

Oxide catalysts for ammonia oxidation in nitric acid production: properties and perspectives

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Received 28 April 1999; received in revised form 28 February 2000; accepted 29 February 2000

Abstract

This paper generalizes the results of long-term efforts aimed at research and development of industrial oxide catalysts for ammonia oxidation in the nitric acid production within two-bed (Pt gauzes+monolithic oxide layers) technology of the high pressure process.

Main factors determining performance of precious metals and oxides in the high-temperature ammonia oxidation are considered. The surface oxygen bonding strength determined by the surface atomic structure appears to be the most important. From this point of view, existing approaches to synthesis of mixed oxide systems including perovskites with controlled nitric oxide selectivity and good stability in the high-temperature process of ammonia oxidation are analyzed. Main features of the bulk oxide monolithic catalysts production technology and principles of a two-bed system design based upon the process mathematical modeling are briefly outlined. Proven economic benefits of this technology recently commercialized in Russia at nitric acid plants are debated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ammonia oxidation; Nitric acid production; Oxide catalysts; Honeycomb monoliths; Perovskites

1. Introduction

Nitric acid production is one of the large-scale processes in chemical industry. The process involves the catalytic oxidation of ammonia by air (oxygen) yielding nitrogen oxide then oxidized into nitrogen dioxide and absorbed in water. The desired product

yield essentially depends on the catalyst selectivity and of course on the operating conditions.

Ammonia usually comprises ca. 90% of the nitric acid production cost [1]. Therefore, the ammonia oxidation efficiency is a key factor for the nitric acid production.

In the first industrial process of nitric acid production by ammonia oxidation designed by Ostwald [2] at the beginning of the 19th century, pure platinum gauzes served as the catalyst. Later pure platinum was displaced by platinum–rhodium alloys, in which the rhodium content varied from 5 to 10%. Despite many

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Table 1
Optimum operating data for ammonia combustion [3]

Pressure	Gauze temperature (°C)	NH ₃ content (vol.%)	Yield (%)	Pt loss (g/t HNO ₃)	Operating time (months)
Atmospheric	810–850	12.0–12.5	97.0–98.0	0.04–0.05	8–12
Medium 3–5 atm	870–890	10.5–11.0	96.5–96.5	0.10–0.11	4–6
High 7–9 atm	920–940	10.3–10.5	94.5–95.0	0.25–0.30	1.5–3

attempts of other type catalyst design to reduce the nitric acid production cost, platinum–rhodium and platinum–palladium–rhodium alloys still serve as the main catalysts.

Table 1 lists the optimum process parameters under various pressures [3]. In commercial plants, the conversion efficiency for nitrogen oxides production ranges within 92–98% allowing no essential improvement. The plant operation is reasonably safe and reliable, and process parameters are well optimized [4,5].

However, there is one serious operation problem related to platinum losses caused by the reaction medium impact on the catalyst especially in high and moderate pressure plants. For new gauzes, reaction induced surface roughening is accompanied by an increase of the catalyst activity [6]. For example, in high pressure (8–10 atm) converters, the maximum nitrogen oxide yield is attained within 3–5 days, thus resulting in a significant loss in the acid production during start-up. As was shown by Farrauto and Lee [6], the increase of the gauze surface by a special pretreatment during its manufacture shortens the time of approach to the optimum regime. However, in all cases, the nitrogen oxides yield continuously decreases during the run. Therefore, one needs to replace the inactivated platinum gauzes by new ones, when reaction selectivity falls below the commercially acceptable level. Moreover, some gauzes never provide high selectivity, since they completely lose their activity in a short time run [3].

In the USA, nitric acid is mainly produced in high pressure (8–10 atm) converters. In Russia as well as in other countries using diluted nitric acid production technology developed in the USSR, the share of high and moderate pressure converters is not less than 50%. Typically, from 10 to 30 gauzes made of the Pt–(Pd)–Rh alloy are arranged on a supporting grid in a reactor chamber with diameters up to 5 m. Therefore, the catalyst loading is quite expensive.

Further, as ammonia is oxidized, Pt is slowly lost from the gauze, mainly in the form of more volatile oxides, though small Pt particles can also detach from gauzes strongly corroded to the end of the run (mechanical losses) [7,8]. The rate of loss depends upon the type of plant being higher for high-pressure plants (more than 1 g/t of ammonia converted). The cost of lost Pt is the second largest expense of the operation, exceeded only by the cost of ammonia feedstock [9]. To recover some of Pt, various approaches were suggested including filters made of various materials to mechanically catch and retain solid particles of Pt, chemical absorbents on the base of supported molten salts or alkaline earth compounds [7,8] etc. The most successfully used technology of Pt recovery is based upon the application of gauzes made of Pd alloys [10]. The recovery alloys are usually used in the form of multiple sheets of woven gauze placed immediately downstream from the catalyst gauze. The recovery reactions consist in the interaction between PtO₂ and Pd on the getter gauze surface followed by the solid-state diffusion of Pt into the bulk of wire thus forming a Pt–Pd alloy. Early technology [10] ensured 35–40% recoveries, while subsequent application of gauzes with a higher Pd content and improved geometries of the individual sheets practically doubled the recovery efficiency [11]. However, the recent surge in the Pd price now exceeding that of Pt makes the application of this technology too expensive.

These facts stimulate the research towards at least partial substitution of Pt gauzes by some less expensive catalytic materials.

With this regard, it is of interest to analyze and generalize the results of recent works aiming at design of essentially less expensive oxide catalysts for this purpose. Thorough systematic studies were performed mostly in the USSR (especially in the State Institute of Nitrogen Industry (GIAP), Moscow) and in China. Starting from the early 1960s, at almost all nitric acid

plants in the (former) USSR operating under atmospheric pressure, a two-bed ammonia oxidation system (one platinum–palladium–rhodium gauze+pelletized oxide catalyst bed) is used in practice [7,12].

For high-pressure plants, design of two-bed catalytic systems meets more difficult problems owing to complexity of the ammonia oxidation processes, the impact of flow hydrodynamics, and to evolution of both platinum and oxide catalysts under the reaction conditions. These problems were overcome due to united efforts of GIAP, Boreskov Institute of Catalysis (Novosibirsk) and Chemical Department of Lomonosov Moscow State University in designing honeycomb catalysts for the high temperature oxidation processes occurring at short contact times [13].

Due to a complex interrelation of all aspects of the problem, it seems reasonable to consider them successively. So, we shall consider: (1) main peculiarities of ammonia oxidation on platinum gauzes; (2) factors determining oxides efficiency in this reaction; (3) main approaches to technology of oxide honeycomb monolith catalyst production; (4) principles for designing the two-bed catalytic system based on mathematical modeling of ammonia oxidation on gauzes and honeycomb oxide catalysts and (5) the industrial application of two-bed systems for ammonia oxidation.

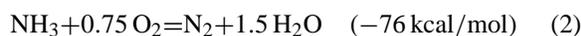
2. Kinetics of ammonia oxidation to NO on platinum metal gauzes

Despite numerous studies related to this important large-scale process, there is no generally accepted kinetic law to describe it. Ammonia oxidation on platinum is considered as a classic example of strongly exothermic heterogeneous catalytic reaction with critical regimes of heat ignition and extinction [14–16]. All attempts to suppress the critical regimes and to obtain intrinsic kinetics for concentrations and temperatures used in industry failed [17,18]. Moreover, for this process, a set of isothermal critical phenomena caused by ignition and extinction were also discovered [16].

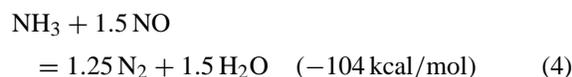
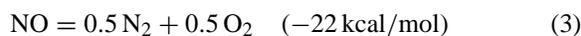
At the same time, these specific kinetic problems disappear at temperatures below 300°C, when molecular nitrogen and N₂O are the main products of ammonia oxidation. For example, the chemical kinetics of the low temperature ammonia oxidation on platinum wire at ammonia pressures ranging from 0.05

to 0.2 atm and at oxygen pressure ranging from 0.2 to 0.95 atm was studied in [19]. According to this study, the experimental data are well described by the first order kinetics with respect to the surface coverage by oxygen and ammonia pressure, activation energy being around 30 kcal/mol (1 kcal=4.18 kJ). For more oxidized product — nitrous oxide, the selectivity is proportional to the surface coverage by oxygen. With increasing contact time, the nitrous oxide yield decreases, which is explained by N₂O interaction with ammonia on the catalyst surface.

Under industrial operating temperatures (800–950°C), the oxidation of ammonia on platinum gauzes produces mainly molecular nitrogen and NO. These products are formed on the catalyst surface by reactions (1) and (2)



As for the side processes which affect the process selectivity, there is no agreement between the researches. Most researchers believe that NO decomposition to N₂ and O₂ and ammonia interaction with nitrogen oxide yielding N₂ and water provides the largest contribution (reactions (3) and (4))



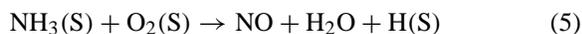
At high temperatures, the total ammonia oxidation rate is limited by the rate of ammonia diffusion to the catalyst, which is typical for the processes with external mass transfer limitation [20,21]. However, the ratio of rates of reactions (1) and (2) is determined by the reaction mechanism, and essentially depends on the composition of platinum gauzes (first of all, on the Rh content), on ammonia/oxygen ratio in the feed and mass transfer intensity [20–24].

Most researchers consider the basic reaction as a pure heterogeneous one, being mass-transfer limited at atmospheric or elevated pressures [4,5,17–28].

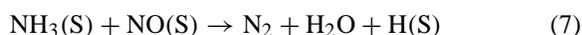
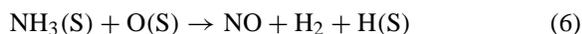
Apelbaum and Temkin studied the reaction under kinetic control at low (about 0.01 Torr) pressures on an electrically heated platinum wire 10 cm long and 0.1 mm in diameter [29]. They found that NO and N₂

desorb from the platinum surface but are never formed from other primary products in the hot gas mixture as was considered earlier [30–32]. More detailed analysis of experiments [29] shows that the reaction order in ammonia is 1.37 and 1 for oxidation towards N_2 and NO, respectively.

Fogel et al. [26,27] used mass-spectroscopy to study the ammonia oxidation at a pressure $\sim 10^{-4}$ Torr. The authors believe the reaction to proceed via the Langmuir–Hinshelwood mechanism without stable intermediates



and/or



According to the data obtained by Kuchaev and Temkin [33], there are two distinct kinetic regions for ammonia consumption rate. In the first region, the reaction rate is proportional to the ammonia partial pressure and does not depend on the oxygen content. In the second region, the reaction rate is proportional to the oxygen partial pressure and does not depend on the ammonia content. The authors conclude that ammonia molecules react in both ways — upon the impact from the gas phase or in the adsorbed state.

For ammonia oxidation on Pt, Rh and Pd wires at 0.1–1.0 Torr, other authors [34,35] concluded that within the 200–900°C temperature range, the reaction rate may be described by a model based on schemes (5)–(7) suggested by Fogel et al. However, as the reaction temperature increases to 1500°C, it is necessary to take into account the direct ammonia decomposition followed by the hydrogen oxidation.

