  $250^\circ C$  on less

TABLE 4. Amount of Decomposed  $N_2O$  per  $1\text{ cm}^3$  of the Composite and Degree of Decomposition at  $250^\circ\text{C}$  in the Presence of Ethanol Vapor

Composite	Layer height, cm	Decomposed amount, $10^2$ mmol	Decomposition degree, %
With conditioning at $700^\circ\text{C}$			
$Al_2O_3$ -AgNO <sub>3</sub>	7.4	5	73.8
$Al_2O_3$ -Ag	7	4	52.7
$Al_2O_3$ -AgNO <sub>3</sub> -Ag	7	5.1	67.4
$Al_2O_3$ -2Ag8Ni	6.8	5.5	70.3
Without conditioning			
$Al_2O_3$	7	0.27	4.8
$Al_2O_3$ -Ag	6.5	1.5	18.5
$Al_2O_3$ -AgNO <sub>3</sub> -Ag	6.5	2	31.5
$Al_2O_3$ -2Ag8Ni	6.4	1	12.4

effective, in terms of preceding studies, catalysts including silver that are not included in Table 3. In addition, it was found that conditioning (heating) of a composite at  $700^\circ\text{C}$  is an important factor influencing the decomposition efficiency.

As one can see from Table 4, the introduction of ethanol vapor in a gas flow increases the degree of decomposition of  $N_2O$  by a very small amount in the presence of unconditioned composites. At the same time, in the presence of composites conditioned at  $700^\circ\text{C}$  the degree of decomposition of  $N_2O$  increases 2–5-fold and exceeds 50% in all cases (see Table 4). In addition, it should be noted that the degree of decomposition of  $N_2O$  in the presence of composites containing 7 wt.% silver does not exceed the degree of decomposition of the composite with 2 and 8 wt.% silver and nickel, respectively.

In summary, the introduction of ethanol vapor into a gas flow makes it possible to increase sharply the degree of decomposition of  $N_2O$  in the presence of composites heated to  $250^\circ\text{C}$ .

**Conclusions.** High-temperature catalytic decomposition of  $N_2O$  is most promising for neutralization. Effective catalysts ( $Al_2O_3$ -Ni,  $SiO_2$ -Ni, and  $SiO_2$ -Co) were found experimentally. They permit decomposition of  $N_2O$  in amounts  $(1.5\text{--}2)\cdot 10^{-2}$  mmol/liter and linear velocity of the gas flow  $\sim 0.01$  m/sec.

It was shown that the introduction of ethanol vapor into a gas flow containing  $N_2O$  gives catalytic decomposition of  $N_2O$  in amounts  $(4\text{--}5.5)\cdot 10^{-2}$  mmol per  $1\text{ cm}^3$  of the composite at initial  $N_2O$  content  $\sim 0.8$  mmol/liter and linear velocity of the gas flow  $\sim 0.02$  m/sec.

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