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Catalytic methods for lowering the amount of nitrogen oxides in exhaust gases on combustion of fuel

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ABSTRACT. The catalytic methods for reducing the amount of nitrogen oxides in exhaust gases on combustion of different types of fuel are analysed: the catalytic combustion method and the method involving the selective catalytic reduction of nitrogen oxides by ammonia.

The bibliography includes 187 references.

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I. Introduction

Nitrogen oxides NO_x (NO and NO_2) are some of the most dangerous contaminants of air. Extremely low maximum permitted concentrations (MPC) have been established in all industrially developed countries for these compounds, which have a pronounced general toxic and irritant activity. Together with sulphur oxides, nitrogen oxides make a large contribution to the formation of acid rain, which leads to the destruction of forests, the poisoning of water reservoirs, and the formation of smog[1].

Considerable amounts of NO_x (up to 770 million tonnes annually) are formed as a result of natural processes—nitrification, forest fires, and storms. As a result of human activity, about 60 million tonnes of NO_x (calculated as NO_2) is produced annually[1,2], but anthropogenic waste is concentrated, in contrast to natural ones, in populated regions and lead to high local ground level NO_x concentrations. The principal sources of nitrogen oxides in industrially developed countries are power generation and transport, giving rise to approximately 95% of NO_x waste, the contribution of chemical industry being less than 5% [2]. Thus the principal amount of anthropogenic NO_x is produced as a result of the combustion of gas, petroleum fuel, coal, and other solid fuels. Further increase in the amount of NO_x waste can lead to irreversible ecological consequences on a global scale and therefore questions concerning the reduction of the amount of such waste are of extremely great current interest. A combined approach, including both the purification of smoke gases and the reduction or prevention of the formation of NO_x in combustion processes is required for the solution of this problem.

II. Sources of nitrogen oxides in fuel combustion processes

Nitrogen oxides can be formed on combustion of fuel both from atmospheric nitrogen ("thermal" and "fast" NO_x) and from bound nitrogen forming part of the composition of nitrogen-containing compounds ("fuel" NO_x).

1. Thermal nitrogen oxides

Thermal nitrogen oxides are formed as a result of the high-temperature oxidation of atmospheric nitrogen via Zel'dovich's radical chain mechanism[1,3]:

$$O_2 + M \overset{k_1}{\rightleftarrows} 2O + M, \quad (1)$$

$$N_2 + O \overset{k_2}{\rightleftarrows} NO + N, \quad (2)$$

$$O_2 + N \overset{k_3}{\rightleftarrows} NO + O, \quad (3)$$

where M is any species. Reaction (3) proceeds much faster than reaction (2) and the rate of formation of NO is therefore specified by the equation

$$\frac{d[NO]}{dt} = 2k_2[O][N_2] = k_{eff}K^{1/2}[O_2]^{1/2}[N_2],$$

where $k_{eff} = 2k_2$ is the effective rate constant and K is the equilibrium constant of reaction (1).

The temperature dependence of the yield of thermal NO_x is exponential. In the temperature range characteristic of the flame combustion of fuel in air (1800 K and above), the equilibrium concentration of NO exceeds 1500 p.p.m. Considerable amounts of NO (up to 500 p.p.m.) can be formed already at 1500 K.

2. Fast nitrogen oxides

Fast nitrogen oxides are formed in the combustion of hydrocarbons as a result of the interaction of hydrocarbon radicals with atmospheric nitrogen. These processes take place mainly in the presence of a deficiency of oxygen[1,2,4]:

$$N_2 + HC \rightarrow HCN + N,$$
$$N + OH \rightarrow H + NO,$$
$$HCN + (H, OH) \rightarrow CN + (H_2, H_2O),$$
$$CN + O_2 \rightarrow CO + NO,$$
$$CN + OH \rightarrow CO + NH,$$
$$NH + OH \rightarrow NO + H_2,$$
$$NH + NO \rightarrow N_2 + OH.$$

3. Fuel nitrogen oxides

Nitrogen-containing compounds entering into the composition of fuels (including basic compounds—derivatives of pyridine, quinoline and acridine, and neutral compounds—various amides, nitriles, derivatives of pyrrole, indole, and carbazole, and other compounds[5]) are also sources leading to the formation of nitrogen oxides.

The formation of NO_x from fuel nitrogen proceeds via a series of intermediates; in particular, in the oxidation of pyridine and pyrrole, cyclic nitriles and CO are formed as intermediates[6]. One of the intermediates is hydrogen cyanide whose formation has been noted in the pyrolysis of pyridine[7] and in the oxidation of various nitrogen-containing compounds in mixtures with fuel in the presence of a deficiency of oxygen.[8,9] Regardless of the nature of the nitrogen-containing additive (NO, NH_3, CH_3CN, pyridine), bound nitrogen is almost fully converted into HCN in the reaction zone of the flame. On moving away from the reaction zone, the amount of HCN diminishes as a result of its conversion into N_2 and NO_x. Ammonia may also be detected together with N_2, HCN, and NO_x in the products of the combustion of nitrogen-containing fuels in the presence of a deficiency of nitrogen[10].

The mechanism of the interconversion of nitrogen-containing compounds in the flame has been considered in a number of studies[9,10–13]. The following mechanism for the conversion of fuel nitrogen has been proposed:

$$\boxed{\text{Fuel nitrogen}} \rightarrow \text{HCN} \rightarrow \text{NH}_x \begin{cases} \rightarrow \text{NO}_x, \\ \rightarrow \text{N}_2 . \end{cases}$$

According to experimental data, the conversion of fuel nitrogen into HCN is rapid and the rate-limiting stage is the oxidation of HCN [13]. The degree of conversion of fuel nitrogen into oxides in flame combustion is 20–50% and above[14–16]; the yield of NO_x is influenced by the content of nitrogen in the fuel (N_f) [14–16], the coefficient of the excess of air α† [17–19], and, to a lesser extent, the combustion temperature[20].

4. Methods for the suppression of the formation of NO_x in flame combustion

In order to combust the waste products comprising thermal nitrogen oxides, methods promoting a decrease in temperature in the combustion zone are employed: recirculation of the combustion products supplied to the combustion chamber, injection of water or steam into the combustion chamber, reduction of the additional heating of air[2,21,22]. These measures are insufficiently effective for the suppression of the formation of fuel NO_x whose sensitivity to temperature is low. The principal methods for the reduction of the amount of fuel NO_x waste involved a decrease in the coefficient of the excess of air and stepwise (two-stage) combustion[23]. In the latter method, air is supplied into the primary combustion zone in an amount less than that required theoretically. This results in a decrease in the O_2 concentration and in the flame temperature and hence in a decrease in the formation of both fuel and thermal NO_x. An amount of air insufficient for the combustion of uncombusted components is introduced to the secondary zone. The temperature in the secondary zone does not then reach the level sufficient for the formation of appreciable amounts of NO_x.

The improvement of the technology of flame combustion and design and technical measures make it possible to reduce somewhat the amount of waste comprising nitrogen oxides from combustion devices, but these possibilities are limited. Furthermore, the application of methods for the suppression of the formation of NO_x such as the recirculation of the combustion products, multistage combustion, and a decrease in the coefficient of the excess of air usually lead to an increase in the content of carbon monoxide, soot, and carcinogenic substances in the effluent gases and also to a breakdown in the stability of the combustion.[24,25] The principal methods for reducing the amount of NO_x waste have been described[21] (Fig. 1).

Norms for the content of NO_x in air have been established in our country[26] and standards are being developed for the maximum permissible amounts of waste (MPW) comprising NO_x for individual undertakings and industrial complexes.[2,27] The requirements for the maximum permissible amounts of waste NO_x have already been established in a number of countries[28,29]. Thus in Japan the NO_x MPW is 60 p.p.m. for large gas-operated boilers, 150 p.p.m. for masout-operated boilers, and 200 p.p.m. for carbon dust-operated boilers[29]. The existing methods for suppressing the formation of NO_x in the flame combustion of fuels cannot ensure the fulfillment of such rigorous requirements as regards the purity of smoke gases and it is therefore necessary to resort to expensive measures such as the catalytic elimination of NO_x from gases[30]. The best results have been obtained in the catalytic reduction of nitrogen oxides by ammonia and this method has been widely adopted in recent years in industrial boiler aggregates in a number of countries.

III. Selective catalytic reduction of nitrogen oxides by ammonia

1. Principles of the method

In contrast to the methods involving the improvement of the technology of flame combustion, the processes in which smoke gases are purified ensure a much greater reduction in the amount of NO_x waste—by 60–90%. The methods for the elimination of NO_x from smoke gases[21,31–33] have come to be divided into "wet" and "dry" (Fig. 1). The wet methods, based on the absorption of nitrogen oxides by aqueous solutions of various compounds, have not found extensive application, since under these conditions there arises, firstly, the problem of the utilisation of the waste water, and, secondly, it becomes necessary to heat the gases after purification before ejection into the smoke tube, which requires a large comsumption of fuel. Among the dry methods, the reduction of NO_x to molecular nitrogen, which need not be utilised, are of greatest interest for practical employment[32].