The literature data related to the nitrogen oxide decomposition (3) are contradicting as well. Some authors report that the NO yield passes through the maximum at a definite gas flow rate or respective contact time [4,28,36,37]. The usual explanation is that nitrogen oxide is unstable, and decomposes at long contact times. However, Apelbaum and Temkin [20,21] proved that decomposition of NO does not occur under the usual operation conditions of ammonia oxidation, since oxygen suppresses this reaction.

As for reaction (4), it may occur via both homogeneous (gas phase) or heterogeneous (catalyst surface)

mechanisms. The rate of heterogeneous ammonia oxidation far exceeds that of the homogeneous route [38].

According to literature [39–41], the homogeneous reduction of nitrogen oxides by ammonia is mostly efficient at 900–1000°C. Hence, the temperature ranges for the ammonia oxidation and homogeneous reaction (4) overlap. Reaction (4) was found to be of a chain type involving many stages and intermediates [42] being well described by the second order equation with respect to reagents [43].

To describe the apparent reaction rate dependence on reaction parameters in industrial conditions, ammonia diffusion rates are used [4,7,28,44–49]. Empirical expressions with numerical coefficients obtained from the experimental data are used to estimate the yield of nitrogen oxide [4,7].

Among the papers on the ammonia oxidation modeling, those guided by Beskov are to be distinguished [50–53]. In these papers, the steady state rates of ammonia consumption are described on the bases of routes (1)–(4). All reactions are assumed to be heterogeneous. The equations and kinetic model parameters were derived from the literature data and from the experimental results of Atroshchenko and Kargin [4,28,38] obtained at conditions of the mass transfer limitation. According to estimations by Beskov et al. [52], in the temperature range 800–1000°C, the rate of NO decomposition into N_2+O_2 is only 2–3 orders of magnitude lower than the rate of reaction (1). Taken into account the results of [20,21], the rate of reaction (3) appears to be overestimated. In contrast, authors [52] clearly underestimated the reaction (2) as being ~ 5 –6 orders of magnitude slower as compared to the reaction (1).

3. Ammonia oxidation on oxide catalysts

3.1. Kinetics peculiarities

3.1.1. Low temperature reaction

The ammonia oxidation on oxide catalysts in an oxygen excess was studied in detail at temperatures below 380°C. In this case, there is no mass transfer limitation, and molecular nitrogen and nitrous oxide are the main reaction products [54–58]. The results obtained and reaction mechanisms considered are reviewed [59,60]. Among simple transition metal

oxides, in the ammonia oxidation, the most active are Co_3O_4 , MnO_2 (Mn_2O_3), Cr_2O_3 , CuO . Moderately active are NiO , Fe_2O_3 , V_2O_5 , ZrO_2 , CeO_2 , La_2O_3 . The activity and selectivity towards nitrous oxide usually correlate, both decreasing as the surface oxygen bonding strength increases and the oxygen and ammonia pressures decrease. The reaction kinetics is rather well described by the reaction mechanism suggested for ammonia oxidation on platinum [19]. However, this mechanism does not take into account that oxygen species on the surface of oxide catalysts are not uniform by bonding strength and reactivity, which also depend on the sample genesis. There were no data on the concentrations of intermediates, their relative stability and reactivity.

In the recent decade, mechanisms of ammonia oxidative transformations were essentially revised, when selective reduction of nitrogen oxides (SCR) by ammonia in an oxygen excess was studied in details for environmental applications. This process is now widely used for NO_x abatement from the flue gases of power plants and industrial sources. Here, ammonia oxidation to nitrogen oxides is an undesired side reaction, attracting thus a keen research attention. Several reviews on the subject were published [61–63] not mentioning a lot of original papers clearly beyond the scope of our present analysis. These experimental data appear to be quite reliable, since they were obtained using in situ IRS, transient response technique, and isotope methods. However, for various oxides, different routes for the surface ammonia transformation were suggested. This may be caused by the different surface chemistry of oxides as well as by inherent difficulties in identification of surface intermediates and estimating their reactivity. Thus, for supported vanadium oxide systems, the route yielding molecular nitrogen is usually ascribed to the interaction of weakly bound or gas phase NO (NO_2) molecules with strongly adsorbed ammonia species such as NH_4^+ , NH_2 [63] or even with the products of their interaction such as hydrazine [64]. At the same time, there are many facts in favor of strongly bound nitrite–nitrate complexes be responsible for N_2 generation via their interaction with ammonia [65–70].

Despite the differences in the suggested mechanisms, various authors agree that strongly bound surface intermediates are required for molecular nitrogen to form on the oxide catalyst surface. A temperature

increase reduces the catalyst coverage by such intermediate species, and the routes of molecular nitrogen and nitrous oxide formation are suppressed, while ammonia oxidation to NO dominates.

3.1.2. High temperature reaction

High temperature ammonia oxidation on pure and promoted bulk oxides of transition metals is discussed in many papers [71–100]. The catalytic performance of mixed oxides of transition, rare earth and alkaline earth metals is considered in [99–113].

The high temperature ammonia oxidation on oxide catalysts is well analyzed [7]. Note that under industrial conditions, when NO dominates among the reaction products, the ammonia oxidation rate on the oxide systems as well as on platinum gauzes is limited by ammonia diffusion from the gas phase to the catalyst surface [71–73,89,90]. This means that the reaction selectivity towards NO attains its maximum, when oxygen nearly completely covers the catalyst surface, and there is almost no ammonia or its partial oxidation products on the surface.

To estimate the ratio of the ammonia oxidation rates on oxides and platinum, the ammonia threshold loads can be compared. A load is defined as the ratio of the volume gas velocity (referred to 0°C and 1 atm) to the catalyst cross-section. A threshold load corresponds to a load when the process extinction is observed [71,72]. As the linear rate of the gas flow increases, the apparent thickness of the diffusion layer decreases, and at some value, the heat evolution rate becomes less than the heat removal rate, and, thus, the catalyst cools down and extinguishes. The threshold load depends on the surface reaction rate constant, and, thus, on the catalyst nature. According to [71], at 1 atm and 10 vol.% NH_3 in air, the threshold load for a 0.09 mm diameter platinum wire is close to $30\,000\text{ L/cm}^2\text{ h}$. For the 4 mm cobalt oxide pellet, it is $10\,000\text{ L/cm}^2\text{ h}$, other conditions being the same [72].

The dependence of the threshold load on the Co_3O_4 catalyst grain size, ammonia and oxygen concentration and total pressure studied by the authors of [84] revealed the following equation for the ammonia oxidation rate:

$$r = K[\text{NH}_3]^{0.36}[\text{O}_2]^{0.14} \quad (8)$$

where K is a constant, $[\text{NH}_3]$ and $[\text{O}_2]$ are the

concentrations of ammonia and oxygen near the catalyst surface, respectively. The reaction activation energy is close to 9 kcal/mol. This equation characterizes the overall ammonia conversion to all products such as nitrogen oxide and molecular nitrogen.

A similar method was used [74,89] for the catalysts based on iron oxides. According to [89], the lower reaction ignition temperature, the higher maximum NO selectivity estimated by the standard procedure [4], the lower effective activation energy and reaction order, hence, the external diffusion limitations are more severe. So, the reaction selectivity towards NO under industrial conditions may serve as a measure for the catalyst activity. Practically in all studies related to oxides, the performance of catalysts was estimated using this approach.

According to the standard procedure [4], such studies are usually carried out under atmospheric pressure in a 40 mm bed, grains size ranging within 1.5–2 mm. At 750–800°C (low-temperature samples) and at 800–900°C (high-temperature samples), the linear gas flow rate ranges from 0.2 to 2 m/s, contact time from 10^{-3} to 6×10^{-2} s, ammonia content from 1.0 to 1.5 vol.%. Under such conditions, the ammonia conversion is complete, but NO selectivity strongly depends on the oxide nature and samples genesis. As a rule, selectivity towards NO goes through the maximum depending on the temperature.

Almost all authors agree that maximum selectivity is shown by such oxides as Co_3O_4 (94% yield), $\alpha\text{-Fe}_2\text{O}_3$ (90% yield), Bi_2O_3 (90–93%), manganese oxides (up to 80% yield). Moderate selectivity is shown by NiO (30–50%), CuO (40–50%), PbO_2 (50%), rare-earth metal oxides (10–50%). Oxides of aluminum, tungsten, molybdenum, tin are not active.

Similar selectivity series for oxides were obtained on ammonia oxidation under pressure up to 8 atm [78–82,85].

Taking into account that under similar operation conditions, on the most active oxides the ammonia conversion is complete at contact times of 10^{-2} s, while on platinum gauzes it is achieved at contact times of 10^{-4} s, the specific catalytic activity of oxide catalysts appears to be at least ~ 2 orders of magnitude lower than that of the platinum group metals. Indeed, according to [7], at 900°C, the effective first order rate constant (in s^{-1}) is 24 600 for the platinum catalyst and 73 for the iron oxide catalyst. This estimation

agrees well with the same scale of the reaction rate differences estimated for oxides and metals in ammonia oxidation to nitrous oxide under the kinetic control at temperatures around 200°C [59]. An essentially higher activity of metals in comparison to that of oxides at the same strength of the oxygen surface bond implies a significant role of the ammonia N–H bond activation (its cleavage or weakening) on the metal surface.

3.2. Factors determining catalytic performance of transition metal oxides

All earlier attempts to find relationships between the oxides activity (selectivity towards NO) and their physical properties such as melting temperature, band gap, conduction type or electron work function failed [7]. At the same time [76], a good correlation was revealed between the activity, the activation energy of oxygen homo-exchange, and the surface oxygen bonding strength estimated by the method of thermochemical cycles [59]. The iron oxide, however, stands apart from these relationships. Nevertheless, all these efforts revealed the significance of oxygen bonding with the surface for ammonia oxidation on oxides.

An important breakthrough in understanding the molecular-scale factors controlling the oxides activity and selectivity in the ammonia oxidation was achieved in works of Ryabchun and co-workers [95–98]. For the industrial iron oxide catalyst, the detailed studies using such methods as thermal desorption, SIMS, X-ray diffraction, epitaxial decoration, laser spectrometry, unsteady state kinetic experiments with a micro-reactor attached to the high-vacuum ‘surface science’ installation have been carried out. The most important conclusion from all these studies was the evidence for a micro-heterogeneity of the working catalyst surface under the reaction conditions. In unsteady state conditions of the surface reduction by ammonia, the maximum selectivity towards NO is attained, when 35% of the oxygen monolayer are removed from the surface accompanied by its reconstruction. This reduction process is of a topochemical character, and proceeds through the expansion of reduced domains from the points of their nucleation. Nitrogen dissolved in the catalyst may play some role in the modification of reduced domains. Oxygen adsorbed on such domains is characterized by the activation energy of desorption ~ 50 kcal/mol, which

coincides with that for the most active catalyst — platinum. In the oxygen excess, the catalyst surface is mostly covered by such an oxygen, though there are also less (adsorption heat, 20–30 kcal/mol) and more strongly bound oxygen species. A weakly bound oxygen favors the oxidation of ammonia to molecular nitrogen, while too strongly bound oxygen is inactive. Independently measured rates of the surface reduction and reoxidation were found to be less than the steady state rate of the overall catalytic process, thus suggesting the reaction to proceed by an ‘associative’ mechanism.

