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Technologies for Simultaneous Low-Temperature Catalytic Removal of NO_x and N_2O from the Tail Gases of Nitric Acid Plants

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Abstract

The reasons for the formation of nitrous oxide (a greenhouse gas with CO_2-equivalent equal to 310) at modern plants manufacturing weak nitric acid are analyzed. The amount of annual N_2O emission depending on the operating conditions of the ammonia converter and on the method of the removal of nitrogen oxides NO_x is estimated. A technological scheme of simultaneous low-temperature removal of NO_x and N_2O from exhaust tail gases is proposed, in which V/Al catalyst for the selective catalytic reduction (SCR) of NO_x with ammonia and Cs/Co_3O_4 catalyst for N_2O decomposition are used. Mathematical modeling of a 2-layer catalytic reactor is carried out; the charges of both SCR catalyst and N_2O decomposition catalyst are determined, which ensures compliance with environmental emission standards for all nitrogen oxides.

Keywords: nitric oxide, nitrous oxide, simultaneous removal, catalysts for SCR, catalysts for low-temperature destruction of nitrous oxide, nitric acid plants

INTRODUCTION

The quality of the environment affects the fortunes of nations, and major pollutants of air and water do not acknowledge national borders. J. Armor [1], a famous American chemist and Head of the Centre for Catalytic Research of Air Products Company, said that simple evident solutions have already been tested, and it is high time to draw attention to advanced and efficient methods in which catalysis is to play a decisive part.

Catalytic technologies have become a generally accepted method to decrease the hazardous effect of technogenic gas emissions on the atmosphere in industrial megapolises.

Estimations of foreign specialists provide evidence [2] that about one third of the world market of catalysts, exceeding 30 billion dollars as a total, is based on the catalysts for environmental protection, and this sector of catalyst branch exhibits a trend to steady growth. Catalytic purification is widely used in motor transport, in manufacturing the products of organic and petrochemical synthesis, mineral fertilizers, sulphur, *etc*. Two different approaches are applied to meet permanently rising requirements of the federal legislation concerning the limitation of the emissions of hazardous substances into the atmosphere. First of all, more efficient and selective basic technologies are under development, providing the formation of decreased amounts of wastes to be utilized or neutralized. Second, permanent improvements of technological processes and arrangements of the devices for ecological purposes are made. Both approaches provide a powerful impetus to the fundamental development of catalysis science and accelerated renewal of the stock of catalysts.

The list of toxic and ozone-destroying substances includes the oxides of nitrogen(II), (IV) and (I) – NO, NO_2 and N_2O, respectively, which are released in the production of weak nitric acid. The necessity of the integrated solution of this problem was stressed in the early 2000-s [3].

First of all, purification of exhaust gases in the production of nitric acid implies the removal of highly toxic nitrogen oxides NO_x (NO and NO_2) because their average daily maximum permissible concentrations (MPC) in the atmosphere are only 0.04 and 0.06 mg/m^3, respectively [4]. Atmospheric concentration of nitrogen (I) oxide is not standardized, however, the Kyoto protocol of 1997 qualifies N_2O (dinitrogen monoxide) as a dangerous greenhouse gas with CO_2-equivalent equal to 310, which causes the destruction of the ozone layer. Chemical industry supplies ~29 % of the total amount of anthropogenic emission of N_2O, and industrial installations for the production of nitric acid belong to the most substantial sources of usual nitrogen oxides (NO_x) and N_2O. The concentration of the latter component in exhaust gases is usually 1000 to 2000 ppm [5]. The factor of nitrogen(I) oxide emission is estimated as 7 kg of N_2O per 1 t of HNO_3 on average, but it may reach 12–20 kg/t for converters operating at high pressure, 7–8 kg/t for medium-pressure converters, and 3–5 kg/t for converters operating at the atmospheric pressure. According to the data of the Institute of Chemical Research in Catalonia (Tarragona, Spain) presented in the report at the 6th Forum on Catalysts, organized by H. Topsøe company, the average emission at 75 plants manufacturing nitric acid in 15 countries of the European Community is 2–9 kg of N_2O per 1 t of HNO_3, with the range 500–1500 ppm N_2O. The world emission of nitrogen(I) oxide from the production of nitric acid is considered to be about 400 thousand tons per year, which makes nitric acid installations the largest stationary source of the industrial emission of N_2O. As a consequence, within the framework of the Kyoto protocol, many industrially developed countries (the USA, Germany and other EC countries) introduce strict limits of N_2O emission for operating and designed facilities for nitric acid production.