The non-selective reduction of nitric oxide by natural gas, hydrogen, or carbon monoxide occurs at 520–670 K in the presence of catalysts[2]:

$$4NO+CH_4 \rightarrow 2N_2+CO_2+2H_2O, \quad (4)$$

$$2NO+2H_2 \rightarrow N_2+2H_2O, \quad (5)$$

$$2NO+2CO \rightarrow N_2+2CO_2. \quad (6)$$

† The coefficient of the excess of air α is defined as the ratio of the amount of air supplied for the combustion of the fuel to the amount of air required theoretically for the combustion of the given mass of fuel.

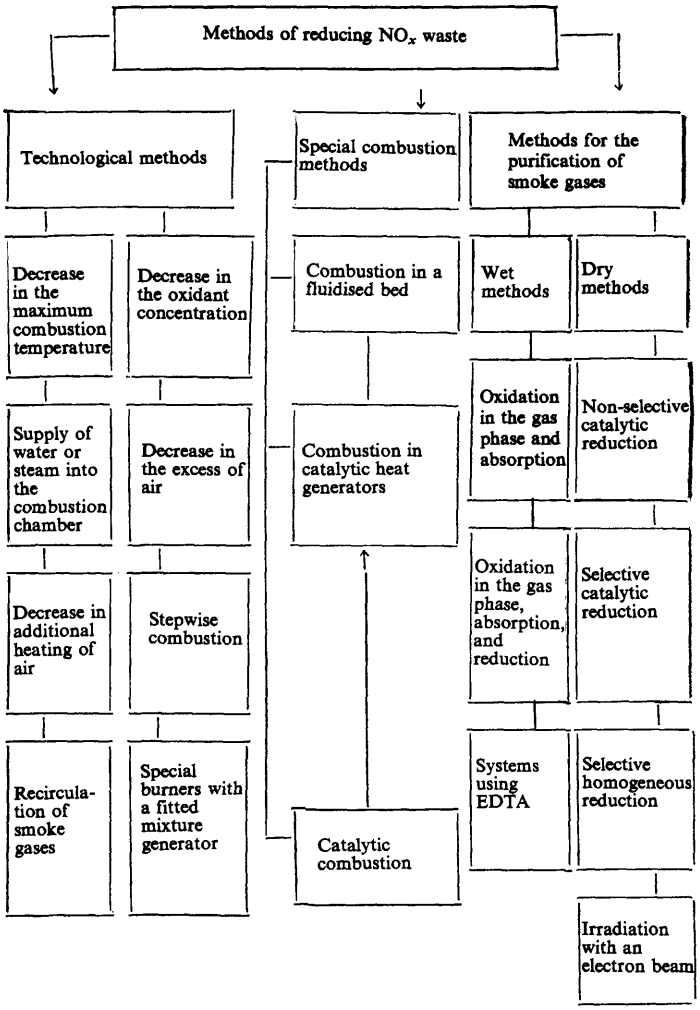


Figure 1. Methods for the reduction of NO_x waste[21].

These processes occur in a medium which contains virtually no oxygen and the first stage of the non-selective catalytic purification is therefore the "burning-off" of the oxygen in the smoke gases by the excess reductant. This consumes an amount of reductant tens of times greater than that consumed in the reaction with nitrogen oxides and methods for the non-selective catalytic reduction have not therefore found applications for the purification of smoke gases from boilers and their employment is limited to the purification of residual gases from plants for the manufacture of nitric acid[31].

The catalytic reduction of NO_x by ammonia with formation of nitrogen and water is at present regarded as the most promising of the catalytic procedures for the purification of smoke gases. This is associated with the fact that, in contrast to other reductants (methane, hydrogen, carbon monoxide, and hydrocarbons), ammonia is capable of reducing selectively nitrogen oxides in the presence of an excess of oxygen in the smoke gases[31].

The method for the selective catalytic reduction (SCR) makes it possible to reduce the amount of NO_x waste in the ideal case by more than 90%, although in practice, owing to the limitations imposed by the volume of the catalytic reactor and the permissible breakthrough of ammonia, a degree of purification of 65–80% is usually attained[32,33].

In the absence of oxygen, the interaction between ammonia and nitric oxide is described by the equation

$$4NH_3+6NO\rightarrow 5N_2+6H_2O. \quad (7)$$

In the presence of oxygen, the reduction of nitric oxide is accelerated[32] and the reaction

$$4NH_3+4NO+O_2\rightarrow 4N_2+6H_2O, \quad (8)$$

takes place. The role of oxygen consists in the reoxidation of the catalyst surface, which is converted into the reduced form following the adsorption of ammonia[31,32]. There exist data[34,35] showing that the rate of reaction of nitrogen dioxide with ammonia is independent of the oxygen concentration. The reaction proceeds in accordance with the equation

$$3NO_2+4NH_3\rightarrow 3,5N_2+6H_2O. \quad (9)$$

In an equimolar $NO-NO_2$ mixture, nitrogen oxides are reduced via the reaction[36]

$$NO_2+NO+2NH_3\rightarrow 2N_2+3H_2O. \quad (10)$$

Reaction (10) is the fastest of those occurring in the $NO_x-O_2-NH_3$ system[34].

Reaction (8) plays the main role in the SCR process, because in most smoke gases 90–95% of nitrogen oxides consists of NO. According to the stoichiometry of reactions (8) and (10), the molar ratio of NO_x and NH_3 should be close to unity. It has been stated[32] that a decrease in the amount of NO_x waste by 60–85% requires that the NH_3:NO molar ratio should be 0.6–0.9 and that the residual ammonia in the effluent smoke gases should be less than 1–5 p.p.m. The temperature necessary to reduce NO_x depends on the type of catalyst and is usually 570–670 K. In order to attain such temperatures without additional heating of the smoke gases, the SCR reactor is as a rule placed between the economiser and the air heater.

In the practical organisation of the elimination of NO_x from gases, it is necessary to take into account all the possible processes which may occur in the system containing the catalyst, ammonia, and smoke gases.

In the presence of oxygen, the ammonia oxidation reactions take place on the catalyst[36]:

$$2NH_3+1.5O_2\rightarrow N_2+3H_2O, \quad (11)$$

$$2NH_3+2O_2\rightarrow N_2O+3H_2O, \quad (12)$$

$$2NH_3+2.5O_2\rightarrow 2NO+3H_2O. \quad (13)$$

Reaction (13), whose occurrence can lead to an increase in the NO concentration compared with its concentration in the initial gas, is especially undesirable. Furthermore, the majority of the catalysts used accelerate the reaction[37]

$$2SO_2+O_2\rightarrow 2SO_3. \quad (14)$$

Following the breakthrough of ammonia and in the presence of SO_3 in the smoke gases, the following reactions can occur:

$$NH_3+H_2O+SO_3\rightarrow NH_4HSO_4, \quad (15)$$

$$2NH_3+H_2O+SO_3\rightarrow (NH_4)_2SO_4. \quad (16)$$

Ammonium sulphate and hydrogen sulphate are formed in these processes. A decrease in the temperature of smoke gases can lead to the contamination by the latter of the heating surfaces or of the catalyst itself. There is a possibility of a version in which the catalytic reactor is placed beyond the apparatus for the desulphurisation of the smoke gases, but in this case the latter must be heated additionally (approximately from 340 to 620 K) by combusting the gas or masout[37], i.e. as a result of an additional consumption of fuel.

Thus the most important requirements which must be met by the SCR catalysts are their high activity in the temperature range 570–670 K and their high selectivity, excluding the appreciable occurrence of the undesirable reactions (11)–(16). The requirements include[38] high resistance to erosion by the ash formed on combustion of the solid fuel, resistance to catalytic poisons present in the ash, the optimum porous structure excluding the blocking of the catalyst pores by dust, and a low hydraulic resistance.

2. Catalysts for selective catalytic reduction

SCR catalysts containing titanium, tungsten, tin, manganese, nickel[39], vanadium, molybdenum, tantalum, boron[40], chromium, iron, copper, cobalt, lanthanide[41], and uranium[42] oxides, platinum metals[43,44], cerium, iron, and manganese halides[45], transition metal ferrites[46], transition metal salts formed by the Si–W, Si–Mo, P–W, and P–Mo heteropolyacids[47], transition metal carbides[48], copper alloys[49], intermetallic compounds of platinum group metals with aluminium, scandium, titanium, and other metals[50], and zeolites[51,52] have been patented as SCR catalysts.

The catalyst carriers employed are aluminium oxide[53,54], aluminosilicates[55,56], alumina, silica[57], calcium silicate[58], titanium dioxide[59,60], a mixture of titanium dioxide and silicon dioxide[61], and zeolites[62,63]. Carriers consisting of sheet metal[64], metallic mesh[65], and ceramic honeycomb blocks[54,66,67] have been patented.