Hence, these results help to elucidate the factors determining the activity and selectivity of oxide catalysts in the high temperature ammonia oxidation to NO. Indeed, to provide an almost complete surface coverage with oxygen at operating temperatures ranging within 800–900°C, the oxygen-surface bond must be strong enough. Note that a reasonably high oxygen bonding strength (the adsorption heat 50–60 kcal/mol O₂) is usually required not for deep oxidation catalysts, but for the catalysts of partial (mild) oxidation such as transition metals molybdates or vanadates [114,115]. Apparently, the optimum oxygen adsorption heat must decrease, if operating temperature decreases.

If at a given temperature the strength of oxygen bonding to the surface is lower than the optimum value, the oxygen coverage will decline generating coordinatively unsaturated surface sites such as reduced cations of transition metals, which will stabilize the adsorbed ammonia species opening the route to molecular nitrogen generation.

At the same time, the oxygen bond strength must not be too strong. The surface oxygen must be able to react with the ammonia molecules with a rate exceeding the rate of their adsorption under given conditions, thus providing the transfer of the reaction into the external diffusion regime, when the surface coverage by ammonia or its intermediates is small. The strengthening of the oxygen bond with the surface will also favor stabilization of strongly bound nitrite–nitrate complexes [116]. As a result, the oxygen-surface bond strength exceeding the optimum one will push reaction to routes yielding molecular nitrogen.

This idea allows to understand why for all oxide systems as well as for platinum group metals, the temperature dependence of NO yield goes through the maximum [7]. Further, the specificity of the platinum

group metals performance can be explained. Thus, for example, at 850–900°C (the typical operating temperatures for platinum), on bulk palladium, ammonia is mainly oxidized to molecular nitrogen, which is explained by a too low surface oxygen coverage due to easy dissociation of the surface PdO [117,118]. At the same time, the rhodium oxide, covering the surface of deactivated platinum gauzes, is practically inactive [3], which may be explained by a too strong rhodium–oxygen bond.

Note that besides the vital importance of the oxygen-surface bonding, a specific activation of the ammonia molecule (*vide supra*) may also play a significant role. Probably, for oxides, high-charge low-coordinated surface cations — Lewis acid sites, including those produced due to the oxygen and/or water desorption from the surface, are of essential importance. At present, however, an analysis of this factor is not possible due to the absence of reliable data on the properties of such sites on the small surface area oxide catalysts characterized in the high-temperature ammonia oxidation.

Analysis of the atomic-scale reasons for various oxygen species appearing on the catalyst surface should be based upon the discrete nature of the energy spectrum of oxygen species on the oxide surface. This means that there are always several surface oxygen species differing by the strength of their bonding (heat of adsorption). These species appear as separate maxima in the spectra of the oxygen thermal desorption [119–121] or as steps on the dependencies of the heat of oxygen adsorption versus coverage registered using isosteric methods [122,123], calorimetry or solid electrolyte potentiometry [114,121].

For a given oxide, the existence of different surface oxygen species is caused by the atomic structure of its faces, by the appearance of point (vacancies) and extended (steps) surface defects, including those emerging in the vicinity of outlets of bulk extended defects [124–128].

In the last decades, a lot of data on the atomic structure of the oxide single crystal faces were accumulated using such methods as LEED, STM, AFM, photoelectron diffraction (see, e.g. [129–131]). For finely dispersed oxides, the atomic structure of their surfaces was studied with the help of such methods as IRS of adsorbed test molecules [132], ESR of adsorbed nitroxides [133], TEM [134–136], ISS [137],

Table 2
Calculated and experimental oxygen desorption heats (kcal/mol) [124]

Oxide	ΔH calculated		ΔH experimental
	Regular sites	Defective sites	
CuO	MO: 9	M–O near (001) twin outlet onto (101) face: 3	10; 25
	M ₂ O: 60		50
Co ₃ O ₄	MO(OH): 40–50	M–O near outlet of (110) stacking fault onto (110) face: 15	15
	MO(Td): 60–70		40
	M ₂ O: 130		120
Fe ₂ O ₃	MO: 35–40 (Oh)	M–O near outlet of (0001) stacking fault onto (0001) and (112 ⁻ 0) face: 18–30	20; 40
	60–70 (Td)		60
	M ₂ O: 130		120
MnO ₂	MO: 32–40	M–O on (110) face, relaxation of surface Mn–O bonds caused by oxygen atom removal: 14	16; 30
	M ₂ O: 60		45

neutron diffraction in the argon adlayer [138,139]. The development of quantum-chemical semi-empirical [125,126,128,140–142] as well as ab initio [140–150] methods of the surface energy and adsorption heat calculation allowed analysis of possible structures of adsorption centers capable to retain oxygen with the strength required for the process considered. Some results are given in Table 2.

According to [124], in an oxidative medium, the well developed densely packed (111) faces of spinel oxides and (0001) faces of corundum-type oxides are mainly covered by strongly bound non-reactive bridged M₂O oxygen species, whose adsorption heats range within 100–120 kcal/mol. The chemically inert stoichiometric (0001) face of hematite is not able to dissociate even water molecules to produce hydroxyls [151].

The structures of such faces annealed in high vacuum and thus weakly reduced, most likely correspond to localization of tri-coordinated cations in the upper layer [152–158]. Theoretical analysis of these structures using non-empirical and semi-empirical methods [143–149,159] has revealed that they must experience a strong relaxation forcing the cation to sink into the surface oxygen layer. At the same time, STM data for the (0001) face of thin hematite layer grown epitaxially on the Pt (111) suggest the existence of domains with the upper layer represented by both oxygen and iron atoms [150]. For the oxidized surface of corundum, AFM [160] shows that the upper layer ends by

the hexagonal package of the oxygen atoms with interatomic distances close to those in the bulk.

For oxide samples prepared from solutions of corresponding salts, IRS of adsorbed CO [124,125,127,132,161–166], IRS of hydroxyls [167–169], neutron scattering in the argon adlayer [138,139], ⁴He ions scattering on the surface [137], ESR of nitroxide radicals applied to diamagnetic oxides (α -Al₂O₃) [133] show that the densely packed faces of spinel or corundum-like oxides do not contain tri- or tetra-coordinated cations in the regular positions. Cations in such coordination are usually present in small amounts, which strongly depend on the sample genesis, allowing to assign them to such surface defects as steps or subsurface stacking faults. For stoichiometric iron and aluminum oxides, configurations of these faces appear to end with the oxygen layer comprising the oxygen ions and hydroxyl groups [167,169]. Some experimental data [170–173] and theoretical analysis [130–141] reveal the hydroxyl groups to play a significant role stabilizing densely packed faces in corundum-like oxides (basal face) and in oxides of rock salt structure (the (111) face).

In CuO (tenorite) and MnO₂ (pyrolusite), M₂O bridged oxygen species bound to the regular sites of the most developed faces have almost optimum bonding strength (50–60 kcal/mol) [124,125,128].

Under oxidative conditions, for corundum-like chromium oxide, the densely packed basal (0001) face is usually covered by chromate groups (tetrahe-

drally coordinated Cr^{6+} cations), where the terminal oxygen has the adsorption heat close to 60 kcal/mol [124,174–176]. Note that in this case, the basal face cations are tetra-coordinated, that agrees well with predictions based on the data obtained with high-vacuum methods (*vide supra*). Apparently, under oxidative conditions, the chromium cation easily changes its oxidation state thus favoring the thermodynamic stability of such configuration, which is not possible in the case of iron or aluminum oxides.

For oxides with the close-packed oxygen sublattice, the terminal (M–O) oxygen species with the adsorption heat close to the optimum value for ammonia oxidation to NO (40–60 kcal/mol) are mostly located on open faces: (1 0 0) and (1 1 0) types in spinel structures (1 1 2⁻ 3) and (1 0 1⁻ 2) in corundum ones. In the case of oxides obtained via the thermal decomposition of precursors (salts, hydroxides) synthesized from water solutions, these faces are not well represented, though their exposition increases with an increase of the calcination temperature. Thus, according to [178], for a sample of cobalt oxide prepared from the nitrate salt, as the calcination temperature increases from 400 to 800°C, the shape of particles changes from platelets with the mostly developed (1 1 1) faces to pyramids with the mostly developed (1 1 0) faces.

Rhombohedral (1 0 1⁻ 2) and pyramidal (1 1 2⁻ 3) faces of hematite are the natural growth faces [148], and in disperse samples, their share also increases with increasing calcination temperature, since their surface energies are lower than that of the basal face [126]. On rhombohedral and pyramid faces, the terminal oxygen species are linked to cations in octahedral or tetrahedral coordination [126,129–131]. Moreover, the terminal oxygen species with a similar bonding strength may appear near steps formed due to the high-temperature reconstruction of prismatic and basal faces [124,130,160,179].

In stoichiometric MeO oxides of the rock salt structure, the (1 0 0) faces are not able to adsorb oxygen without changing the cation charge, though they do contain penta-coordinated cations required for such an adsorption. As a result, the stoichiometric perfect face of NiO is practically inert to reduction by CO or hydrogen at moderate temperatures [129–131,180]. For dispersed nickel oxide, such faces are well developed only in samples obtained via plasma thermolysis of nitrate solution [181]. At the same time,

in samples obtained via traditional thermal decomposition of nitrate solution, the particles morphology is mainly determined by (1 1 1) faces covered by strongly bound oxygen species probably stabilized by hydroxyl groups [182].

In oxides with a broad range of the surface/bulk non-stoichiometry (cobalt and manganese spinel oxides, nickel oxide), the terminal oxygen species appear on the densely packed faces when cation vacancies are generated due to the oxygen excess [124,183–186]. This excess oxygen is removed at 400–500°C. Therefore, at temperatures typical for the ammonia oxidation process, such generation of terminal oxygen species will hardly be of importance for the application in concern.

In transition metal oxides, the most weakly bound oxygen species (heat of adsorption 10–30 kcal/mol) are mainly located on coordinatively unsaturated cluster sites appearing in the vicinity of outlets of extended defects such as dislocations, twins, stacking faults and intergrain boundaries [124–128]. Usually, the density of extended defects is determined by the oxides preparation procedure. The dislocation network in the surface layers of oxide particles is also generated during phase transitions, when, e. g. magnetite phase nuclei emerge during the hematite reduction [124,125,127], or when Co_3O_4 transforms to CoO at high temperatures [178]. Such cluster sites may also appear due to reconstruction of the (1 0 0) and (1 1 0) faces of spinel [187–190], and (1 1 1) face of rock salt-like oxides [191] caused by a loss of oxygen and/or hydroxyls. Though weakly bound oxygen species determine the activity of some transition metal oxides [124] and perovskites [192–199] in oxidation of CO and hydrocarbons at temperatures up to 400°C, in the high temperature ammonia oxidation those sites obviously will cause a lower NO selectivity owing to their inability to keep oxygen at operating temperatures. Indeed, after oxygen removal, clusters of coordinatively unsaturated cations will appear at the surface being able to retain the intermediate complexes of ammonia oxidation, and, hence, to accelerate the N_2 generation (*vide supra*). Moreover, extended defects are known to be the potential sites for the nucleation of reduced phases [200], which are less selective towards NO [7].

For perovskite systems, the effect of the synthesis procedure on the development of certain faces is far less studied than for simple transition metal

oxides. Depending on the system and synthesis conditions, the perovskite particles morphology may be presented by spheres comprised of the cubic micrograins [195,201,202], platelets including hexagonal ones [195,203], prisms with sharpened tops, pyramids, octahedrons [203,204]. These data combined with the results of the selective electron diffraction [201–205] and HREM [204,205] imply that the surface of particles may be represented by the (100), (110) and (111) faces as indexed in the cubic space group.