The participants of the Round Table organized in March 2019 on the initiative of the Federation Council stressed [6] that active work is carried out with the aim at the legislative provision of the creation and functioning of the state system of monitoring and control of greenhouse gas emissions. At present, basic regulations determining the architecture of state control over the emission of greenhouse gases have been adopted. These acts include:

1) The climatic doctrine of the Russian Federation, upheld by the decree of the President of the Russian Federation on 17.12.2009, No. 861-rp.

2) The integrated plan for the implementation of the Climatic doctrine for the period till 2020, adopted by the arrangement of the Government of the Russian Federation on 25.04.2011 No. 730-r.

3) Edict of the President of the Russian Federation of 30.09.2013 No. 752 “About decrease in the emission of greenhouse gases”.

4) Schedule of measures for the provision of the reduction of greenhouse gas emission by 2020, adopted by the Government of the Russian Federation on 02.04.2014 No. 504-r.

The state policy is focused on the development of the system of state monitoring of the emissions of greenhouse gases and the support for the voluntary projects aimed at the reduction of greenhouse gas emissions by economic subjects. At the same time, the enterprises are solving this problem relying on their economic and technological possibilities.

The UN Conference on climate was held in November 2015 in Paris. At this conference, the Russian Federation supported a new agreement within the UN Framework Convention on climate change (1992) instead of the Kyoto protocol (1997). Russia is planning to decrease the emission of greenhouse gases by 2030 down to 70 % of the level of 1990. Elaboration of new efficient economic factors should stimulate the economy to broader involvement of the modern technologies against greenhouse gases including N_2O.

The possibilities of the realization of integrated low-temperature catalytic purification of gases formed in the production of nitric acid (tail gases) from nitrogen oxides (NO, NO_2) and nitrogen (I) oxide (N_2O) in one reactor are considered in the present paper.

THE FORMATION OF NITROGEN(I) OXIDE IN THE PRODUCTION OF NITRIC ACID

Technological schemes of the production of nitric acid include the reactor of catalytic oxidation of ammonia with the boiler utilizer, heat exchangers, absorption column, reactor of the catalytic purification from nitrogen oxides, and auxiliary equipment. Depending on the scheme, the catalytic process of ammonia oxidation is carried out at high, medium or atmospheric pressure.

Ammonia oxidation in low-capacity aggregates (45–50 thousand tons per year) is carried out at atmospheric pressure at the stage of ammonia conversion and at a pressure of 3.5 bar at absorption stage (combined schemes); UKL systems have a nominal capacity of 120 thousand tons per year and operate at a pressure of 7.16 bar at all units; ammonium oxidation in large-scale aggregates AK-72 (AK-72M) with the productivity of 360–380 thousand tons per year occurs at a pressure of 4.2–4.7 bar, and absorption is carried out at a pressure of 10–11 bar. The residual NO_x content after absorbing columns is 0.05–0.08 vol. % in UKL systems, and 0.1–0.15 vol. % in AK-72 systems. The following reasons leading to the emission of N_2O may be named:

– homogeneous interaction of NH_3 with O_2 before the gauzes because of overheating of the reaction mixture (pre-catalysis);

– the side reaction proceeding during ammonia oxidation on Pt/Rh gauzes:

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \quad (1)$$

– interaction of ammonia slipped through the gauzes with NO according to the reaction:

$$4NH_3 + 4NO + 3O_2 = 4N_2O + 6H_2O \quad (2)$$

– excess supply of NH_3 into the reactor of selective reduction of NO_x (reactions proceeding in this case are listed below).

So, the amount of released N_2O depends on the conditions of ammonia converter operation, on the type of gauzes used in the installation, and on the conditions of purification from NO_x.

Removal of nitrogen oxides from exhaust gases by means of their reduction to molecular nitrogen (DeNO_x processes) may be carried out using different methods. *Selective non-catalytic reduction* proceeds at a temperature above 800 °C, under these conditions NO_x is reduced by ammonia without any catalysts. The use of a catalyst allows NO_x reduction at substantially lower temperatures.

During *non-selective catalytic reduction* (in the absence of oxygen), possible reducing gases may be purge gas of ammonia cycle (mainly H_2), hydrocarbons (natural gas, propane, butane); not only NO_x but also N_2O is reduced in this process. Process temperature depends on catalyst nature and kind of reducing agent [3, 7]. In large-scale aggregates AK-72 for the production of nitric acid, purification of exhaust gases from NO_x is performed by means of high-temperature reduction with natural gas on Pd-containing catalysts at 720–770 °C [8], at the same time, the level of N_2O in exhaust gas does not exceed 50 ppm, and additional purification from N_2O is not required. It may be noted that the reduction of nitrogen oxides with methane in the case of non-optimal O_2/CH_4 ratio may be accompanied by the appearance of such pollutants as greenhouse gases CO_2 and CH_4, as well as CO. With the use of the natural gas, at first oxygen is burnt out, and then nitrogen oxides are reduced according to the following main reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (3)$$
$$CH_4 + 0.5O_2 = CO + 2H_2 \quad (4)$$
$$2NO + 2H_2 = N_2 + 2H_2O \quad (5)$$
$$4NO + CH_4 = 2N_2 + CO_2 + 2H_2O \quad (6)$$
$$3N_2O + CH_4 = 3N_2 + CO + 2H_2O \quad (7)$$
$$4N_2O + CH_4 = 4N_2 + CO_2 + 2H_2O \quad (8)$$