Analysis of the patent literature shows that the principal component of the catalyst carriers used to ensure the safety of the smoke gases from thermal electric power stations is titanium dioxide, which is highly stable as regards the sulphur oxides present in the smoke gases. Titanium dioxide is used both in a pure form[59,60] and together with other oxide additives: SiO_2 [61], WO_3 [68,69], MoO_3 [69], various SiO_2, Al_2O_3, ZrO_2, or ThO_2 compositions[67], as well as clay substances of the type of kaolin, montmorillonite, halloysite, pyrophyllite, or their mixtures[70]. Compounds of vanadium (V_2O_5 [59,62,63], $VOSO_4$ [71], or vanadium oxides with added TiO_2 or other metal oxides), niobium[67], silicon or zirconium[72], tungsten or molybdenum[73,74], the lanthanides[75,76], and tin[74,77,78] are usually employed as the active components of industrial catalysts. The oxides of elements in the following combinations can also serve as active components: Mn and Sn, Mn and Cd, Fe and Ni, Fe and Bi, Cr and Ni, Cr and Sb, Cu and Mo, and Co and Pb[79]. Other combinations of metal oxides, chosen from the following groups have also been proposed: Cu, Mn and Cr, on the one hand, and V, Mo, Cl, and Sn, on the other[80]. Group VB, VIB, VIIB, and VIII metal oxides are also active SCR catalysts[81].

Noble metals exhibit a high activity at 370–470 K, but their use is limited by the reduction of NO_x in the pure gases, in which there are no catalytic poisons, especially SO_2 [82]. Platinum can be employed in the range 440–520 K: the lower limit is determined by the possibility of the deposition of explosive ammonium nitrite and nitrate and the upper is set by the reaction involving the oxidation of ammonia to nitrogen oxides.

The activity of metals (deposited on Al_2O_3) diminishes in the sequence Pt $\simeq$ Pd $\gg$ Ru > Ni for the $NO-NH_3$ system, Pt $\gg$ Pd $\gg$ Ru > Ni for the $NO-NH_3-O_2$ system, Ru $\gg$ Pt, Pd, Ni for the $NO-NH_3-SO_2$ system, and Pt $\gg$ Pd, Ru > Ni for the $NO-NH_3-SO_2-O_2$ system[83,84].

In the absence of SO_2, oxygen accelerates the reduction of NO_x on platinum, ruthenium, and nickel catalysts but lowers the rate of reaction on the palladium catalyst, which can be explained by the reversible oxidation of the metal surface. In the presence of SO_2, the metal surface is covered by a monolayer of S^{2-} ions and the activity falls by 3–5 orders of magnitude; the ruthenium catalyst, whose activity falls only by a factor of 4, exhibits a notable resistance to poisoning by sulphur. The addition of oxygen to this system leads to the partial restoration of activity. Noble metals promote the ammonia oxidation side reactions in the presence of oxygen, the main one being the N_2O formation reaction (12) [83].

The activity of substituted type Y zeolites containing transition metals varies in the sequence $Pt^{II}-Y > Fe^{III}-Y > Ni^{II}-Y > Co^{II}-Y$ [85]. The zeolites are active in the temperature range 370–470 K. The presence of oxygen increases the rate of reduction of NO_x. Sulphur dioxide lowers the degree of conversion at T > 530 K, inducing the partial decomposition of the zeolite with formation of sulphates, in particular $(NH_4)_3Al(SO_4)_3$. Their deactivation in the presence of water vapour is a significant disadvantage of zeolites[86].

The activity of transition metal oxides increases in the sequence Ni < Ti, Sn, Co, Zn < W < Mo < Cr < V, Fe, Cu, Mn [31,87]. The oxides are also poisoned by sulphur, iron and vanadium oxides being the most stable. Apart from oxides, transition metal salts are active in SCR reactions: in terms of their influence on the relative catalytic activities of catalysts containing copper or iron, the counterions can be arranged in the sequence $Br^- > Cl^- > SO_4^{2-} > O^{2-}$ [88]. In the conformity with this, copper and iron oxide are less active in the absence of SO_2 than the sulphates; on the other hand, in the presence of SO_2, the oxides are converted into sulphates and their activities become similar. The activities of metal oxides in the presence of SO_2 diminish in the sequence $CuO > Fe_2O_3 > Co_3O_4 >$ NiO, while water vapour has hardly any influence[87]. Under industrial conditions, the majority of oxide catalysts, including even the most active and sulphur-resistant iron and iron-chromium catalysts deposited on alumina, lose their activity after working for several hundreds of hours as a result of poisoning by sulphur. The industrial application of the SCR method has become possible only as a result of the development of TiO_2-based catalysts, which possess a high activity and resistance to poisoning by sulphur over a wide temperature range (470–720 K) [89].

Industrial SCR catalysts usually consist of TiO_2 and a second component chosen from the oxides V_2O_5, MoO_3, WO_3, Fe_2O_3, CoO, NiO, MnO_2, Cr_2O_3, CuO, etc. Catalysts comprising TiO_2 and semiconducting *n*-type oxides (V_2O_5, $Mn_2O_3.Fe_2O_3$) are the most active in the reaction $NO+NH_3\rightarrow N_2+H_2O$, while the most active catalysts in the NO_2 reduction reaction are those based on TiO_2 and *p*-type semiconducting oxides (CoO, NiO). The anionic vacancies in the catalysts of the first type apparently promote the adsorption of

NO, while the cationic vacancies in catalysts of the second type favour the adsorption of NO_2.

It may be that TiO_2 plays the role of not only the carrier but also of a promoting agent, since the activity of mixed catalysts based on TiO_2 is higher than that of the individual oxides forming part of their composition[89].

The activity of the TiO_2-based catalysts hardly changes over a period of 2000 h and their useful lifetime during industrial employment has been estimated as 5 years. The SCR reactions on various catalysts containing the Fe, Cr, Cu, Al, Ti, and Mg oxides have been studied[89]. The $Fe_2(SO_4)_3-\alpha$-$Fe_2O_3-TiO_2$ catalyst is one of the most active both in the presence and absence of SO_x. The addition of MoO_3 or WO_3 to this catalyst increases its resistance to poisoning by sulphur and the selectivity of the reduction of NO.[89] The study of the reaction of NO with NH_3 in the presence of O_2 on V_2O_5/TiO_2 and V_2O_5/Al_2O_3 shows that the first of these catalysts is more active than the second[90]. This has been explained by the greater number of V=O surface groups participating in the reaction on the catalyst deposited on TiO_2.

3. Kinetics and mechanism of the selective catalytic reduction reactions

Reviews of studies on the kinetics of the reduction of NO by ammonia have been published[31,32,91]. On platinum, the observed reaction order with respect to NH_3 is close to unity, while the order with respect to NO is 0–0.5 [31]. Apart from nitrogen, N_2O is formed during the reaction. The mechanism of the reaction on platinum has been established with the aid of labelled nitrogen ^{15}N incorporated in the composition of NO and NH_3 [92]:

$$NH_3 \rightleftarrows NH_3(ads.),$$
$$NH_3(ads.) \rightleftarrows NH_2(ads.) + H(ads.),$$
$$NO \rightleftarrows NO(ads.),$$
$$NO(ads.) + NH_2(ads.) \rightarrow [\text{surface complex (I)}] \rightarrow N_2 + H_2O,$$
$$\vdots \quad \ldots\ldots\ldots\ldots \rightarrow N_2O + 2H(ads.),$$
$$H(ads.) + NO(ads.) \rightarrow HNO(ads.),$$
$$2HNO(ads.) \rightarrow [\text{surface complex (II)}] \rightarrow N_2O + H_2O,$$
$$\vdots \quad + 2H(ads.) \rightarrow N_2 + 2H_2O.$$

The rate of the reaction of NH_3 with NO on copper-containing zeolites is described by the kinetic equation[86]

$$w = \frac{kK_{NO}K_{NH_3}p_{NO}p_{NH_3}}{(1 + K_{NH_3}p_{NH_3} + K_{H_2O}p_{H_2O})^2},$$

where k is the rate constant for the reaction of the adsorbed NH_3 and NO, K_i the equilibrium constant for the adsorption of the corresponding components of the reaction mixture, and p_i are the corresponding partial pressures. This equation corresponds to the mechanism in which the rate-limiting stage is the interaction of the strongly adsorbed NH_3 with the weakly coordinated NO. The equation indicates the cause of the inhibition of the reaction by water: water displaces ammonia, competing with it for the surface centres.

The following mechanism has been postulated for the SCR reaction on copper oxide and copper sulphate catalysts[87]:

$$NO \rightleftarrows NO(ads.),$$
$$NH_3 \rightleftarrows NH_2(ads.) + H(ads.),$$
$$O_2 \rightleftarrows 2O(ads.),$$
$$2H(ads.) + O(ads.) \rightleftarrows H_2O,$$
$$NO(ads.) + NH_2(ads.) \rightleftarrows N_2 + H_2O.$$

According to this mechanism, the overall rate of the process is determined by the rate of the stage involving the reaction of the adsorbed NO with the dissociatively adsorbed NH_3.