Since the perovskite structure is formed by the dense packing of mixed lanthanum-oxygen layers, transition metal cations being located between the layers in oxygen octahedrons, each type face may have a different termination. Thus, along the (100) direction, alternated are layers LaO and MeO₂, along (110) — layers O₄, MeO and La₄Mn₂O₂, along (111) — densely packed lanthanum-oxygen layers in the cubic sequence abc with the layers of transition metal cations in between.

In general, there are no data which face termination comprise the surface. Considering the XPS and SIMS data [195,199,201,206,207], one may conclude that in most cases the ratio between the lanthanum cations (or sum of lanthanum and — alkaline-earth cations for samples with such a substitution in the lanthanum sublattice) and transition metals in the subsurface layer differs insignificantly from that in the bulk, though may vary depending on the conditions of sample synthesis and pretreatment. Thus, a reductive treatment favors segregation of transition metal cations, while an oxidative treatment in humid atmospheres enriches the surface with lanthanum and alkaline-earth cations [208,209]. Hence, the most developed faces of perovskites appear to be represented by all possible terminations with a nearly equal probability.

On any perovskite face, the oxygen atoms bound to lanthanum cations in the regular positions seem to be chemically inert at all temperatures of catalysis. The faces of the (110) type shall be mainly covered by bridged oxygen species bound to either two manganese cations or manganese and lanthanum cations. The (100) faces with MeO₂ composition may contain penta-coordinated cations of transition metals, which are sites for oxygen adsorption in the terminal MO form. From stoichiometric lanthanum cobaltites, ferrites, nickelates and manganites, such oxygen species are usually desorbed at 700–800°C [210–213].

In the perovskite matrix, owing to diluting effect of lanthanum cations, clustered transition metal cations-sites for ammonia oxidation to N₂ (vide supra) will hardly appear in the vicinity of extended defects. Indeed, in the rock salt-like oxides, at a mono-atomic step on the (100) face, the lifting of screening by oxygen anions allows interaction between cations lying at the top and bottom of step. On the contrary, in the perovskite structure, the step bottom is comprised by the lanthanum–oxygen layer allowing no interaction between the transition metal cations [129,131]. Clustering becomes possible only in the vicinity of such extended defects as clusters of oxygen vacancies, twins, or intergrowth structures where the local enrichment by transition metal cations occurs [125,196].

If in perovskite-like oxides some lanthanum cations are replaced by the alkaline-earth cations, various defects are generated depending on the degree of substitution and the nature of transition metal cation. Among them, cation and/or anion vacancies, ordering of modifying cations in some planes, microstrains and other extended defects like micro-domain interfaces, intergrowth of phases with different composition, cooperative distortion of lattice, which may even produce phases of other symmetry and/or structure were revealed [113,192,199,201,205,206,211–219]. Oxygen vacancies appearing due to this partial substitution will affect the catalyst performance only if they emerge on the surface. It certainly takes place for partially substituted lanthanum manganites, ferrites, cobaltites and nickelates, where appearance of oxygen species desorbing at temperatures below 500°C and probably related to ion-radical O[•] species bound with the surface oxygen vacancies is well documented [102,105,113,211,220]. These radical species can be associated with a new O1s peak in the XPS spectra of substituted samples lying at ~2 eV above the level typical for oxides and non-promoted perovskites [113,207,215,217,220]. However, at least in part, this peak may also correspond to surface hydroxyls bound to lanthanum cations [216].

If oxygen vacancies appear in the coordination sphere of transition metal cations in perovskites, the oxygen octahedron easily transforms into another polyhedron (tetrahedron, bipyramid, etc.) thus removing the vacancy [204,205,214]. Therefore, one may assume that relatively stable surface oxygen vacancies are most likely present in the lanthanum-containing

faces. This means that oxygen ion-radicals appears to be mainly linked to the subsurface transition metal cations. Hence, a cation substitution produces the active oxygen species on rather inert lanthanum-containing faces of perovskites. The ion-radical form of oxygen is coordinated to subsurface transition metal cations in part screened by the lattice oxygen anions. Hence, the removal of ion-radical due to desorption at temperatures of ammonia oxidation will not lead to undesired stabilization of ammonia oxidation intermediates.

From the point of view of the surface oxygen bonding strength, the NO selectivity pattern in the high temperature ammonia oxidation on oxide systems can be considered.

Since the heat of oxygen adsorption in on-top positions on the regular centers of cobalt oxide is lower than that for platinum, the optimum temperature of the ammonia oxidation into NO (650°C) is also lower. An increase of the temperature of maximum NO yield in going from Co_3O_4 (650°C) to $\alpha\text{-Fe}_2\text{O}_3$ (700–800°C) and to $\alpha\text{-Cr}_2\text{O}_3$ (850°C) [7,76] apparently correlates with the increasing strength of MO form bonding with the regular surface cations [121,124,126].

The maximum NO selectivity on cobalt oxide (96%) and chromium oxide (94%) is higher than that on hematite (89–93%). This qualitatively agrees with the fact that on the former two oxides we have a high (up to a half of monolayer) surface coverage by the terminal oxygen form with the adsorption heat ca. 40–60 kcal/mol [121,176,177], whereas on hematite this coverage hardly attains 20% of a monolayer [124].

High maximum NO yields on perovskites systems, which competes or even exceeds those on pure transition metal oxides [7,103–113], are well explained by the fact that the strength of the terminal oxygen bonding to a transition metal cation in former systems is higher than that for simple oxides.

A specific behavior of the oxides faces towards stabilization of various adsorbed oxygen species as well as an undesired effect of extended defects explains the dependence of NO selectivity on the synthesis procedure for different samples of the same oxide phase [7]. Beside the effect of some non-controlled alkaline cation admixtures (vide infra), the oxide particles may also change their shape and defect structure when the nature of the precursor phase or conditions of its decomposition are varied.

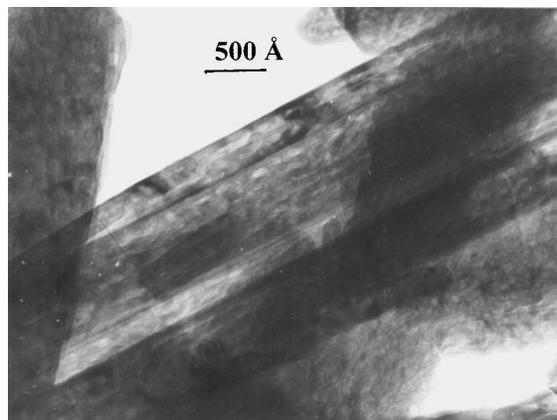


Fig. 1. Typical TEM image of the hematite particles prepared by thermal decomposition of goethite.

Thus, when hydroxides, oxohydrates or basic metal carbonates, whose surface is usually represented by the densely packed hydroxyl layers, are used as precursors, the oxides surface is also mainly formed by the densely packed faces [121,124,127,178,179]. Moreover, the precursor phase lattice transforms to that of the oxide phase in a topotactic manner, which helps to generate a great number of extended defects such as twins, dislocations and stacking faults [182,221–223]. Fig. 1 illustrates such highly defect iron oxide particles obtained through the goethite decomposition. In this case, the particles surface is mainly composed by basal and prismatic faces characterized by a low reactivity of regular centers.

If iron oxides are obtained through decomposition of a nitrate solution, their particles are usually elongated, roundly shaped (Fig. 2) and contain few extended defects. The particles roundness implies presence of high index stepped faces, on which the terminal oxygen species bound to the regular cations may appear. Experiments [7,82,83] show that indeed NO selectivity is higher for samples of iron oxides prepared from the iron nitrate, which appears to correlates with a higher surface coverage by oxygen whose adsorption heat is about 60 kcal/mol [221].

Round-shaped particles are usually formed when the non-equilibrium methods are used for the oxide synthesis. Among these methods are spray-drying and calcination in the heat carrier flow, the plasma thermolysis of salt solution [195,196] or mechanochemical activation [193]. Fig. 3 shows that iron oxide particles

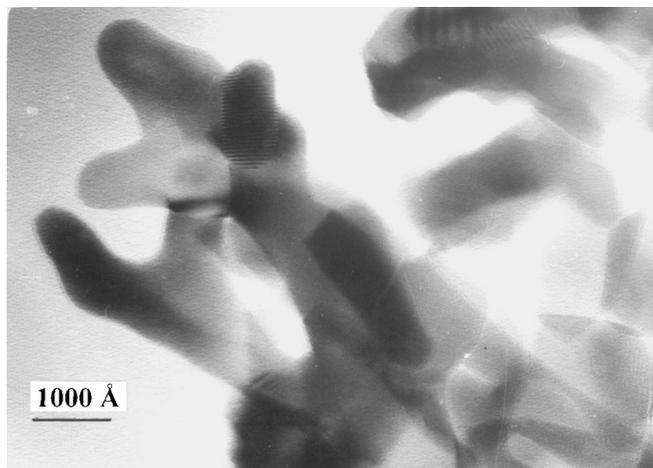


Fig. 2. Typical TEM image of hematite particles prepared by thermal decomposition of nitrate solutions.

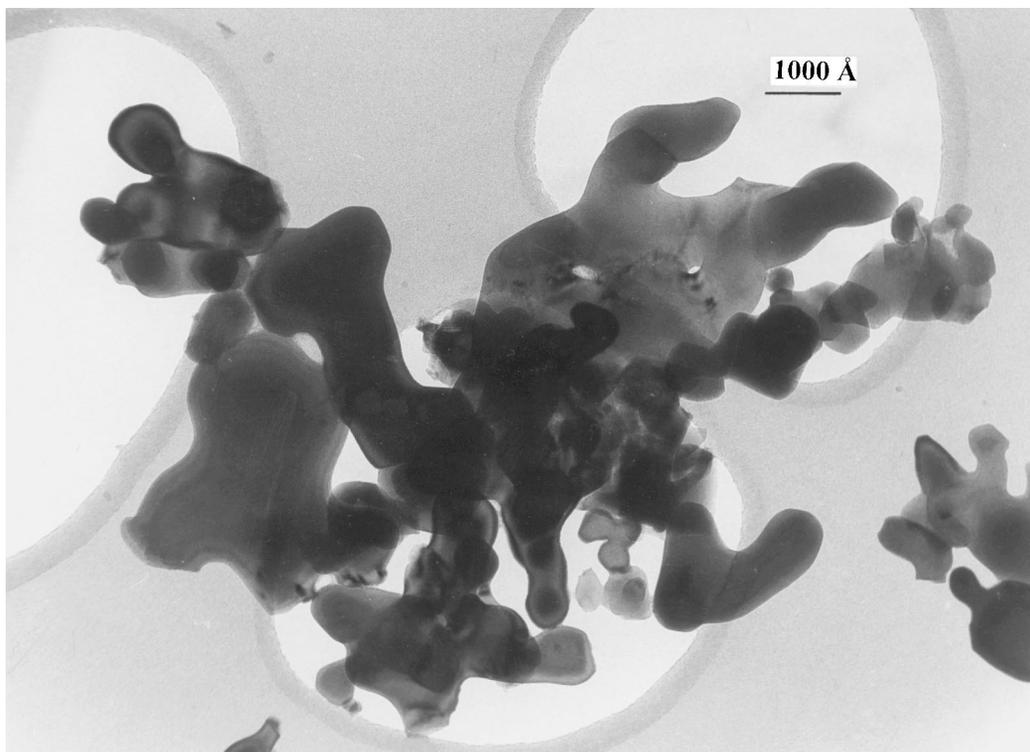


Fig. 3. Typical TEM image of hematite particles prepared by spray-drying of chloride solutions.