Selective catalytic reduction (SCR) of NO_x with ammonia proceeds in the presence of oxygen and takes place at a temperature of 200–450 °C. Many catalysts in the form of supported oxides MnO_2, CuO, Fe_2O_3 and zeolite systems for low-temperature SCR have been described [9–12]. In Russia, commercially applied catalysts include alumina-vanadium catalysts like AVK-10, AOK-78-55 based on V_2O_5, in particular those modified with MnO_2 [8, 13], and aluminium-copper-zinc catalyst AMTs-10. Alumina-vanadium catalysts are widely used for the purification of exhaust gases from NO_x, they are most active and less sensitive to catalyst poisons [14, 15]. The following basic reactions proceed during the reduction of nitrogen oxides by ammonia:

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O \quad (9)$$
$$8NH_3 + 6NO_2 = 7N_2 + 12H_2O \quad (10)$$

Side reactions leading to the formation of N_2O are also possible:

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \quad (11)$$
$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad (12)$$
$$4NH_3 + 4NO = 4N_2O + 6H_2 \quad (13)$$

Selective catalytic reduction of nitrogen oxides by ammonia on the catalysts listed above is used in UKL-7 schemes and in old-fashioned installations with low capacity operating according to the combined scheme. However, under the conditions of low-temperature SCR the level of N_2O does not decrease, moreover, nitrogen(I) oxide may be formed in the excess of ammonia according to reaction (13) [16].

Installations for the production of nitric acid with the medium pressure at ammonia conversion stage and increased pressure at absorption stage are widespread in industrial countries. Due to the high technological level, very low NO_x con-

TABLE 1

Industrial installations for the production of nitric acid and evaluation of annual emissions of N_2O

Production scheme	Number of installations (in particular in the RF), pc.	Annual emission of N_2O from 1 installation, t	Total annual emission (in particular in the RF), t
Combined 1/3.5	43	200	8600
UKL-7.3	80	457	36 560
AK-72	12 (9)	10–100	(90–900)
AK-72M	3 (1)	3000	9000 (3000)

TABLE 2

Level of N_2O emission in typical schemes of nitric acid production before and after the reactor of catalytic purification from NO_x [16]

Production scheme	Method of purification from NO_x	N_2O concentration, ppm	
		Inlet	Outlet
Combined 1/3.5	Selective reduction of NH_3 (~280...300 °C)*	500–800	900–1200
UKL-7.3	High-temperature reduction of CH_4 (~700 °C)	870–1390	20–50
UKL-7.3	Selective reduction of NH_3 (~280...300 °C)*	~560	~780
UKL-7.3	Selective reduction of NH_3 (~280...300 °C)**	900–1200	900–1000
AK-72	High-temperature reduction of CH_4 (~700 °C)	1000–1200	3–50

*Because of variations in the concentrations of nitrogen oxides in exhaust gases, in the case of insufficiently precise regulation of ammonia dosing, excessive amount of NH_3 may be supplied for the reduction of NO_x; ammonia in excess causes the production of an additional amount of N_2O in the reactor.

**In case of precise ammonia dosing into the reactor of selective purification, N_2O production does not proceed.

tent in tail gases is provided. In Russia, only upgraded AK-72M aggregates are equipped with efficient absorption systems. The cold of liquid ammonia evaporation is used for more efficient heat removal in absorption column, which results in an increase in the degree of absorption of nitrogen oxides. Instead of high-temperature purification of exhaust gases on a Pd-containing catalyst APK-2, the scheme of AK-72M involves low-temperature purification with ammonia on an aluminium-copper-zinc catalyst AMTs-10 at a temperature of 280–300 °C [8, 17]. However, because of the high N_2O content, in this case it is necessary to provide purification from this oxide (Table 1).

Estimations of the average annual emission of nitrogen(I) oxide in the production of non-concentrated nitric acid (55–60 %) in the Russian Federation and FSU countries are presented in Table 1. Estimated data on N_2O content taking into account the methods of catalytic purification of exhaust gases after absorber from nitrogen oxides are shown in Table 2.