In a study[91] of the kinetics of the reaction of NO with NH_3 on the $V_2O_5/SiO_2.TiO_2$ industrial catalysts, the rate of the process was fitted by the kinetic equation $w = kc_{NO}^{n_1}c_{NH_3}^{n_2}c_{O_2}^{n_3}$. At temperatures in the range 550–650 K, the reaction orders are 0.7–0.8 with respect to NO, 0.1–0.3 with respect to NH_3, and 0.1–0.3 with respect to oxygen. Internal diffusion conditions occur in this temperature range and the activation energy is 28 kJ mol^{-1}. The mechanism of the reaction on V_2O_5 proposed by Miamoto et al.[90] relates the activity of the catalyst to the concentration of the surface V=O groups:

$$V{=}O + NH_3 + NO \rightarrow V{-}OH + N_2 + H_2O,$$
$$3V{=}O + 2NH_3 \rightarrow 3V\square + N_2 + 3H_2O,$$
$$V\square + 0.5O_2 \rightarrow V{=}O,$$
$$V\square + NO \rightarrow V{=}O + 0.5N_2,$$

where V□ is a V–OH group or an oxygen vacancy on the surface. In contrast to this, it has been shown[93] that N_2 is formed predominantly on the single crystal faces coated by hydroxy-groups and that there is a correlation between the number of adsorbed NH_4^+ ions and the amount of N_2 formed. The following mechanism is consistent with similar ideas:

$$V^{5+}{-}OH + NH_3 \rightarrow V^{5+}{-}ONH_4,$$
$$2V^{5+}{-}ONH_4 + V^{5+}{-}O{-}V^{5+} + 2NO \rightarrow$$
$$2N_2 + 3H_2O + V^{5+}OH + V^{4+}\square V^{4+},$$
$$V^{4+}\square V^{4+} + 0.5O_2 \rightarrow V^{5+}{-}O{-}V^{5+},$$

where □ is an oxygen vacancy on the surface.

4. Industrial use of selective catalytic reduction

In order to eliminate NO_x from smoke gases with a high content of SO_x and solid particles, mainly only two types of block catalysts are employed in industry: lamellar catalysts made from cast metal plates and monolithic catalysts with a ceramic honeycomb structure.

The lamellar catalysts developed by the Hitachi company (Japan) consist of steel sheets plated by the plasma sputtering of stainless steel with subsequent deposition of the catalytic mass. The catalyst plates, the gap between which is 5–6 mm, are assembled into 450 × 450 × 500 mm blocks. Jointly assembled 10–20 blocks comprise catalyst modules weighing from 1.11 to 2.02 tonnes.

The reduction temperature is 570–690 K. Depending on the temperature of the gases and their content of SO_x and ash, different modifications of the catalysts are employed[94].

Different types of honeycomb catalysts on a ceramic base have been developed by the Mitsubishi and Sakai companies (Japan). Depending on the type of fuel, different ratios of the active substances—titanium dioxide, tungsten trioxide, and vanadium pentoxide—are used. The catalysts are made in the form of rectangular blocks 500–1000 mm long and with a 150 × 150 mm cross-section. In each block there are 20 × 20 or 33 × 33 honeycomb cells; the longitudinal cross-sections through the honeycomb cells range from 3.5 × 3.5 to 6 × 6 mm. The surface of the catalyst varies from 430 to 678 m^2 per m^3 of its volume. The catalysts are assembled into modules containing between 36 and 100 blocks[95].

The SCR method has found the most extensive application in Japan, where 20 devices, fitted on large carbon dust energy units, began to operate in 1980–1986. In addition, towards the end of 1985, a further 200 devices for the catalytic purification of smoke gases operated in Japan on thermal electric power station boilers with an overall power of 30 GW [33].

Industrial SCR devices are being introduced in the Federal Republic of Germany[96], Australia[97], and West Berlin[98]. Experimental studies on SCR are being prosecuted in Sweden[99].

The experience gained in the use of industrial SCR devices has shown that the guaranteed useful lifetime of the catalysts is between 1 and 2 years. In fact, the average useful lifetime reaches 5 years in the combustion of liquid fuel and 7 years in the combustion of gas[100]. In order to prolong the useful lifetime of the catalyst, it is essential to free the gases from dust, which erodes the active surface. However, fine dust particles, which are difficult to remove, can block the pores of the catalyst, which also reduces its useful lifetime[100].

Each MW of the measured power of the energy unit usually requires 2 m^3 of the catalyst, costing 30 000 German marks (10 000 roubles) per m^3 [101].

The specific cost of the purification of smoke gases using the SCR method depends comparatively little on the power of the plant and varies from 106 to 222 German marks per kilowatt (40–80 roubles/kW) for energy units with power ranging from 150 to 700 MW. The cost of the catalyst itself is then 40% of the overall cost of the apparatus[33].

The requirements which must be met by the catalysts in the purification of gases by the SCR method are more stringent than in the catalytic combustion of fuels. In many cases, especially in the generation of heat for domestic purposes or for various technological processes, ecologically pure catalytic combustion can compete with flame combustion combined with purification of smoke gases.

IV. Catalytic combustion as a method of preventing the formation of nitrogen oxides

1. Principles of catalytic combustion

The catalytic combustion of fuels is a special case of total oxidation. The specific features of catalytic combustion consist in the fact that the catalyst should ensure the complete combustion of highly concentrated mixtures of hydrocarbons under conditions where the ratios of the reaction components are close to the stoichiometric ratios and when a large amount of heat is evolved. The total oxidation catalyst can therefore be used, in principle, also for catalytic combustion. However, these catalysts must exhibit an improved heat resistance, stability, and resistance to catalytic poisons which may be present in the fuel. The history of the problem and the principles governing the selection of catalysts have already been examined in detail[102–109]. The principal results of the latest studies on the catalytic combustion of fuels have been described in reviews[108–112].

Studies on the use of catalytic combustion for domestic, energy generating, and technological requirements are developing in several directions. Small catalytic heat sources for the heating of domestic and industrial accommodation and means of transportation are being created[113–124]. Extensive studies are being prosecuted on the catalytic combustion in the combustion chambers of gas turbines[125–134]. The catalytic combustion of gases with a low heat of combustion and a low temperature of the effluent gases in a number of industrial undertakings is believed to be extremely promising[135]. In all the devices listed, the fuels are combusted in a stationary catalyst bed consisting of noble metals deposited on fibrous and block carriers at temperatures in the range 1100–1600 K.

The principal advantage of the catalytic combustion of fuels is believed by the majority of workers to be the possibility of a significant decrease in the amount of harmful waste[131,132]. Indeed, the use of a catalyst makes it possible to increase the degree of conversion of the hydrocarbon fuel and to eliminate the formation of CO and of carcinogenic hydrocarbons usually formed in flame combustion. In the catalytic combustion of fuels which do not contain bound nitrogen in gas turbines at 1200–1500 K, the concentration of NO_x in the effluent gases diminishes from 150 to 2 p.p.m.[129,130] In model boiler plants with catalytic combustion of a gaseous fuel at 1400–1600 K, a tenfold decrease in the amount of NO_x waste (from 150 to 15 p.p.m.) is achieved[130]. The advances made concern principally pure fuels (petroleum gas and petroleum distillates) and arise from the fact that the decrease in temperature makes it possible to rule out completely the formation of high-temperature "thermal" nitrogen oxides. At the same time the problem of reducing the amount of waste "fuel" nitrogen oxides in working experimental devices has apparently not yet been solved. Thus, in the combustion of nitrogen-containing fuels, an almost complete conversion of the nitrogen of the fuel into nitrogen oxides has been observed in the catalytic chamber of the gas turbine[130]. Other difficulties and limitations accompanying the employment of devices with a stationary catalyst bed in the form of honeycomb structures or other blocks have also been discovered. The catalytic combustion is accompanied by extensive adiabatic heating, as a consequence of which the catalyst blocks must possess a series of unique properties. On the one hand, they must have a minimal wall thickness and must be characterised by a minimal hydraulic resistance and, on the other hand, they should exhibit the maximum stability as regards large temperature drops during prolonged use. The employment of platinum group metals as the active component leads to an appreciable increase in the cost of the catalytic devices. Platinum and palladium may be poisoned by catalytic poisons and are suitable only for the combustion of fuel free from such poisons[135]. The devices described are not suitable for the combustion of liquid fuels obtained by the hydrogenation of coal or masout, since they contain catalytic poisons and cannot be fully vaporised to be supplied into the catalytic chamber in the vapour phase.

Catalytic heat generators (CHG) for the combustion of fuel have been developed by the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[103,111,136–138]. The combustion of

fuels in CHG is based on four principles: (1) the use of total oxidation catalysts; (2) the use of a fluidised bed of catalyst particles; (3) the combustion of nearly stoichiometric fuel–air mixtures; (4) the combination of heat evolution and heat removal in a single catalyst bed.