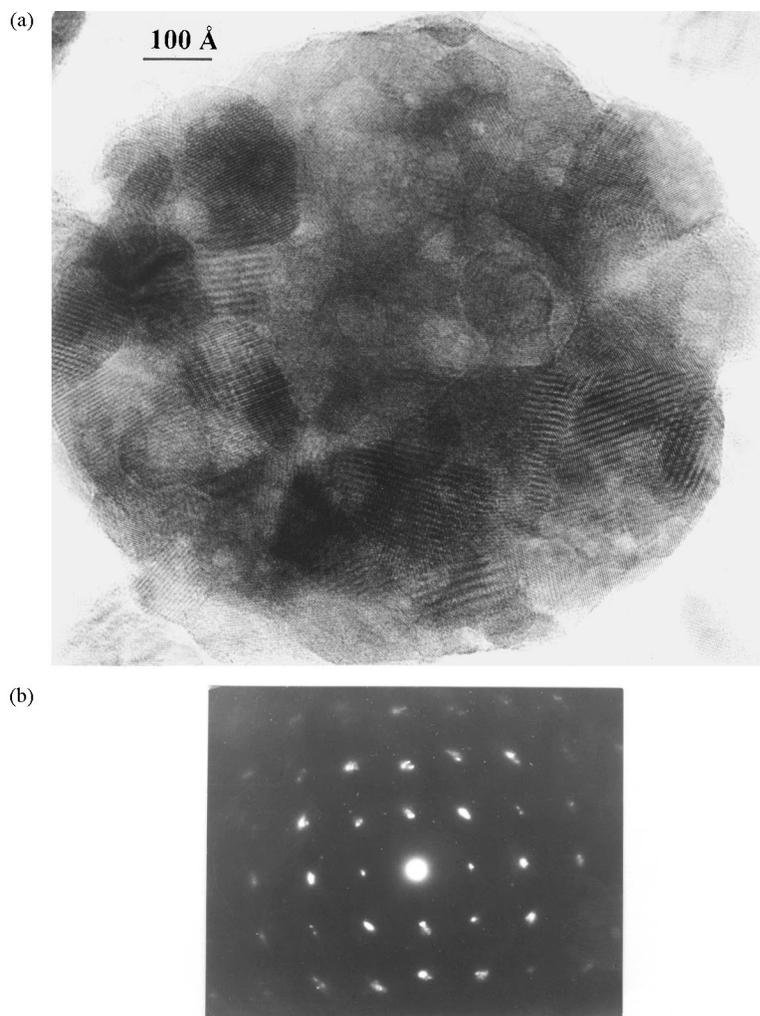


Fig. 4. Typical TEM image of lanthanum manganite particles synthesized via arc plasma thermolysis of mixed nitrate solution (a) and corresponding microdiffraction in the (100) zone (b).

obtained through the iron chloride solution decomposition in the spraying columns (a commercial hematite sample, the West Siberia smelter) followed by calcination at 800°C are indeed round-shaped and show high selectivity in the desired reaction [99,206,224,225]. The lanthanum manganite particles obtained through the arc plasma thermolysis of mixed nitrate solutions are also spherical (Fig. 4) [201,202,226]. In this case, the particles are comprised of micrograins, whose surface is represented by the (100) faces. At the same time, the lanthanum manganite particles prepared

by the thermal decomposition of co-precipitated hydroxides are usually platelets with mostly developed (110) and, probably, (111) faces. As the result, these samples are less active in redox reactions [195].

From the practical point of view, the oxides, which can be used for synthesis of commercial catalysts, must not transform to lower oxides at the temperatures of catalytic process in a slightly reducing medium. With this regard, pure manganese oxides MnO_2 and Mn_2O_3 though initially selective, are inevitably con-

verted to less selective Mn_3O_4 spinel oxide due to their reduction.

Similarly, the phase transition $\text{CuO} \rightarrow \text{Cu}_2\text{O}$, which occurs in the surface layer of oxide particles earlier than in their bulk and yields a dislocation network [227], also does not allow to use a pure copper oxide as a base for the commercial catalyst. A moderate selectivity of CuO may be explained by such a phase transition, though copper oxide has a lot of surface oxygen with the appropriate bonding strength. A low selectivity of Cu_2O [7] may be caused by a high concentration of regular coordinatively unsaturated Cu^+ cations on the most developed stoichiometric (100) and (110) faces [228,229], which stabilize the ammonia oxidation intermediates.

Pure oxide Co_3O_4 , showing the maximum selectivity at 650°C [7], can be used only under the atmospheric pressure and at lowered ammonia content, otherwise it transforms to less selective CoO . Pure $\alpha\text{-Fe}_2\text{O}_3$ is more stable catalyst than spinel cobalt oxide. However, it is also reduced to less selective Fe_3O_4 (or even FeO) under the industrial conditions, if the oxygen content is below the optimum value [230].

Another problem can be a volatility of metal oxides under the reaction conditions. Thus, one of the most selective oxides, bismuth oxide, easily sublimates at operating temperatures of ammonia oxidation into NO . Therefore, bismuth oxide is used only as an admixture to other transition metal oxides [7]. Chromium oxide also shows a noticeable volatility, especially under high-pressure conditions, because CrO_3 sublimates from the surface [7].

Hence, all the most selective simple transition metal oxides cannot be used in the industrial high-pressure process due to their poor stability in the reaction conditions. Therefore, it is necessary to modify the basic oxides by introducing promoters able to increase their thermal stability, suppress reduction and improve (or at least not worsen) their selectivity.

3.3. Control of NO selectivity for catalysts based on transition metal oxides

For basic oxides of cobalt, iron and chromium, a lot of other oxides were tested as additives. Mainly, these were non-reducible oxides of alkaline, alkaline-earth and rare-earth metals. Moreover, oxides of other transition metals were used to promote the iron and cobalt

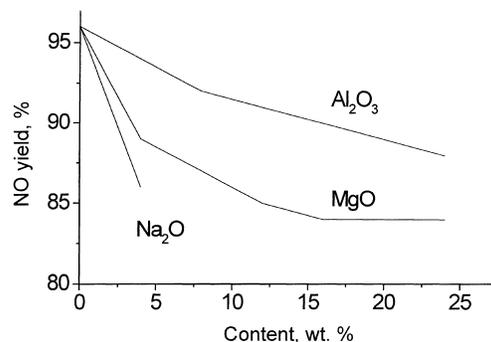


Fig. 5. Dependence of NO yield on the content of additives in Co_3O_4 samples [7]. 650°C , GHSV $(6\text{--}10) \times 10^4 \text{ h}^{-1}$.

oxides. As a rule, promoters were introduced into the oxide bulk using decomposition of a mixed nitrate solution or co-precipitation of hydroxides (hydroxycarbonates) from such solutions [7].

Most papers report no data on the promotion-induced change of the phase composition, defect structure and surface chemistry of oxides or strength of the surface oxygen bonding. Hence, those results can be interpreted only regarding similar systems characterized by modern physical and chemical methods in details.

Almost all promoters decrease the NO selectivity of oxide systems in comparison with pure oxides tested under the same conditions [7] (see Figs. 5–10 for illustration). The alkaline cations provide the most negative effect on selectivity. In this case, the terminal oxygen bond with the surface transition metal cation becomes stronger due to electron donating effect of alkaline cations in the neighboring positions. Thus,

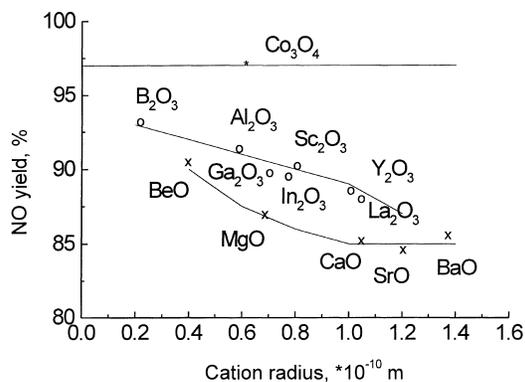


Fig. 6. NO yield vs. radius of added cation for modified Co_3O_4 samples [7]. 650°C , GHSV $(6\text{--}10) \times 10^4 \text{ h}^{-1}$, promoter content 5%.

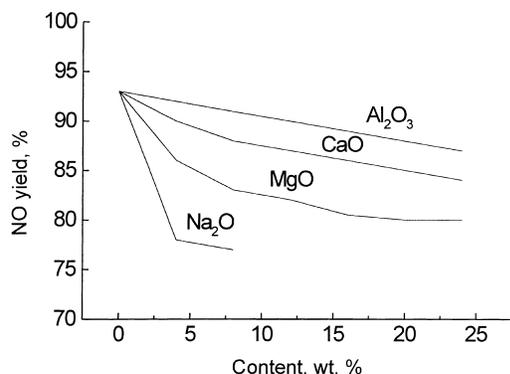


Fig. 7. Dependence of NO yield on the content of additives in Fe_2O_3 samples [7]. 750°C , GHSV $(6\text{--}10)\times 10^4 \text{ h}^{-1}$.

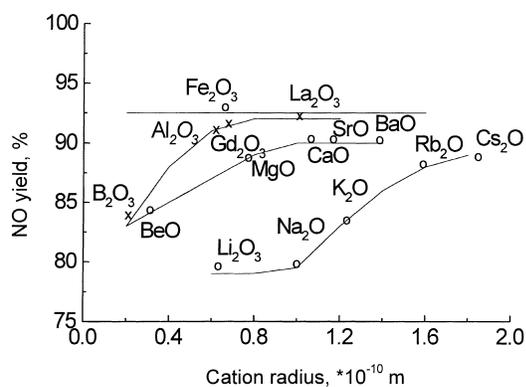


Fig. 8. NO yield vs. radius of added cation for modified Fe_2O_3 samples [7]. 750°C , GHSV $(2\text{--}8)\times 10^4 \text{ h}^{-1}$, promoter content 5%.

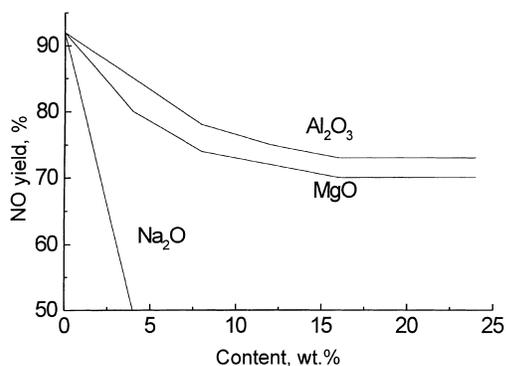


Fig. 9. Dependence of NO yield on the content of additives in Cr_2O_3 samples [7]. 850°C , GHSV $(6\text{--}10)\times 10^4 \text{ h}^{-1}$.