According to the analysis performed in [16] (Table 2), N_2O content is not high in the schemes involving high-temperature reduction with natural gas, so additional purification is not necessary. In the schemes using SCR with ammonia, N_2O content in exhaust gases may reach 1500 ppm, and in this case purification from nitrogen(I) oxide is necessary.

So, the main sources of the emission of N_2O in the production of nitric acid in the Russian Federation are UKL and AK-72M installations equipped with low-temperature purification from NO_x on the basis of SCR with ammonia. Emissions of N_2O from installations with high-temperature catalytic purification are very small.

METHODS TO REMOVE N_2O. INTEGRATED PURIFICATION FROM NITROGEN OXIDES NO_x AND N_2O

Above-listed reasons of the formation of nitrogen(I) oxide in the production of nitric acid lead to different methods to decrease its emission. The group of **primary methods** (primary abatement) promoting suppression of N_2O formation during the oxidation of ammonia and in the secondary processes of reaction product interaction with overshot ammonia include optimization of the composition of platinoid gauzes pack and operation conditions, introduction of free volumes for homogeneous decomposition of N_2O at high temperatures. **Secondary methods** (secondary abatement) imply mounting a catalyst for the decomposition of N_2O directly after the gauzes pack. Yara, BASF, J. Matthey, Heraeus companies proposed high-temperature catalysts based on precious metals or

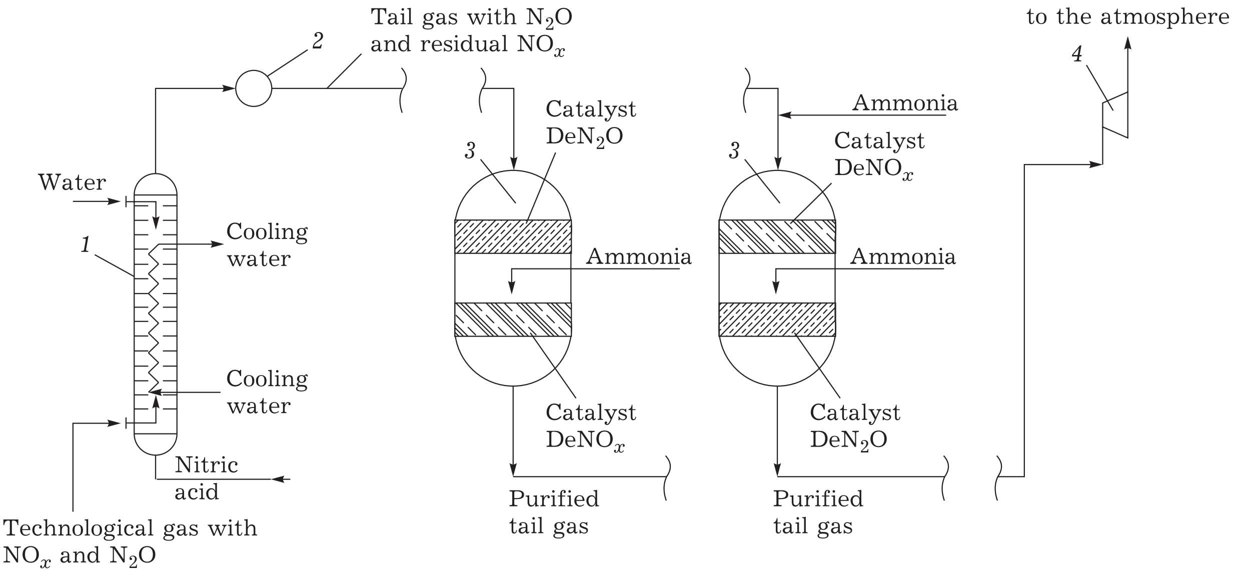

Fig. 1. Scheme of EnviNOx® technology: *a* – version 1 (catalytic decomposition of N_2O and reduction of NO_x by ammonia); *b* – version 2 (NO_x reduction with ammonia and N_2O reduction by hydrocarbons). *1* – absorption column; *2* – heater of tail gas; *3* – reactor; *4* – turbine of tail gas.

metal oxides supported on ceramics. For example, in one of the projects implemented by Heraeus company (Germany), a “secondary” catalyst for the decomposition of nitrogen(I) oxide HR-SC is mounted in a basket immediately under the net pack. The catalyst is formed as aluminium oxide Raschig rings 8×8×2 mm, with a precious metal as the active component [18]. **Tertiary methods** (tertiary abatement) include the removal of N_2O (along with NO_x) from tail gases after absorption column by means of non-selective catalytic reduction or decomposition at moderate temperatures.