Thus the non-flame combustion of fuels in CHG takes place on the surface of catalyst particles in a fluidised state. Like any fluidised bed apparatus, the CHG consists of a hollow vessel in the lower section of which there is an air distributing grid. Fluidisation occurs during the ascending movement of a mixture of air with the fuel as well as the combustion products through the bed of spherical catalyst particles. The useful removal of heat from the CHG is achieved either through the surface of a heat exchanger in contact with the fluidised catalyst bed or via a working body in direct contact with the catalyst. The fundamental advantage distinguishing the CHG from the devices described in the literature for the combustion of fuels in a fluidised catalyst bed[139–145] is the presence of a horizontal sectioning grid with a specified live section and a rigorously specified diameter of the apertures. This results in the creation of two zones of a free fluidised bed—below the sectioning grid and above it. The height of the lower zone should be such that complete oxidation of the fuel is ensured. The sectioning grid limits the circulation of the catalyst particles and hence the thermal conductivity of the bed. It plays the role of a non-isothermal packing and divides the apparatus along its height into two isothermal zones: the lower zone whose temperature is necessary for the complete oxidation of the fuel (700–1000 K) and the upper zone whose temperature is determined by the conditions in the heating of the working body[111,146,147] (Fig. 2). The presence of the non-isothermal packing and the removal of heat from the upper part of the apparatus make it possible to reduce the temperature of the effluent gases to 420–450 K.

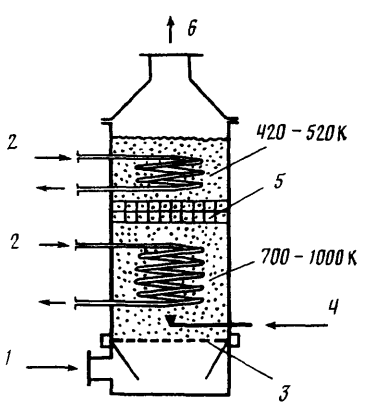


Figure 2. Schematic illustration of a non-isothermal catalytic heat generator[111]: *1*, air; *2*, water; *3*, gas distributing grid; *4*, fuel; *5*, non-isothermal head-piece; *6*, effluent gases.

Analysis showed that catalytic combustion makes it possible to solve the ecological problems arising in the use of the so called "pure fuels" without bound nitrogen. Unfortunately the fraction of such fuels with diminish as the trends which have arisen towards the employment of coal, masout, and coal liquefaction products intensify. Such fuels contain bound nitrogen which can form during catalytic combustion an amount of nitrogen oxides which is not less than in flame combustion. The specific features of the extensive oxidation reactions of nitrogen-containing compounds consist in the fact that both molecular nitrogen and nitrogen oxides can be formed from them:

$$RN + O_2 \rightarrow CO_2 + H_2O + N_2, \quad (17)$$

$$RN + O_2 \rightarrow CO_2 + H_2O + NO_x. \quad (18)$$

In catalytic combustion processes, it is important to achieve a decrease in the yield of fuel NO_x via reaction (18) as a result of the preferential occurrence of reaction (17). To solve this problem, it is essential to investigate the kinetics and mechanism of the catalytic oxidation of nitrogen-containing compounds of different classes.

2. Kinetics and mechanism of the catalytic oxidation of nitrogen-containing compounds

(a) Oxidation of ammonia and hydrogen cyanide. The catalytic oxidation of ammonia has been studied in very great detail, since this reaction is one of the most important processes in heterogeneous catalysis[148,149]. It can proceed via three principal pathways described by Eqns. (11)–(13). All the reactions indicated are almost irreversible.

The present state of the theory of catalytic oxidation of ammonia has been described satisfactorily by Il'chenko[150]. By analogy with the oxidation of organic compounds, molecular nitrogen should be regarded as the product of mild oxidation, while nitrogen oxides are products of extensive oxidation. In the presence of many catalysts, three nitrogen-containing products (N_2, N_2O, NO) in various proportions are formed simultaneously at 673–773 K. On the other hand, by using selective catalysts and by carrying out the reaction under specified conditions, one can ensure the preferential occurrence of one of the processes. Thus at high temperatures (1073–1173 K) on platinum catalysts, the yield of nitrogen oxides can reach 96–99%, which is achieved in practice in the manufacture of nitric acid. The oxidation of ammonia on platinum begins at 423–473 K where the only nitrogen-containing reaction product is molecular nitrogen. With increase in temperature, N_2O appears, its yield passing through a maximum. At temperatures of the order of 573 K, the formation of nitric oxide begins. The yield of this product gradually increases and can exceed 90% at 973–1273 K [148,150].

The oxidation of ammonia on other catalysts proceeds similarly but the temperature limits in the formation of the products of mild and extensive oxidation can be different. The specific catalytic activity of metals in the oxidation process decreases in the sequence Pt > Pd > Cu > Ag > Ni > Au > Fe > W > Ti. The corresponding activity series for oxide catalysts has also been found: Co_3O_4, MnO_2 > CuO > ZnO > CaO_2 > NiO > Bi_2O_3 > Fe_2O_3 > V_2O_5 > TiO_2 > CdO > PbO > SnO_2 > ZrO_2 > MoO_3 > WO_3 [149–152]. The decrease in activity is associated with the increase in the bond energy between oxygen and the metal surface. The selectivity in the extensive oxidation (to N_2O and NO) diminishes in approximately the same sequence. The point is that, in the extensive oxidation process, a larger number of oxygen–catalyst bonds are broken that in the formation of the mild oxidation product (N_2). With increase in the bond energy between oxygen and the metal surface, the rate of extensive oxidation should therefore

diminish more rapidly than the rate of mild oxidation, which in fact leads to a change in selectivity in the series quoted above[148,149].

A similar behaviour has been observed in the study of the catalytic oxidation of hydrogen cyanide[153]. In this case, the activity and selectivity of the catalysts are also determined by the bond energy between oxygen and the catalyst surface[148].

(b) Oxidation of organic nitrogen-containing compounds. Comparatively few data on the kinetics of the extensive oxidation of organic nitrogen-containing compounds have been described in the literature. The studies carried out have been devoted mainly to the selection of conditions governing the use of catalysts for the additional combustion of the waste from different industries.

Thus the oxidation of dimethylformamide has been studied on the AVK-10 (10% V_2O_5/Al_2O_3), NIIOGAZ-7D ($Cr_2O_3+CuO+V_2O_5$), ShPK (0.2% Pt/Al_2O_3), and AP-56 (0.5% Pt/Al_2O_3) industrial catalysts at 573–623 K [154]. The formation of nitrogen oxides at concentrations up to 18 p.p.m. has been observed on platinum catalysts. On oxide catalysts, NO_x were either not formed or were evolved in trace amounts.

The kinetics of the oxidation of dimethylacetamide in the presence of the NIIOGAZ-7D catalyst were investigated on a flow-circulation apparatus in the temperature range 503–653 K [155]. The amount of nitrogen oxides formed increased with increase in the initial dimethylacetamide concentration and temperature.

The possibility of making safe the dimethylamine-containing waste water by the vapour phase catalytic oxidation of dimethylamine has been studied on a flow apparatus[156]. At 700–750 K and at a vapour–gas flow rate of 2000–4000 h^{-1}, the GIPKh-105 catalyst ensured 94% conversion of dimethylamine via the reaction

$$4(CH_3)_2NH+15O_2\rightarrow 2N_2+8CO_2+14H_2O.$$

The formation of nitrogen oxides in the catalytic oxidation of ammonia and ethylenediamine has been investigated in flow apparatus on AP-56, NTK-1 (53% ZnO, 24% Cr_2O_3, and 12% CuO) and GIPKh-105 (40% CuO and 40% Cr_2O_3) catalysts[157], whose efficiency was estimated from the degrees of conversion of the compounds indicated in extensive oxidation reactions. The GIPKh-105 catalyst, ensuring 100% conversion of both ethylenediamine and ammonia at 573 K, a 15000 h^{-1} space velocity, and a concentration of 10 mg $litre^{-1}$ proved to be best. In the oxidation of ammonia (c = 15 mg $litre^{-1}$) the degree of conversion of the bound nitrogen into oxides was 3% at 623 K, while the degree of conversion in the oxidation of ethylenediamine (c = 6.8 mg $litre^{-1}$) was 38%. On reducing the temperature to 473 K, the concentration of NO_x diminishes severalfold. In the joint presence of ethylenediamine and ammonia, the yield of nitrogen oxides is appreciably lower than in their separate oxidation. The authors believe[157] that one of the stages involved the reaction of nitric oxide, formed in the oxidation of ethylenediamine, with the ammonia present in the gas mixture in accordance with the scheme

$$NO(ads.)+NH_3(ads.)+O(ads.)\rightarrow N_2+H_2O+OH(ads.).$$

As a result of this, the yield of nitrogen oxides in the oxidation of a mixture of ethylenediamine and ammonia is significantly reduced. The complete elimination of pyridine from the waste in chemopharmaceutical industries is achieved on aluminoplatinum, copper–chromium, copper–manganese, and aluminocopper catalysts at a temperature of about 623 K [158–160]. The selectivity with respect to N_2 is 85–92% [159].