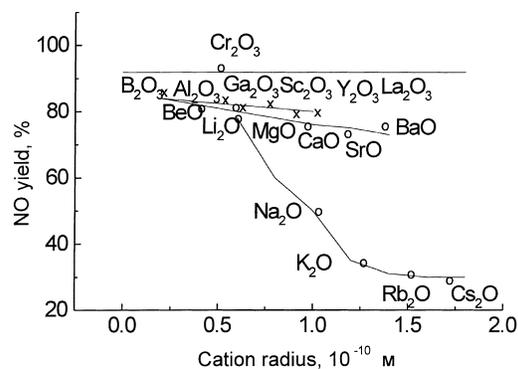


Fig. 10. NO yield vs. radius of added cation for modified Cr_2O_3 samples [7]. 850°C , GHSV $(3\text{--}12)\times 10^4 \text{ h}^{-1}$, promoter content 5%.

according to [123], introduction of only 2 wt.% of potassium into hematite substantially increases the isosteric heat of oxygen adsorption from the optimum value (50–60 kcal/mol) (Fig. 11). Probably, the sharpness of the effect is caused by the tendency of potassium cations to segregate on the surface of transition metal oxides due to the difference between the radii of transition metal and potassium cations [231–233]. Such a segregation intensifies with the increase of calcination temperature [221], thus appearing to be the main factor strongly decreasing the NO selectivity of alkaline promoted oxides.

Although there are no reliable data showing the segregation of alkaline metal cations on the surface of cobalt and chromium oxides, most likely the mechanism of their effect on NO selectivity in the high-temperature ammonia oxidation is the same. In

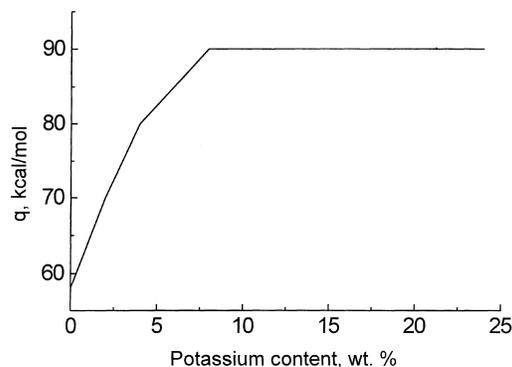


Fig. 11. Heat of oxygen adsorption at the surface of potassium-modified iron oxide samples vs. potassium content. Degree of surface reduction –2% of monolayer.

any case, micro-admixtures of alkaline metal cations in cobalt and chromium oxides are known to decrease the oxides activity in CO oxidation [121,176]. With chromium oxide, the alkaline admixtures can also stabilize the surface phase of alkaline metal chromate, which provides a stronger oxygen bonding and less reactivity in comparison to those of chromate groups on pure chromium oxide [176,234,235].

Alkaline earth cations and Me^{3+} cations like aluminum, whose radii are comparable to those of cobalt cations, are relatively easy dissolved in Co_3O_4 forming a mixed spinel, in which Co^{2+} cations may occupy tetrahedra, while Me^{3+} cations occupy octahedra [235,236]. Since reactive terminal oxygen on the (100) and (110) faces is bound to both tetra- and octa-coordinated cobalt cations, their substitution by non-reactive species bound to admixed cations decreases the oxide NO selectivity. In agreement with this model, the NO selectivity of Co_3O_4 modified by such admixtures depends only weakly on the admixture content (Fig. 5). At the same concentration, more bulky La^{3+} and Y^{3+} cations decrease the NO selectivity of cobalt oxide sharper as compared with Al^{3+} cations, most likely due to their higher tendency to segregation. According to [237,238], large promoting cations introduced into the cobalt oxide increase the sample dispersion as well as concentration of microstrains. Hence, at least in part, the observed NO selectivity decline for cobalt oxide promoted by large cations, may be assigned to generation of extended defects and associated weakly bound surface oxygen species localized on cluster centers.

Alkaline-earth and aluminum cations introduced in hematite produce a less strong effect on the reaction selectivity towards NO than in the case of cobalt oxide. The reason is that the hematite structure contains a lot of vacant octahedra. According to [239,240], the admixed cations of different charges (2+, 4+) are preferably located as chains in the regular and interstitial positions, while some neighboring Fe^{3+} cations are shifted into interstices. Bulky rare-earth cations can segregate as microinclusions or even X-ray detected separate phases, such as perovskites LnFeO_3 [92]. As a rule, the rare-earth admixtures increase the specific surface area of modified hematite samples most likely owing to suppression of sintering.

Introduction of alumina into the iron oxide produces a solid solution thus changing the lattice parameters

[241]. The X-ray energy-dispersive analysis [179] revealed that aluminum cations prefer to segregate on the extended defects (twins etc.) in the bulk of iron oxide, thus decreasing their surface concentration. The segregation of aluminum cations near the extended defects in transition metal oxides supported on alumina suppresses the oxides reduction by hydrogen [242–244] and CO [128], first of all, due to a stronger bonding of oxygen located in vicinity of these defects. Since the hematite reduction to magnetite proceeds topochemically, the nuclei of magnetite forming near the outlets of extended defects [245], the alumina addition improves stability of hematite-based oxide catalysts in the reaction of high-pressure ammonium oxidation [7].

On hematite, the maximum selectivity towards NO either decreases, when aluminum or alkaline earth cations are introduced, or increases, when cerium or lanthanum cations are added [7]. In the latter case, the optimum temperature of the catalyst operation increases indicating a stronger bonding of oxygen with the surface.

For chromium oxide, which, as hematite, has a corundum-type structure, the same admixtures impose a far stronger effect on the selectivity towards NO (Figs. 9 and 10). Moreover, chromium oxide and hematite show the opposite dependencies of NO yield on the radius of promoter cation. This distinction, which earlier found no explanation [7], can result from the difference in the nature of oxygen species responsible for selective ammonia oxidation to nitrogen oxide, and, in particular, from the specific features of chromate groups stabilized on the Cr_2O_3 surface. In accordance with the rules of the acid-base interaction, basic cations, appearing on the chromia surface, produce salt-like surface chromates phases, where the oxygen bonding becomes stronger. The more basic is cation, the stronger is its interaction with the chromate anion, and, hence, the chromium-oxygen bond. The basicity of cation increases, when its radius increases, charge being the same, as well as when the cation charge decreases, radius being the same. This fact explains the observed features.

Another interesting effect, not explained earlier, is that for mixed oxide systems $\text{Co}_3\text{O}_4\text{--Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$, NO selectivity is lower than for pure oxides. This effect was observed for a rather broad range of temperatures (700–850°C) [230]. The decline of NO selectivity for cobalt and iron oxides due

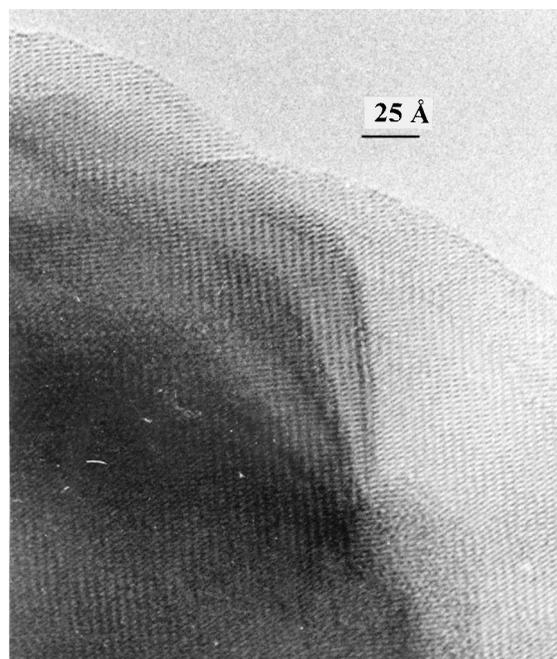
to chromium addition can be ascribed to appearance of the surface chromate phase, which strengthens the oxygen bonding. However, such a simple explanation does not work when Fe and Co cations are introduced into the chromium oxide. In this case, admixed cations with a lower strength of oxygen bonding are expected to increase the NO selectivity, at least, at temperatures close to optimum ones for iron and cobalt oxides, which does not take place. The most plausible explanation stems from the fact that even small admixtures of guest cations affect the decomposition of metal salts thus increasing the density of extended defects-twins and stacking faults [246,247]. Thus, cobalt oxide nuclei formed in the course of decomposition of the cobalt nitrate solution with a small admixture of the iron nitrate, were shown to be surface-enriched by iron [178]. Stacking of such nuclei produces a stacking fault with the local hexagonal sequence of the oxygen layers typical for hematite (a corundum-like structure) but not spinel structure. The admixed cations present in the vicinity of extended defects stabilize these defects by preventing their annealing on calcination at elevated temperatures.

Even in the case when the host and guest cations have the same charge and provide the same type of the oxide structure, this mechanism of defects generation continues to operate, as shown for the chromium oxide with a small (1%) admixture of Fe cations. In this case, stacking faults in the prismatic planes dominate (Fig. 12) [124]. At the same temperatures of calcination, samples modified with iron cations contain more defects than pure samples (Fig. 13).

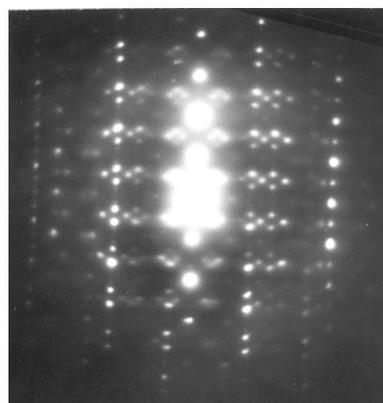
From the molecular point of view, the increase of the density of extended defects implies the increase of the concentration of surface centers where weakly bound oxygen is adsorbed (*vide supra*). At operating temperatures of ammonia oxidation, such an oxygen is removed from these sites, making them coordinatively unsaturated and capable to stabilize the intermediate products of ammonia oxidation. As the result, the route of ammonia oxidation to molecular nitrogen becomes more efficient.

3.4. Systems based on complex oxides of perovskite structure

Complex oxides with a perovskite structure show a high selectivity towards NO at operating tempera-



(a)



(b)

Fig. 12. High resolution TEM image of the chromium oxide particles prepared by thermal decomposition of nitrate solution (a) and corresponding microdiffraction in the (112^-0) zone (b) [124].

tures around 900°C, even when composing transition metal oxides such as copper and nickel oxides are not selective by itself (Table 3).

Obviously, manganese, iron and cobalt-containing perovskites, as compared with pure transition metal oxides, show a higher maximum selectivity at higher temperatures. In contrary, in the reactions of deep oxidation of hydrocarbons and CO, cobalt, nickel

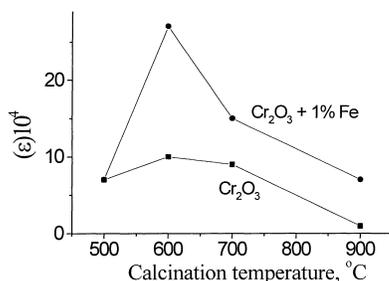


Fig. 13. Density of microstrains in pure and promoted samples of chromium oxide vs. calcination temperature.

and copper-containing perovskites exhibit a far lower activity than individual oxides [196]. This fact was explained by a lower probability for cluster active sites to form in the perovskite matrix (vide supra). Hence, the beneficial effect of perovskite structure on the catalytic properties of transition metal cations in the high temperature ammonia oxidation into NO appears to stem from stabilization of these cations in the octahedral coordination. This provides the optimum strength of the terminal oxygen bonding on the (100) faces, thus ensuring a high NO selectivity.