Integrated purification from NO_x and N_2O is at present the leading technological trend, and its actual application in the installations of nitrogen acid production in the USA and in Europe includes several hundred industrial lines [19].

A concept of the technology of integrated purification was developed by different companies. In particular, it was implemented by ThyssenKrupp Uhde company (Germany) under the trademark of EnviNOx® [20] at medium temperatures in a double-bed reactor which is mounted directly between the overheater of tail gases and a turbine, in two versions depending on the temperature of tail gases.

Version 1 (Fig. 1, *a*) involves the catalytic decomposition of N_2O proceeding on the Fe-zeolite catalyst in the first bed at a temperature of 425–520 °C according to the reaction:

$$2N_2O = 2N_2 + O_2 \quad (14)$$

then ammonia is introduced before the second bed, and catalytic reduction of NO_x by ammonia to N_2 proceeds in the second bed on the similar catalyst according to reactions (9) and (10). As NO_x promotes the decomposition of N_2O, the $DeNO_x$ stage is located after the DeN_2O stage.

This version is recommended for application at the tail gas temperature higher than 425 °C. In the cases when tail gas temperature is within a lower range of 300–450 °C, *version 2* is used (Fig. 1, *b*): ammonia is introduced together with tail gases. In the first bed, SCR of nitrogen oxides with ammonia proceeds according to reactions (9) and (10), and hydrocarbons (natural gas or propane) are introduced before the second bed for the reduction of N_2O according to reactions (7) and (8). In this case, it is necessary to remove NO_x from tail gases completely because NO_x inhibit the reduction of N_2O.

In addition to an analogue of version 2, the version in which the catalyst of N_2O decomposition is placed after the SCR catalyst is described in [21] for simultaneous removal of NO_x and N_2O from the combustion gases of engines operating with lean fuel mixtures. According to this scheme, selective catalytic reduction of NO_x with propylene leading to the formation of N_2O is carried out in the first catalyst bed (Pt on activated carbon) at a low temperature 200–220 °C. The second bed may contain either the catalyst of N_2O decomposition or the catalyst of N_2O reduction (Co compounds on hydrotalcite, Fe-ZSM-5) by hydrocarbon, in the latter case propylene is introduced before the second bed. In both cases, the second bed operates at 430–480 °C. A substantial difference

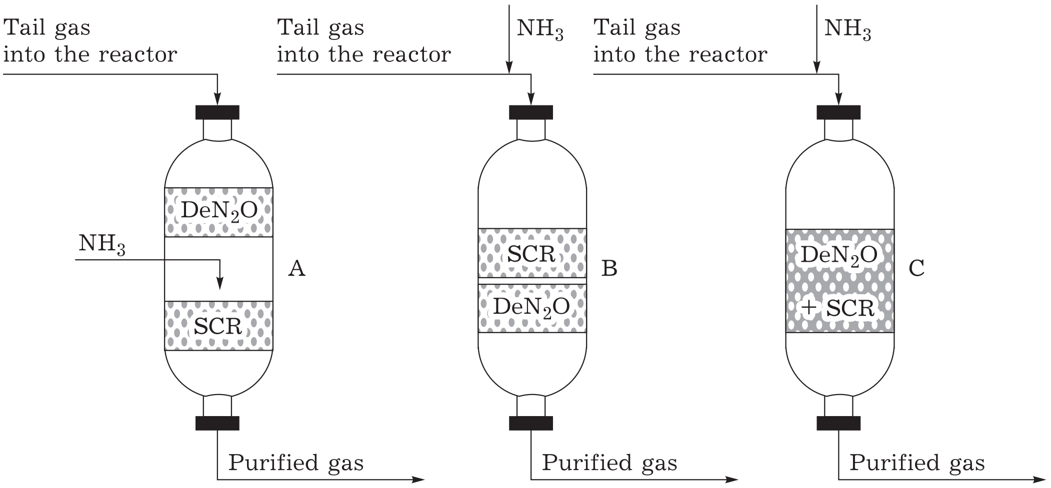

Fig. 2. Schemes of combined loading of the reactor for gas purification from nitrogen oxides.

between the optimal temperature windows of the catalysts does not allow considering the proposed schemes as promising for the purification of tail gases of nitric acid production. In the systems of integrated purification from nitrogen oxides, the use of the catalyst of N_2O decomposition in the second bed may be preferable, though this would require choosing a corresponding catalytic composition.