The extensive aniline oxidation reaction in the presence of the aluminoplatinum catalyst has been studied in greatest detail[161,162]. The experiments were performed in a flow-circulation apparatus at an initial aniline concentration of (0.5–240) × 10^{-6} M and at space velocities of the stream of 250–10000 h^{-1}. The rate of oxidation of aniline obeys the equation

$$w = k\frac{c_A c_{O_2}^{0.5}}{1+k'c_A},$$

where c_A and c_{O_2} are the stationary concentrations of aniline and oxygen respectively, k = 8.14 × 10^{10} $e^{-84018/RT}$ $litre^{1.5}$ $mol^{0.5}$ h^{-1} g^{-1}, k' = 2.24 × 10^3 $e^{21736/RT}$ litre mol^{-1}. The contents of nitrogen oxides in the reaction products for a degree of conversion of aniline of 0.9 and at 473, 573, and 673 K are respectively 0.2, 5.1, and 10.7% relative to the aniline which has reacted. The extensive aniline oxidation reaction has been described by a scheme incorporating twelve stages[162] of which the first five concern the reaction of bound nitrogen:

(1) $O_2\rightleftarrows 2O(ads.)$,

(2) $C_6H_5NH_2+O(ads.)\rightleftarrows C_6H_5NH_2O(ads.)$,

(3) $C_6H_5NH_2O(ads.)+O(ads.)\rightleftarrows C_6H_5NOOH_2(ads.)$,

(4) $C_6H_5NOOH_2(ads.)\rightleftarrows C_6H_5(ads.)+NO+H_2O$,

(5) $C_6H_5NH_2O(ads.)+NO\rightarrow C_6H_5O(ads.)+N_2+H_2O$.

It has been suggested that stages 1–3 virtually correspond to equilibrium, stage 4, representing the decomposition of compounds of the peroxide type, is slow, while stage 5 as well as the remaining stages not quoted here are rapid and irreversible. The following kinetic equations follow from the above scheme on the assumption of high coverages of the catalyst surface:

$$w = k_4\frac{K_1K_2K_3p_{O_2}p_A}{K_1p_{O_2}^{0.5}+K_1K_2p_{O_2}^{0.5}p_A+K_1K_2K_3p_{O_2}p_A},$$

where K_1, K_2, and K_3 are the equilibrium constants of stages 1, 2, and 3 and k_4 is the rate constant for stage 4. This equation is converted into the experimental expression when $K_1K_3 \ll 1$.[162]

The above scheme makes it possible to account for the virtually complete absence of nitrogen oxides in the oxidation of aniline on the catalyst: NO is formed slowly in stage 4 but is rapidly consumed in stage 5. Indeed, in the oxidation of aniline adsorbed on the catalyst by nitric oxide, mainly molecular nitrogen was formed. Detailed kinetic studies on the extensive catalytic oxidation reactions of a series of nitrogen-containing compounds were carried out in order to establish the principles governing the decrease in the NO_x concentration in the catalytic combustion of nitrogen-containing fuels[163–169]. The objects of study were compounds differing in the nitrogen-containing functional groups. Catalysts developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences for catalytic heat generators as well as a series of other typical total oxidation catalysts, especially industrial final combustion catalysts IK-12-1 and AK-64, were used.

In the study of the pyridine oxidation reaction[163,164,169] in the temperature range 513–820 K, the initial pyridine concentration was varied in the range 0.05–2.0 vol.% and the oxygen concentration

was varied in the range 4.2–50 vol.%. The oxidation products were CO_2, H_2O, N_2, and NO_x (NO and NO_2). In the kinetic region (at 633 K and below), the order of the extensive oxidation reaction with respect to pyridine was zero and that with respect to oxygen was close to unity on all the deposited catalysts. The NO_x formation reaction was also zero order with respect to pyridine. The kinetic parameters of the extensive oxidation reactions and the nitrogen oxide formation reactions as well as the degrees of conversion of bound nitrogen into oxides (X_{NO_x}) on certain catalysts are listed in Table 1. A significantly smaller amount of NO_x is formed on oxide catalysts than on the platinum catalyst under the same conditions. Oxide catalysts propagate the oxidation to molecular nitrogen with a high selectivity, the degree of conversion of bound nitrogen into oxides not exceeding as a rule several per cent. In the presence of the copper–chromium catalysts, the rate of formation of nitrogen oxides increases with increase in the content of copper chromite in the catalyst.

Table 1. Kinetics of the catalytic oxidation of pyridine (c_{RN} = 0.5%)[163,164,169].

Catalyst	Sample, g	Extensive oxidation		Formation of NO_x			
		10^{-10} w, mol C_5H_5N cm^{-2} s^{-1}, 573 K	E_{act}, kJ mol^{-1}	10^{-8} w, mol NO_x cm^{-2} s^{-1}, 573 K	E_{act}, kJ mol^{-1}	c_{NO_x}, p.p.m., 573 K	x_{NO_x}, %, 573 K
5% $CuCr_2O_4/\gamma$-Al_2O_3	2.18	0.5	154±26	1.3	170±26	8	2.6
11% $CuCr_2O_4/\gamma$-Al_2O_3	2.09	2.2	170±3	2.5	—	9	1.1
30% $CuCr_2O_4/\gamma$-Al_2O_3	0.29	0.8	182±12	9.0	170±6	11	11.1
28% $NiCr_2O_4/\gamma$-Al_2O_3	1.02	2.0	184±12	3.9	—	9	2.0
26% CuO/γ-Al_2O_3	1.8	4.0	170	7.1	—	27	1.8
0.64% Pt/γ-Al_2O_3	1.8	2.0	158±8	50.0	125±17	48**	25.0
γ-Al_2O_3	1.8	0.002*	221±11	—	—	1***	0.1

* Found by extrapolating the experimental data to temperatures above 623 K.
** At 543 K.
*** At 623 K.

The catalytic oxidation of acetonitrile, nitromethane, and dimethylformamide has been investigated[165,167]. Their extensive oxidation reactions were investigated in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 catalyst in the range of initial acetonitrile concentrations from 0.12 to 3.0 vol.%, nitromethane concentrations from 0.24 to 1.95 vol.%, and dimethylformamide (DMF) concentrations from 0.01 to 0.68 vol.%. The oxygen concentration in the oxidation of CH_3CN was varied from 13 to 50 vol.%, while in the oxidation of CH_3NO_2 and DMF it was always 50 vol.%. The studies were performed on flow-circulation apparatus in the temperature range 453–793 K. The principal kinetic parameters of the extensive oxidation reactions are listed in Table 2.

Above 623 K, the nitrogen-containing compounds are fully converted into oxidation products. The degree of conversion of bound nitrogen into NO_x in such a complete reaction is determined by the nature of the active component of the catalyst employed, the concentrations of the substance oxidised and oxygen in the reaction mixture, and temperature. In the oxidation of pyridine, acetonitrile, and DMF in the presence of oxide catalysts, the main bulk of the bound nitrogen is converted into N_2, while the yield of nitrogen oxides does not exceed several per cent. An appreciably higher degree of conversion of bound nitrogen into NO_x is characteristic of the platinum catalyst—up to 40% in the case of pyridine and up to 90% in the case of acetonitrile (Fig. 3). At a constant temperature and in an excess of oxygen, the quantity X_{NO_x} in the presence of all the catalysts investigated falls with increase in the initial concentration of the oxidised substance in the reaction mixture.

Table 2. Kinetics of the extensive oxidation of certain nitrogen-containing compounds in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 (c_{RN} = 0.5%) catalyst[165–167]

Compound	T, K	10^{-10} w, molecules cm^{-2} s^{-1}	E_{act}, kJ mol^{-1}	Reaction order	
				w.r.t. RN	w.r.t. O_2
Acetonitrile	573	29.0	100	0	0.9
Nitromethane	573	100	100	0	—
Dimethylformamide	513	10	53	0.5	—

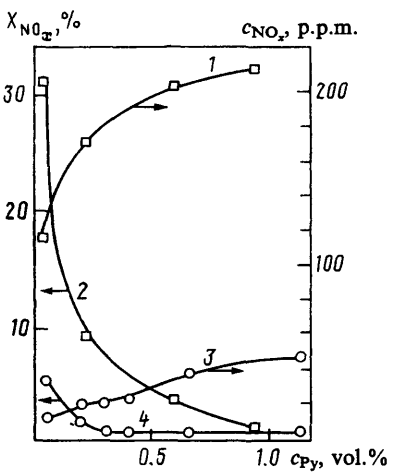


Figure 3. Dependence of the NO_x concentration (curves *1* and *3*) and of the degree of conversion of bound nitrogen into NO_x (curves *2* and *4*) on the initial pyridine concentration at 673 K in the presence of the 0.64% Pt/γ-Al_2O_3 (curves *1* and *2*) and 5% $CuCr_2O_4/\gamma$-Al_2O_3 (curves *3* and *4*) catalysts[164].

The NO_x concentration depends little on the oxygen concentration, while the coefficient of the excess of oxygen $\alpha > 1.5$ and diminishes sharply as the reaction mixture approaches the stoichiometric composition. An increase in temperature entails an increase in X_{NO_x}. For copper–chromium catalysts, the dependence of the amount of

nitrogen oxide formed and X_{NO_x} on the concentration of the active component ($CuCr_2O_4$) in the catalyst was obtained. The NO_x concentration and X_{NO_x} increase in the sequence γ-Al_2O_3 < 5% $CuCr_2O_4/\gamma$-Al_2O_3 < 11% $CuCr_2O_4/\gamma$-Al_2O_3 < 30% $CuCr_2O_4/\gamma$-Al_2O_3.