Table 3
Selectivity of some perovskite systems towards NO

Basic system, optimum composition	NO yield, % (at T, °C)	Reference
La _{1-x} Sr _x NiO _{3-λ}		
LaNiO _{2.92}	97.3 (700)	[106]
La _{1-x} Ce _x Co _{1-y} B _y O _{3+δ} (B=V, Cu, Fe, Ni, W)		
La _{0.8} Ce _{0.2} Co _{0.9} Fe _{0.1} O _{3+δ}	99.5 (700)	[110]
La _{1-1.33x} Th _x NiO _{3-λ}		
La _{0.6} Th _{0.3} NiO _{2.95}	98.7 (700)	[113]
Ca _x La _{1-x} MnO _{3+δ}		
Ca _{0.9} La _{0.1} MnO _{2.97}	97.8 (800)	[113]
Sr _x La _{1-x} CoO _{3+δ}		
Sr _{0.09} La _{0.91} CoO _{2.986}	98.8 (700)	[113]
Sr _x La _{1-x} FeO _{3+δ}		
Sr _{0.4} La _{0.6} FeO _{2.954}	96.9 (800)	[113]
(LaCe)MnO ₃ ^a	93.8 (900)	[13]
CaMnO ₃ ^a	88.2 (920)	[13]
Ca ₂ Fe ₂ O ₅ ^a	84.7 (940)	[13]
(LaCe)FeO ₃ ^a	86.9 (920)	[13]
(DyY)MnO ₃ ^a	86.8 (925)	[13]
(DyY)FeO ₃ ^a	83.5 (920)	[13]
(DyY)Mn _{0.3} Fe _{0.7} O ₃ ^a	83.1 (920)	[13]
	60 (900)	

^a Samples contain up to 20% of alumina binder.

Mixed oxides with a K₂NiF₄ structure such as La₂CoO₄, La₂CuO₄, La₂NiO₄, which are composed of alternating perovskite (ABO₃) and rock salt (AO) layers, are also rather selective [248,249]. Selective enough are structures like calcium manganite, strontium cobaltite (defect perovskite) and calcium ferrite (braunmillerite) (see Table 3). A partial substitution of one transition metal cation for another (cobalt for manganese, iron for cobalt, etc.) also improves NO selectivity [103–105].

A very attractive feature of perovskites is that they meet practice demands to retain their structure, composition and catalytic properties at the operating temperatures of industrial ammonia oxidation process [113].

In general, perovskites or perovskite-like systems are selective even in the case when their surface contains no weakly bound forms of oxygen desorbing below 700°C [113,250]. Nevertheless, a partial substitution of lanthanum by other cations, producing weakly bound oxygen species desorbing within 200–600°C range, is usually accompanied by a small increase of selectivity, at least to some degree of substitution dependent upon the nature of perovskite [113]. However, it does not prove that a weakly bound oxygen is responsible for ammonia oxidation into NO on perovskite systems. Thus, for La_{1-x}Sr_xCoO₃, the amount of strongly bound oxygen species desorbing at 800°C increases with the strontium content, correlating with NO selectivity as well [212]. Accompanying increase of the surface concentration of cobalt [199] implies these oxygen species are bound with cobalt cations.

In some cases, experiment shows the NO selectivity of perovskites to change contrariwise to the density of extended defects (microstrains and inter-grain boundaries) [107,113]. New phases evolving at some substitution degree (mixed oxides of braunmillerite structure, transition metal oxides, promoting oxides, lanthanum carbonates) unambiguously cause the decrease of NO selectivity [106,113]. As a rule, heterophase oxide systems have a well developed dislocation network at the interfaces. This agrees well with the assumption that in the oxide systems extended defects decrease the NO selectivity in ammonia oxidation (vide supra).

For ammonia oxidation to nitrogen oxide on perovskites, the ammonia molecule is assumed to

be activated on the surface Me^{3+} cations then interacting with the ion-radical oxygen species adsorbed on vacancies [106,107,113]. Ammonia may also directly interact with activated oxygen species [113]. Although such stages may participate in the routes of NO generation, they hardly are dominating, since a high NO selectivity was obtained for unpromoted perovskites as well.

In lanthanum ferrites and cobaltites, at some degree of La substitution, the braunmillerite structure fragments appear [205,214], in which transition metal cations are in the tetrahedral coordination. This provides the terminal oxygen species more strongly bound to those cations, while bonding of ion-radical oxygen species becomes stronger as well [113]. As the result, calcium substituted ferrites and lanthanum cobaltites decrease their NO selectivity estimated at the same temperature [113]. This model is supported by the fact that calcium substituted lanthanum manganite, in which there is no change of transition metal cation coordination, gains in selectivity until a defect calcium manganite phase starts to form [113].

4. Industrial oxide catalysts for ammonia oxidation to nitrogen oxides and technologies for their production

4.1. Catalyst compositions

Search for oxide catalysts for ammonia oxidation started at the beginning of the 20th century. Thus, in 1902 Ostwald patented catalysts based on transition metal oxides. During 1914–1916, for NO production, a German chemical company BASF used the catalyst containing iron oxide doped with oxides of bismuth, chromium, manganese, uranium. At 750–800°C, the NO yield on this catalyst was 92–94% at an ammonia content 7.5%.

In the 1960s, intensive studies resulted in development of some catalyst compositions, which operated in industry. Research attention was focused on the cobalt oxide systems, since they allowed operation without platinum gauzes [83,251].

Hedler's catalyst [62] is cobalt oxide stabilized by various admixtures. It allowed a 93–94% NO yield and worked for 1 year.

African Explosives [252,253] patented a catalyst based on cobalt oxide promoted with scandium, yttrium and/or other rare earth metals, which at 800–850°C and 1000 m³/m² h provided NO yield mounting to 95–96%.

The ICI catalyst [83] consists of cobalt oxide supported on magnesium–aluminum spinel with specific surface 350 m²/g. This catalyst works at 700–1000°C and provides NO yields close to that obtained on industrial platinum catalysts. Note, however, that according to [94], a large surface and developed pore structure of cobalt oxide catalysts cause the NO selectivity to decrease.

The Stamicarbon catalyst [83] may work at temperatures not higher than 850°C at a volume gas flow rate of up to 100 000 h⁻¹, ammonia content mounting to 10%.

Some data on the oxide catalyst compositions suggested in the recent years are given in Table 4.

If only oxide catalysts are used, the contact time usually ranges from 10⁻² to 10⁻¹ s, which is essentially longer than on platinum gauzes. Moreover, the oxide catalysts selectivity towards NO is always lower than that of Pt gauzes, which is ascribed to a larger chemical sorption capacity of oxides [7]. In our opinion, it may also be caused by a larger impact of the homogeneous reaction between ammonia and NO.

With regard to industrial process economics, which is primary determined by the nitric acid yield and possibility to use the same reactors without serious rewamping, it is better to use oxide catalyst together with a fewer number of platinum gauzes [7].

The possibility to use two catalysts beds for ammonia oxidation to nitrogen oxides was first mentioned in patent [252,253]. In the 1950s, GIAP designed the iron–chromium oxide catalyst KN-2 for the second bed of ammonia oxidation system and determined operating parameters for the two-bed system for ammonia oxidation (single Pt gauze+oxide catalyst bed) under atmospheric pressure [12].

Later some patents suggested ammonia oxidation by oxygen containing gas over the catalyst comprised by platinum (or its alloy) gauzes with granulated oxide catalysts loaded over gauzes (iron oxide, manganese oxide, bismuth oxide [254], cobalt oxide [255], catalysts containing iron oxide, chromium oxide, bismuth oxide, lead oxides and other promoters [256,257], catalysts containing iron oxide, cobalt oxide nickel

Table 4
Composition and NO selectivity of some oxide catalysts

Optimum composition	NO yield, % (at T , °C)	Reference
LaNiO ₃	99 (663)	US Patent 4812300
La _{0.75} Sr _{0.21} MnO ₃	98 (663)	
MeO/support Me=Co, Fe, Cr, Mn, Bi	55 (650)	E Patent 0562567 A1
MeO/support Me=Co, Pt	95 (760–800)	US Patent 5242882
α -Fe ₂ O ₃	91–98 (620–720)	DE Patent 3126675 A1
α -Fe ₂ O ₃ +Ga ₂ O ₃ (Ce ₂ O ₃)+1–2 Pt gauzes	92–97	SU Patent 856540; 1148151
α -Fe ₂ O ₃ +3–4 Pt gauzes	95.5 (900–950)	SU Patent 1153981 A
Mixed oxides of Y, Be, Ba, Cu	92 (900–950)	SU Patent 1759446 A1
α -Fe ₂ O ₃ , Cr ₂ O ₃	98 (800)	SU Patent 300057
α -Fe ₂ O ₃ +ZrO ₂	94.3 (850)	SU Patent 805514
α -Fe ₂ O ₃ , Al ₂ O ₃ , MgO+1 Pt gauze	98.1 (900–950)	SU Patent 1676141 A1
α -Fe ₂ O ₃ , Al ₂ O ₃ , MgO+1 Pt gauze	98 (850–920)	SU Patent 771958
Co ₃ O ₄ +alumina (5–15%), thoria, ceria, zinc and calcium oxides pellets or extrudates	Up to 97 (850–900)	SU Patent 325761; US Patent 3962138, 4036935
Co ₃ O ₄ +0.1–10% Li ₂ O pellets, grains, monoliths	97 (850–900)	US patent 3931391
Co ₃ O ₄ or Bi ₂ O ₃ promoted by rare earth element or thorium, may also contain at least one of oxides of Mn, Fe, Mg, Cr or Nb	97 (850–900)	US patent 3985681
α -Fe ₂ O ₃ -MAl ₂ O ₄ -Bi ₂ O ₃ -Ce ₂ O ₃ (M=Mg, Mn, Ca, Sr, Ba)	95–97 (850–900)	US patent 5336656
CoO _x , Pt/support	95–97 (850–900)	RU Patent 1383563
α -Fe ₂ O ₃	95–97 (850–900)	RU Patent 1541833
α -Fe ₂ O ₃ , Al ₂ O ₃ , MgO	95–97 (850–900)	RU Patent 1541833
Mixed Fe ₂ O ₃ , Al ₂ O ₃ , Cr ₂ O ₃ +Pt gauze	97.6–98.2 (795–810), 1 atm	Bu Patent 31092
α -Fe ₂ O ₃		RU Patent 1626495

oxide [258]). For these systems, the nitrogen oxide yield at atmospheric pressure was within 92–98%. Some other compositions are listed in Table 4. Note that the two-bed system is used only in NIS and in other countries where the ammonia oxidation technology developed in the USSR is used (Poland, Bulgaria, etc.) [7,88,93,100].

When a non-platinum catalyst is installed downstream from the platinum gauzes, its operating conditions differ significantly from those experienced if it is used alone. The gas mixture exiting the platinum gauzes contains NO, water, less oxygen (5–9%) and ammonia (1–2%). As a result, the demand towards catalyst selectivity increases (that is to minimize the occurrence of reaction between NO and ammonia on the catalyst surface), but the demand in activity is far less severe, since platinum gauzes make the process auto-thermal, and not more than 15% of the inlet ammonia concentration comes to the oxide catalyst bed inlet.