It is reasonable to solve the problem of the arrangement of integrated purification of exhaust gases from nitrogen oxides taking into account the features of production layout. The UKL installations for nitric acid production operating in the RF are already equipped with the reactors for low-temperature catalytic purification by means of SCR. The dimensions of the free volume and the design of the bearing internal supporting structures for the reactor of catalytic purification in UKL installations allow the arrangement of not only the layer of SCR catalyst but also a layer of the catalyst of N_2O decomposition 0.5–0.7 m high. Because of this, the integrated purification of tail gases may be implemented in the same apparatus by making a catalytic system that secured both SCR of NO by ammonia, and the decomposition of N_2O within temperature range 250–300 °C [21].

The possibility to implement known technological schemes of integrated low-temperature purification of tail gases from a mixture of NO_x and N_2O for UKL aggregates is now to be considered, taking into account the fact that the commercial catalyst of SCR of NO_x by ammonia is used to remove NO.

The versions of the catalyst arrangement in the adiabatic reactor are shown in Fig. 2.

Version A: the catalyst of N_2O decomposition is placed in the first layer as the gas enters the reactor, while the ammonia is introduced before the second layer on which the catalyst of SCR of NO_x is placed. This method will require precise ammonia dosing to avoid the additional formation of N_2O during SCR. Version B: the catalyst of SCR of NO_x with ammonia is placed in the first layer (NH_3 is introduced together with tail gases), while the catalyst of N_2O decomposition is in the second layer. For the efficient implementation of this version, both catalyst beds should have close temperature regions of operation. Version C: purification from N_2O and NO_x proceeds on a hypothetic bifunctional catalyst (or on a mixture of catalysts), ammonia for SCR is introduced together with tail gases. In this method, the catalyst of N_2O decomposition should be stable not only to the presence of NO and water but also to the action of ammonia.

In view of the actual temperature modes of the operation of the catalysts of SCR and N_2O decomposition, the most reasonable method is version B, which may be adapted to the existing industrial conditions.

PROMISING CATALYSTS FOR NO_x AND N_2O REMOVAL

Catalytic technologies are very successfully used to solve ecological problems connected with the emission of dangerous nitrogen-containing gases in the industrial production of nitric acid.

At present, in the RF at the plants producing nitric acid, selective catalytic reduction of NO_x with ammonia on alumina-vanadium catalysts AVK-10, AOK-78-55 with the mass fraction of V_2O_5 12–12.5 %, sometimes with MnO_2 admixture in the amount of 1–1.5 mass % is used to decrease NO_x level to the content admissible by ecological standards (<50 ppm). Improvement of the technology of the preparation of V/Al catalysts for SCR was carried out at the Boreskov Institute of Catalysis SB RAS (BIC SB RAS), which results in a successful decrease in V_2O_5 content to 5–7 mass % [22] (in comparison with 12–15 % [13]) with the retention of the high activity of the catalyst in SCR and selectivity with respect to molecular nitrogen, which allows enhancing the efficiency of the use of this catalyst. Results showing a comparison between catalyst activities are presented in Table 3.

The temperature region of the operation of V/Al catalysts without a decrease in selectivity with respect to N_2 is 220–280 °C, which sets the problem to develop a catalyst of N_2O decomposition operating in a close temperature range.

In the technology of integrated purification from nitrogen oxides known under the trademark of EnviNOx® [20], Uhde Company (Germany) uses a Fe-zeolite catalyst as the catalyst of N_2O decomposition. The advantages of this kind of catalysts include relatively low cost of production, high stability during long-term operation, and bifunctional nature, that is, efficiency in $DeNO_x$ and DeN_2O reactions. However, catalytic systems based on zeolites get deactivated in the presence of water and cause the decomposition of N_2O at a temperature above 350 °C [23], which may require additional energy consumption for gas heating in the case if this catalyst is used together with the V/Al catalyst [24]. Cobalt spinels in which Co is partially substituted by Ni are able to decompose N_2O into nitrogen and oxygen at 200–300 °C [25]. The high activity of the systems of this kind is due to the ease of the transition $Co^{3+} \leftrightarrow Co^{2+}$ as a result of rapid adsorption and desorption of oxygen, which has a substantial effect on the rate of the limiting stage of N_2O decomposition – oxygen desorption.

Experimental data on the catalytic activity of different systems in the decomposition of N_2O at low and medium temperatures are shown in Table 4.