Table 3. The formation of nitrogen oxides in the complete oxidation of nitrogen-containing compounds in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 catalyst[165–167].

Compound	Catalyst sample, g	c_{RN}, vol.%	T, K	c_{NO_x}, p.p.m.	X_{NO_x}, %
Acetonitrile	0.53	1.09	623	16	0.2
	0.53	0.95	723	26	0.3
	7.04	2.45	768	159	0.7
Dimethylformamide	3.17	0.66	673	17	0.3
	3.17	0.66	723	234	3.6
Pyridine	2.28	1.09	673	122	1.1
	2.28	1.09	723	588	5.4
	15.06	0.95	793	1 336	14.4
Nitromethane	1.19	1.07	673	7 910	76.8
	6.05	1.07	758	10 220	99.2

Table 3 presents data concerning the influence of the nature of the oxidised compound on the yield of NO_x in the range of high temperatures (>620 K) in the presence of the 30% $CuCr_2O_4/\gamma$-Al_2O_3 catalyst. The maximum amount of NO_x is formed in the oxidation of nitromethane, which is apparently associated with the presence of the NO_2 group in the molecule. On the basis of the set of kinetic relations obtained as well as literature data concerning the forms of adsorption of pyridine and the extensive oxidation of organic compounds, the following mechanism for the conversion of pyridine has been proposed[168,169]:

$$C_5H_5N \xrightarrow{k_1} C_5H_5N(ads.),$$

$$C_5H_5N(ads.) + O_2 \xrightarrow{k_2} HN-C_5H_4OO(ads.),$$

$$HNC_5H_4OO(ads.) + O_2 \xrightarrow{k_3} NH(ads.) + CO_2 + C_4H_4OO(ads.) \xrightarrow[fast]{}$$

$$\rightarrow CO_2, H_2O, N_2, NO_x.$$

In the first stage, pyridine is adsorbed on the surface, in the second stage the aromatic ring is cleaved, while in the third stage a C–N bond is ruptured with formation of surface groups. The kinetic equation which follows from the last scheme on the assumption that $k_1 p_{C_5H_5N} \gg k_2 p_{O_2}$ and $k_3 p_{O_2}$ has the form $w = k p_{O_2}$. It describes adequately the experimental data. It must be emphasised that all observations indicate the dissociation of C–N bonds in the first stages of the oxidation process. Compounds with such a bond, including HCN, were not detected in the reaction products. Furthermore, in special experiments on the oxidation of pyridine and acetonitrile under the conditions of a deficiency of oxygen, the degree of conversion of bound nitrogen into NH_3 reached 10%, while HCN was formed in trace amounts. The oxidative reactions of the type NH_x surface groups formed apparently proceed via the mechanism proposed for the ammonia oxidation reaction[148]:

(1) $NH(ads.) + O(ads.) \rightleftarrows HNO(ads.)$,

(2) $NH(ads.) + HNO(ads.) \rightleftarrows N_2 + H_2O$,

(3) $HNO(ads.) + HNO(ads.) + O(ads.) \rightleftarrows 2NO + H_2O$,

(4) $NO + O(ads.) \rightleftarrows NO_2$.

Apparently stages 1 and 2 take place preferentially on oxide catalysts, while on aluminoplatinum catalysts stages 3 and 4 also make a significant contribution, i.e. the catalysts differ in the ratio of the rate constants for the corresponding stages.

The above investigations have led to the conclusion that the possible routes to a decrease in the waste nitrogen oxides in the catalytic combustion of nitrogen-containing fuels involve the use of oxide catalysts, a decrease in temperature, and a decrease in the coefficient of the excess of air.

3. Characteristic features of the formation of fuel NO_x in the catalytic combustion fuels

A series of studies on the reactions of nitrogen in fuels during catalytic combustion have been published[130,134,170–182]. The yield of fuel NO_x is influenced by the combustion temperature, the coefficient of the excess of air α, the nitrogen content in the fuel, and the nature of the catalyst (Table 4).

It has been established[171] that in the combustion of mixtures of propane with ammonia and methylamine, the form of the nitrogen-containing additive does not affect the yield of nitrogen oxides. The degree of conversion of nitrogen into NO_x increases with increase in temperature[171,172]. Thus, in the combustion of propane with added NH_3 and CH_3NH_2, the quantity X_{NO_x} increases from 30% at 1100 K to 80% at 1400 K. A further increase in temperature to 1600 K hardly affects the increase in X_{NO_x}, which is 80–90%[171].

The dependence of the degree of conversion of the fuel nitrogen into NO_x on the coefficient of excess of air α has been studied in greatest detail. In the range $1.2 \leqslant \alpha \leqslant 2.0$, the degree of conversion of bound nitrogen into oxides depends little on α and diminishes by a factor of 2–3 as the fuel–air mixture approaches the stoichiometric composition[130,170–181]. For $\alpha \leqslant 1$, the combustion products contain ammonia and hydrogen cyanide. Under these conditions, a decrease in the amount of air leads to a further decrease in the NO_x concentration owing to the increase in the N_2, NH_3, and HCN concentrations[130,131,170]. For certain values of α, which are usually in the range 0.6–0.9, the maximum degree of conversion of bound nitrogen into N_2 is attained (up to 80–90%). It has therefore been suggested[171] that the catalytic combustion be carried out in two stages: $\alpha < 1$ is established in the first stage (usually between 0.5 and 0.9), while in the second stage an excess of air is supplied to achieve the final combustion of the uncombusted substances. On average $\alpha \geqslant 1$ for the entire process. The two-stage catalytic combustion at 1400–1500 K ensures a decrease in the degree of conversion of fuel nitrogen into oxides from 80–100% (for single-stage combustion) to 10–30%[130,172,176,177]. However, an increased deactivation of the catalyst as a consequence of its saturation by coke is then observed in the first stage[172]. A scheme for the two-stage combustion of liquid nitrogen-containing fuels using a catalyst only in the second stage has been proposed.[134]

Table 4. The formation of NO_x in the catalytic combustion of fuel (literature data).

Fuel combusted	Catalyst	Nitrogen-containing additive	N_f^*, %	T, K	α	Studied dependence of X_{NO_x} on				Refs.
						α	N_f	type of catalyst	temperature	
$CO+H_2+CH_4+N_2$ (model mixture)	2.1–6.3% Pt on a monolithic carrier with a variable cross-section of channels	NH_3	0.0471	1273	0.4–2.3	+	–	–	–	[174]
CH_4	ditto	NH_3	0.9417	1273	0.4–2.3	+	–	–	–	[174]
CH_4, C_3H_8	Pt, NiO+Pt on a monolithic carrier	NH_3 or CH_3NH_2	0.003–3.6	1100–1600	0.6–2.2	+	+	+	+	[171]
C_3H_8	0.18% Pt on monolithic cordierite ite covered with Al_2O_3	NH_3	2.0	1000	0.8–1.0	+	+	–	–	[175]
$CO+H_2+CH_4+N_2$ (model mixture)	Pt/Al_2O_3, NiO/ZrO_2	NH_3	0.05–0.24	1480	0.4–1.2	+	–	+	–	[177]
C_3H_8, CH_4	Noble metal on a monolithic carrier	NH_3	0.2	1000–1500	0.5–1.3	+	–	–	–	[130]
CH_4	Co_2O_3, NiO+Pt, Co_2O_3+Pt, Pt on a monolithic carrier	NH_3	0.2–2.0	1100–1900	0.5–2.0	+	+	–	+	[172]
CH_4	ditto	»	»	»	»	+	+	+	+	[176]
C_3H_8	5.63% $Cr_2O_3+Co_2O_3$	NH_3	1.0	1200–1300	0.5–1.8	+	–	–	+	[178]
Kerosene	0.2% Pt on a carrier with a honeycomb structure	C_5H_5N	0.3	1470–1770	0.9–1.1	+	–	–	–	[134]
Diesel fuel	2% Pt on a monolithic carrier	C_5H_5N	0.125; 0.535	1000–1700	1.0–4.0	–	+	–	–	[179]
Diesel fuel	5.3% Pt on a monolithic carrier	none	0.0135	1100–1400	1.0	Independent of conditions				[182]
Artificial liquid fuels from coal, diesel fuel	2% Pt/Al_2O_3, 2% Pt on a monolithic carrier	none	0.31–0.86	1370–1530	0.7–1.7	+	–	–	–	[180]
Diesel fuel	Noble metal on a monolithic carrier	C_5H_5N	0.5	1000–1500	2.0–3.5	+	–	–	–	[181]
Masout	Monolithic catalyst with a variable cross-section of channels	none	0.85	1370–1930	0.8–3.0	+	–	–	–	[170]

Note. For liquid fuels, the nitrogen content in the fuel is indicated in weight percentages, while for gaseous fuels it is indicated in volume percentages.

A significant decrease in the yield of NO_x is achieved as a result of the interaction of the nitrogen oxides formed with soot:

$$2NO+C \rightarrow N_2+CO_2.$$

A decrease in the NO_x concentration in the effluent gases on apparatus of this type can occur also by virtue of the interaction of NO with CO [172].