The oxide catalyst based on $Ni_xCo_{3-x}O_4$, doped with Cs cations, has a spinel structure and is the

TABLE 3

Comparison of the activity of industrial and experimental samples of catalysts for SCR

Temperature, °C	Sample made at the BIC SB RAS [22]		Commercial sample		Conditions of laboratory tests
	X_{NO}, %	S_{N_2}, %	X_{NO}, %	S_{N_2}, %	
220	61.25	99.5–99.9	59.36	99.7	Flow isothermal reactor; Volume flow rate 24 000 h^{-1}; fraction 0.25–0.50 mm; [NO]: ~1000 ppm, $[NH_3]$: ~1200 ppm, $[O_2]$: 4.1–4.5 %, He – balance
240	86.12		84.72	99.6	
250	97.90		–	–	
260	98.78		98.98	99.4	
280	99.29		99.08	99.3	
300	99.06		98.85	–	
350	96.60		98.47	–	

Note. 1. $X_{NO} = (C^0_{NO} - C_{NO})/C^0_{NO}$; $S_{N_2} = C_{N_2}/(C^0_{NO} - C_{NO})$, where C^0_{NO} and C_{NO} are initial and final concentrations of nitrogen oxide; C_{N_2} is the concentration of molecular nitrogen. 2. Dash means the absence of data.

TABLE 4

Catalytic activity of oxide systems in the decomposition of N_2O

Catalyst	T*, °C	Reaction conditions (composition of initial gas, carrier gas, and the volume flow rate)	Reference
Fe/ZSM-5	450	700 ppm N_2O, 1000 ppm NO, 1100 ppm NH_3, 4.5 vol. %. O_2, 2 vol. % H_2O, in He; 7200 h^{-1}	[24]
$Pb_{0.04}CoO_x$	414	2000 ppm N_2O, 500 ppm NO, 5 vol. %. O_2, in He; 20 000 h^{-1}	[26]
$K\text{-}Co_{2.6}Zn_{0.4}O_4$	350	900–1050 ppm N_2O, 400–530 ppm NO, 1100 ppm NH_3, 1–1.3 vol. %. O_2, 0.3–0.5 vol. % H_2O, in He; 20 000 h^{-1}	[27]
$Cs\text{-}Ni_xCo_{3-x}O_4$	220	1500 ppm N_2O, 1000 ppm NO, 1100 ppm NH_3, 2.5 vol. %. O_2, 3 vol. % H_2O, in He; 7200 h^{-1}	[28]

*Minimal reaction temperature at which N_2O conversion exceeds 90 %.

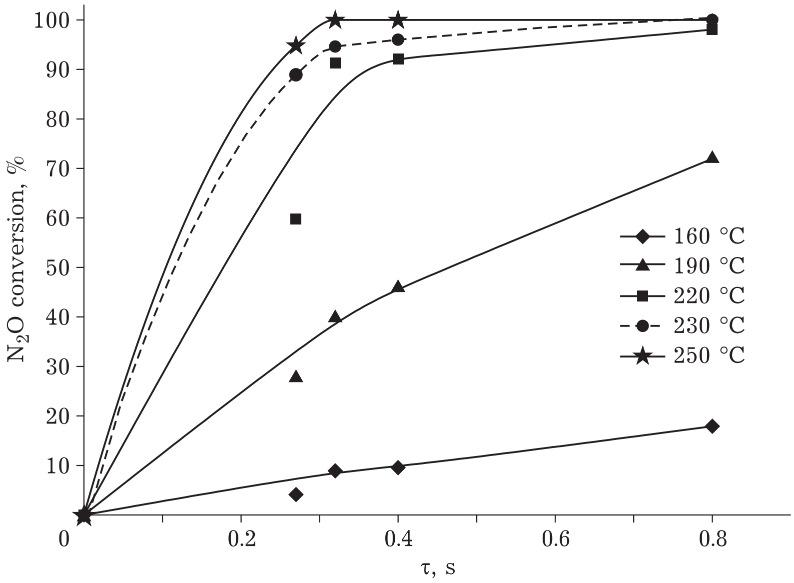

Fig. 3. Dependence of N_2O conversion on the oxide Ni-Co-containing catalyst on contact time at different temperatures. The graphs were plotted in OriginPro 9.1 software, the curves were approximated by the Akima-Spline function.

most active system for N_2O decomposition at 220–300 °C. The presence of a modifying agent in the form of the cations of alkaline metals, in particular Cs, simplifies oxygen desorption and increases catalyst activity in the decomposition of N_2O [29]. The advantage of the systems based on Co_3O_4 is in the fact that they do not lose their activity in the presence of water and oxygen.

A catalytic system based on Ni and Co compounds, modified with alkaline metals, is proposed at the BIC SB RAS for the low-temperature decomposition of N_2O [28, 30]. Determination of the activity was carried out using a laboratory set-up with a flow isothermal reactor within the volume flow rate Q range of 4500–14 000 h^{-1}; the catalyst was tested in the form of the size fraction 0.25–0.50 mm, the initial mixture contained 1500 ppm N_2O, 2.5 % O_2, ~3 % H_2O, trace amounts of NO and NH_3, He – balance. The results of studying the dependence of N_2O conversion on conventional contact time τ ($\tau = 3600/Q$, s) at different temperatures are shown in Fig. 3. The data on conversion stabilized in the reaction medium are presented. These data were later on used to model the reactor and to calculate the volume of the catalyst of low-temperature decomposition of N_2O.