The nature of the catalyst exerts a major influence on the yield of fuel nitrogen oxides. The use of oxide catalysts makes it possible to attain lower degrees of conversion of bound nitrogen into NO_x than in the case where catalysts based on noble metals are employed. In the single-stage combustion of a gaseous fuel with added NH_3 in an excess of air [177], the degree of conversion of bound nitrogen into NO_x reaches 70–80% in the presence of the NiO/ZrO_2 catalyst and 90–95% in the presence of the Pt/Al_2O_3 catalyst (combustion temperature 700–900 K). In the multistage combustion using the NiO/ZrO_2 catalyst in the first stage, the degree of conversion of bound nitrogen into NO_x is 10%, while in the presence of the platinum catalyst 35% of the fuel nitrogen is converted into oxides.

The combustion of mixtures of propane with ammonia has been studied on a catalyst containing chromium and cobalt oxides [178]. The temperature profile in the catalyst bed affects the yield of nitrogen oxides. Under optimum conditions with $\alpha > 1$, it is possible to decrease the degree of conversion of bound nitrogen into NO_x to 5–20%.

With increase in pressure, the yield of NO_x can both increase [179] and decrease [172,176]. Data concerning the influence of the nitrogen content in the fuel on the degree of conversion of bound nitrogen into oxides are just as uncertain: an increase in the concentration of bound nitrogen (in the form of NH_3) in the gaseous fuel was accompanied by a decrease [171] and an increase [175] in X_{NO_x}. An increase in the pyridine content in the liquid fuel resulted in some decrease in X_{NO_x} [179]. Overall, the problem of reducing the fuel NO_x waste in the combustion of fuels in a stationary catalyst bed requires further work.

The characteristics of the formation of nitrogen oxide in the combustion of nitrogen-containing fuels in a fluidised bed of granulated catalysts, specially developed for catalytic heat generators, have been examined [164,183–187]. The experiments were performed on a pilot apparatus with a power of 20 kW. Experiments were performed initially on the combustion, in catalytic heat generators, of fuels virtually free of bound nitrogen in order to determine the possible contribution of thermal NO_x to the overall amount of nitrogen oxides. In the combustion of n-decane and diesel and furnace fuels on catalysts containing 5 and 30% $CuCr_2O_4$

on γ-Al_2O_3, the observed values of c_{NO_x} did not exceed 10 p.p.m., i.e. the equilibrium concentration calculated for 1000 K and α = 11 [164].

The characteristic features of the formation of fuel NO_x were investigated by combusting both a fuel with the natural abundance of bound nitrogen of 0.1% (masouts M100 and M40) and specially prepared mixtures of fuels with nitrogen-containing additives. In the combustion of diesel fuel with added pyridine, giving rise to a nitrogen concentration up to N_f = 1 wt.%, the CO_2 and NO_x concentration profiles increased in parallel along the reactor height and attained a constant level at the height corresponding to the complete conversion of the fuel (500–600 mm) [164]. Nitrogen oxides were formed in the catalytic oxidation of the fuel in the fluidised catalyst bed and additional formation of NO_x over the bed was not observed.

In the combustion of model mixtures of isopropyl alcohol with nitrogen-containing compounds (caprolactam, acetonitrile, monoethanolamine, or pyridine) the degree of conversion of bound nitrogen into NO_x was determined mainly by the combustion conditions and depended little on the nature of the oxidised nitrogen-containing substance. At a catalyst bed temperature of 1023 K, N_f = 1 wt.%, and α = 1.22, the degree of conversion of nitrogen into NO_x is 11–15% [185,187].

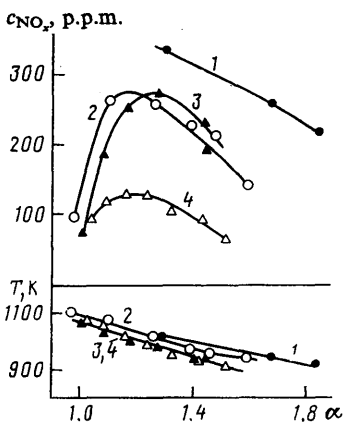


Figure 4. Dependence of the NO_x concentration and catalyst bed temperature on α in the combustion of a mixture of diesel fuel with pyridine [187] in the presence of different catalysts: *1*, Pt/γ-Al_2O_3; *2*, chromium oxide catalyst; *3*, 25% $CuCr_2O_4$/γ-Al_2O_3; *4*, 5% $CuCr_2O_4$/γ-Al_2O_3.

The dependence of the NO_x concentration on α was investigated in the combustion of masouts M40 and M100 with added ammonium nitrate and pyridine in the presence of the $CuCr_2O_4$/γ-Al_2O_3 catalyst [183,184]. The curves obtained had a maximum and the concentration of NO_x fell as α approached unity. For a bound nitrogen content of 0.2%, the NO_x concentration was 40–80 p.p.m., while for N_f = 1% it amounted to 80–150 p.p.m., which is much lower than in the flame combustion of such fuels [4,21]. The degree of conversion of bound nitrogen into NO_x is between 5 and 15%.

The dependence of X_{NO_x} on N_f was investigated by combusting mixtures of isopropyl alcohol with pyridine and of diesel fuel with pyridine [185,187]. With increase in N_f, the NO_x concentration rises, but the degree of conversion X_{NO_x} falls. Industrial waste with a high content of bound nitrogen can be made safe by its combustion in a catalytic heat generator. Even for N_f = 8%, the NO_x concentration is less than 520–540 p.p.m., which is significantly lower than the value 3000–5000 p.p.m. expected in the flame combustion of a similar mixture [185,187].

The nature of the active component of the catalyst used in the catalytic heat generator also affects the formation of NO_x in the combustion of nitrogen-containing fuels (Fig. 4). Aluminoplatinum catalysts afford the greatest amount of nitrogen oxides, while oxide catalysts produce a smaller amount of such oxides. In full agreement with experiment [186,187], a decrease in the concentration of the active component of the deposited catalyst promotes a decrease in the emission of nitrogen oxides (Fig. 4). An increase in temperature leads to an increase in the concentration of nitrogen oxides (as the temperature rises by 150 K, the NO_x concentration is doubled) [187].

We shall now analyse the problem of the amount of nitrogen oxides evolved in the combustion of fuels in a catalytic heat generator and in the traditional flame combustion [1,2,21] relative to the c_{NO_x} level calculated from the equilibrium constants of the reaction $N_2 + O_2 \rightleftarrows 2NO$ for α = 1.1 (Fig. 5). In the temperature range (1500–2000 K) where real combustion takes place, the calculated equilibrium NO_x concentration varies from 400 to 2500 p.p.m.[1] The NO_x concentrations observed in flame combustion are lower than these values, because, owing to the insufficiently long residence time of the fuel–air mixture in the combustion chamber, equilibrium cannot be attained. In the catalytic combustion, the yield of thermal NO_x is extremely low (less than 5 p.p.m.) while the concentration of fuel NO_x is higher than the equilibrium values corresponding to the temperature range of this method of combustion but is lower by a factor of 5–10 than in flame combustion in devices with a combustion chamber.

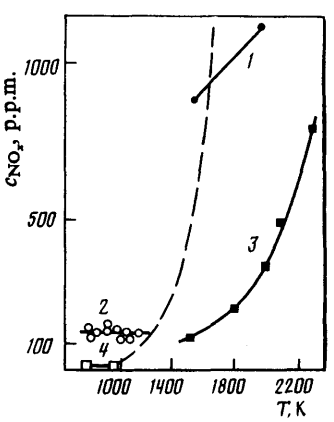


Figure 5. Dependence of the concentrations of fuel (curves *1* and *2*) and thermal (curves *3* and *4*) NO_x on temperature in the flame (curves *1* and *3*) and catalytic (curves *2* and *4*) combustion (α = 1.1); the data for the fuel NO_x were obtained at N_f = 1 wt.%; dashed line—equilibrium NO_x concentrations [1,2,187].

Catalytic combustion can be used successfully in various domestic and industrial combustion chamber devices in order to decrease the degree of incomplete chemical combustion and the amount of thermal NO_x waste. However, the problem of reducing the fuel NO_x waste formed in the combustion of fuels containing bound nitrogen in devices with platinum catalysts operating at high temperatures and under severe thermal conditions has not yet been solved. The study of the kinetics of the oxidation of nitrogen-containing compounds on solid catalysts has shown that a decrease in the yield of fuel NO_x can be attained by using oxide catalysts instead of platinum catalysts, by reducing the temperature, and by adjusting the coefficient of the excess of air to values close to unity. A decrease in temperature is usually accompanied by a fall in the power and efficiency of the device. The use of a fluidised bed in catalytic heat generators makes it possible to carry out technological processes with much heat evolution and at a low temperature in the combustion zone (770–1070 K) by combining the heat evolution and heat removal processes in a single catalyst bed. It is important to emphasise that a decrease in the concentration of nitrogen oxides in catalytic combustion is ensured by the method of combustion itself and by the selection of the optimum process conditions and catalysts. There is then no need for the expensive removal of nitrogen oxides from smoke gases.

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