MODELING OF THE CATALYTIC REACTOR FOR COMBINED PURIFICATION FROM NO_x AND N_2O

It is assumed in the present work that the integrated catalytic purification of tail gases from NO_x and N_2O in UKL installations is carried out according to scheme B (Fig. 2), that is, in a two-bed shell reactor. The volume flow rate of tail gases entering the reactor is 46 000 m^3/h (under normal conditions); the temperature and composition of tail gases at the inlet correspond to the industrial data shown in Table 2; the inner diameter of the apparatus is 3.8 m. Calculation of the volumes of catalyst charging into the reactor was carried out by means of mathematical modeling, the algorithm involved the determination of conventional contact time in each layer which was necessary for the achievement of the maximum permissible concentration in purified gas after the first layer: NO_x (50 ppm), and after the second layer: N_2O (50 ppm).

The mathematical model of the process of catalytic purification in the adiabatic reactor takes into account the convective transfer of mass and heat in each layer, the observed rates of chemical transformation of NO_x and N_2O and heat evolution as a result of exothermal reactions. It was previously established in experiments that the kinetic model of the selective catalytic reduction of nitrogen oxides by ammonia in the presence of the V_2O_5/Al_2O_3 catalyst is described by the equation of the first order with respect to NO_x [30]. The kinetic model of N_2O decomposition into nitrogen and oxygen on the oxide Co-containing catalysts is described by the equation of the first order with respect to N_2O [32]. Rate constants were related to the unit volume of the

TABLE 5

Basic calculated parameters of the reactor for the integrated catalytic purification of tail gases in the production of nitric acid

Technological parameters for tail gas flow rate equal to 46 000 m^3/h (under normal conditions)	The first layer $DeNO_x$	The second layer DeN_2O
Working temperature range, °C	220–240	230–260
Conventional contact time, s	0.38	0.48
Catalyst layer height, m	0.42	0.53
Degree of purification, %, not less than	98.0 (with respect to NO_x)	98.0 (with respect to N_2O)
Volume of catalyst in the layer, m^3	4.76	6.0
Pressure drop, kPa	3.5	6.2

TABLE 6

Composition of the major impurities at the inlet and outlet of the reactor of integrated catalytic purification

Composition of impurities	at the inlet, ppm	at the outlet, ppm
NO_x	700–1500	22–50
NH_3	700–1500	43–60
N_2O	900–1200	30–50
O_2 (vol. %)	1.9–4.5	1.9–4.5

catalyst layer, and thus both the activity of the catalyst and the porosity of the layer were taken into account.

Calculations were carried out for atmospheric pressure; after the first layer in which either an industrial V/Al catalyst of SCR process in the form of cylinders ∅5×15 mm or the promising catalyst [22] was used, with the conventional contact time 0.35–0.45 s and within working temperature range 220–240 °C, the residual content of NO_x is not more than 20–50 ppm. Then the gas enters the second layer, where a Ni-Co-containing catalyst of N_2O decomposition is placed. It was demonstrated by varying the size of the particles of Ni-Co-catalyst that loading catalyst grains in the form of cylinders ∅4×8 mm with the conventional contact time 0.4–0.5 s and temperature within the range 230–250 °C ensures the degree of N_2O decomposition not lower than 98 %. Under these conditions, N_2O content in exhaust gases will be lower than 30–50 ppm. With the nominal load with tail gases, the total pressure drop in two layers will be no more than 100 kPa.

The main technological and design characteristics of the reactor for the integrated catalytic purification of exhaust gases of nitric acid production from NO_x and N_2O in UKL installations are presented in Tables 5 and 6.

CONCLUSION

The state of NO_x and N_2O emission in typical nitric acid installations operating in Russia is analyzed. A possible technological scheme of integrated low-temperature single-reactor purification of exhaust tail gases from NO_x and N_2O with the use of V/Al catalysts of the SCR of NO_x by ammonia and a Cs/Co_3O_4 catalyst of N_2O decomposition is proposed.

For the UKL installation, calculations of a two-bed arrangement of the catalysts of SCR of NO_x and the decomposition of N_2O in the reactor of catalytic purification were carried out, and estimated values of the load of SCR NO_x and N_2O decomposition catalysts providing the ecological standards of the emission of nitrogen oxides were obtained.

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