The thermal stability of the second bed catalysts is of key importance. For catalyst working under the atmospheric pressure it means temperatures around

800°C. Under 7–10 atm, the catalyst must resist heating up to 900–950°C. As a result, the oxide iron–chromium second bed catalyst, which provides 6 years stable operation under the atmospheric pressure [7], is quickly deactivated on operation under elevated pressures due to its reduction to magnetite, wustite and even metal iron [230].

This obstacle predetermines requirements towards the composition of oxide catalysts operated under different pressures. For elevated pressures, among the most selective are iron–aluminum oxide catalysts promoted by other oxides (ceria, vanadia, etc.) [7,83]. Their selectivity is quite stable in high pressure converters, though on operation, they lose their specific surface from 10–25 to 1 m²/g, and their pore structure changes (small pores disappear and large pores appear) [241]. Such changes may reduce the mechanical strength of the catalyst granules regarding their possible attrition and weight loss [259]. Chemically unbound highly dispersed corundum segregating on the surface of some iron–aluminum oxide catalysts may increase the dust generation thus reducing the catalyst selectivity [260].

4.2. Catalyst synthesis methods

Though modified iron oxides prepared from mixed nitrates solutions [261,262] are mostly selective, nitrates shortage and high prices stimulated a search for alternative raw materials and synthesis methods. Good results were obtained by the acid kneading of commercially available iron oxide (e.g., semi-product for the middle-temperature water gas shift iron–chromium oxide catalyst) with alumina and other additives. The mechanical activation of this paste is used to improve the interaction between the components [263–269]. The paste is either extruded as cylinders or tubes or decomposed to produce powders then pressed and sintered [270].

The dispersed powders of perovskites are usually produced via such routes as sintering of the oxides mixture, co-precipitation of mixed hydroxides, oxalates or other non-soluble compounds followed by calcination [271]; spray-drying or arc plasma thermolysis of mixed nitrates solution [181,195,196].

Mechanochemical activation of solid reagents in high power ball mills is also used for perovskites synthesis [193,196–198]. Unlike traditional ceramic procedures, sintering of mixed activated reagents at reasonably low (600–800°C) temperatures rapidly produces highly dispersed monophase powders of complex oxides. The rate of solids interaction during activation and/or subsequent annealing was shown to be proportional to the difference of their acid–base properties determined by the cation charge and anionic composition [272]. The particles of perovskites thus obtained are spherical or almost spherical. Since the single phase composition and rounded particle shape are of critical importance for perovskites exhibiting high NO selectivity, this synthesis technology seems to be rather promising for production of catalysts to be used for ammonia oxidation to nitrogen oxides. The specific surface area of complex oxides produced via the mechanochemical method is 10–20 m²/g, whereas samples obtained through the ceramic technology have the specific surface area values not exceeding 1 m²/g.

4.3. Honeycomb oxide catalysts for the second bed of ammonia oxidation to nitrogen oxides

In USSR in 1970s, the catalyst based on iron oxides and designed for the second bed of ammonia

oxidation to NO was successfully operated in high pressure (up to 10 atm) converters. A bed of tablets (5–6 mm × 5–6 mm) or extrudates (15 mm long, 5–6 mm in diameter) was loaded into special baskets.

However, granulated oxide catalyst met some operating problems, since it sometimes contained dust, and its loading required a specially designed basket. The pressure drop in the granular catalyst bed was too large (up to 1000 mm of water). Moreover, the granular bed is not uniform in thickness providing by-pass for the gas flow and a non-uniform gas flow rate within itself as well as in platinum gauzes [13].

All these problems stimulated development of the two-bed catalytic system for ammonia oxidation using a honeycomb monolith oxide catalyst. The honeycomb catalyst bed has the following advantages over the bed of granular catalyst:

1. no special basket is required for the bed;
2. a high mechanical strength, resistance to thermal shocks, the absence of dust provide the uniform filtering of the ammonia–air flow through the catalyst bed;
3. a uniform gas permeability of the honeycomb catalyst equalizes the gas flow through the platinum gauzes;
4. the honeycomb catalyst bed has a low pressure drop.

The technology for honeycomb oxide ammonia oxidation catalysts was developed in the 1990s [99,196–198,210,224–226,273–277]. It is based on the wet kneading procedure allowing a waste-less catalyst production [278,279]. The active component powder is first mixed with organic and inorganic additives and a binder. Then water and electrolytes are added to produce pastes, which then are extruded through proprietary extruding heads (spinnerets). Then monoliths are dried and calcined.

Reinforcing alumina–silica fibers are added into the pastes on mixing to improve the catalyst resistance to thermal shocks. Aluminum oxynitrate or pseudo-boehmite serves as the aluminum binder also allowing alumina introduction into the iron oxide to improve its thermal stability. For a better rheology of pastes and pore structure, various surfactants were added such as ethylene glycol, polyethylene oxide, carboxymethyl cellulose, polyvinyl alcohol, glycerin, etc.

Optimized regimes of drying in controlled humidity conditions and calcination up to 950–1000°C suppress

cracking and provide monoliths with good mechanical strength.

Optimum composition monoliths with active components based on perovskites and iron oxide are 75 mm × 75 mm in cross-section and 50–100 mm long with desired channel size and wall thickness. After calcination at 900°C, the monoliths have the following parameters: specific surface 30 m²/g, integral pore volume up to 0.3 cm³/g, crushing strength 8–10 MPa. The best catalysts survive up to 100 thermal cycles from room temperature to 800°C without cracking.

Pilot-industrial batches of the honeycomb oxide catalysts for the second bed of ammonia oxidation are produced using the facilities of Boreskov Institute of Catalysis [13].

5. Two-bed ammonia oxidation: process peculiarities

Detailed studies regarding the two-bed ammonia oxidation with granulated catalyst [4,12,81,280,281] allowed the estimation of main process parameters under various operation conditions (load and pressure). These parameters were then used in attempts to optimize the catalyst loading and bed geometry. However, in fact, all parameters for the two-bed systems with granulated oxide catalyst bed were obtained empirically with no physical model for the process description.

A high pressure drop within the oxide catalyst bed stimulated its geometric optimization. Converters working under 7.16 atm with platinum gauzes and the oxide catalyst disposed on a cone or a semi-spherical surface show a several fold lower pressure drop at the same yield of nitrogen oxide. Moreover, the platinum loading is reduced by 2–2.5 kg, and platinum losses are by 50% lower [281].

With the honeycomb oxide catalyst, all technological parameters (such as the number of platinum gauzes, optimum configuration and size of honeycomb catalyst channels, the bed height and number of beds, the distance between the beds) were determined using the mathematical modeling [282].

A two-phase model of the ammonia oxidation process on the platinum gauzes and honeycomb catalyst was developed for this purpose. According to the model, the process is limited by the mass transfer

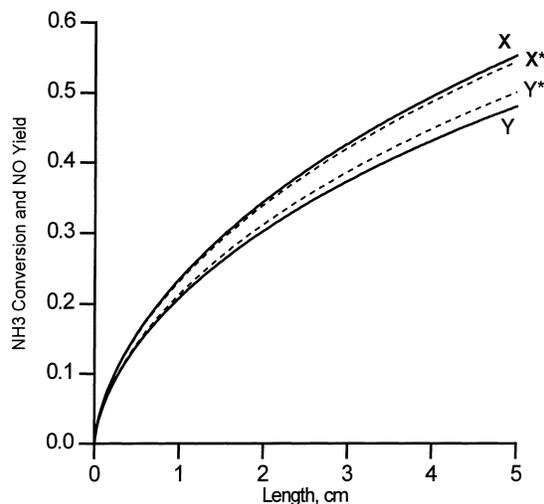


Fig. 14. Calculated ammonia conversion and NO yield along the monolith length with regard to inlet ammonia concentration accounting for (X, Y) and without accounting for (X*, Y*) the homogeneous reaction. Process parameters: pressure 0.7 MPa, superficial gas velocity 7 m/s, inlet temperature 915°C. Monolith characteristics: square channels of 2 mm, wall thickness 1 mm.

between the gas phase and catalysts. The process selectivity towards NO is provided by ammonia oxidation to NO and N₂ on the catalyst surface, and by the side homogeneous reaction of NO and ammonia yielding N₂ thus decreasing the process efficiency.

Fig. 14 shows how ammonia conversion and NO yield change along the monolith length. At the channel inlet, the ammonia oxidation rate is high due to very fast mass transfer, and conversion along the monolith quickly increases. As the gas velocity profile stabilizes along the channel, the mass transfer rate decreases, and the homogeneous reaction contribution increases. The homogeneous reaction rate is far lower than that of the desired reaction, but it has a great effect on a choice of the monolith channel configuration and second bed geometry: channel size, wall thickness, length and number of monolith layers and their mutual disposition. These parameters should be optimized with a restriction imposed by a permissible pressure drop.

The pressure drop of the second bed is an important factor effecting the efficiency of the whole reactor. Modeling results demonstrate that honeycomb monoliths used as the second bed perform not only as catalysts. Owing to their regular structure, the

Table 5
Operation parameters of two-bed system working under 7.3 atm [13]

Month	NH ₃ conversion (%)	NH ₃ /air ratio (%)	T (°C)	NH ₃ load (nm ³ /h)	HNO ₃ (t)	Capacity (HNO ₃ t/h)	Run (h)
March	94.10	9.36	866	6000	8406	14.8	568
April	94.07	9.15	866	5800	8114	13.5	601
May	93.64	9.15	868	5700	9299	13.0	715
June	93.77	9.08	865	5650	9819	14.4	684
July	92.95	9.13	862	5550	9145	12.9	708

gas flow distribution inside the gauzes pad becomes more uniform. This results in more uniform and lower mechanical and chemical losses of platinum, thus improving the gauzes efficiency and increasing their operation life.

Computational fluid dynamics study was performed to investigate the effect of monolith catalyst geometry and disposition [283]. The results demonstrated that the optimal distance between two catalyst beds can be defined.

6. Industrial operation of the two-bed catalytic system

A long term experience in industrial operation of the two-bed catalytic system with granulated catalysts is summarized in [4,7,13,28].

Since 1985 till 1990, in two-bed systems, granulated iron–aluminum oxide catalyst was used in UKL-7 converters at seven nitric acid plants. The number of UKL converters varied from 7 to 20 depending on the catalyst and baskets supply. If all design and operation requirements were strictly followed, the NO yield was the same as in the case of the standard loading of platinum gauzes. The platinum metal loading was thus reduced by 20–25%, and the irreversible platinum losses were cut for 15% [7,13].

Two pilot batches of the honeycomb oxide catalyst were produced in 1995 and loaded into the UKL-7 converters at JSC ‘Azot’ in Cherepovets (Russia) and JSC ‘Azot’ in Berezniki (Russia). The catalyst was represented by rectangular prisms 50 mm high with the square section 70 mm×70 mm. The catalyst (100 L) was loaded in a single layer across the converter on a Nichrome screen covering a support grid. The catalyst was covered by another Nichrome screen, and then pad of one used and nine new gauzes made of

GIAP5 alloy [7] were installed. The average nitrogen oxides yield was 94%, and no ammonia slip was observed.

The full-scale resource testing of the honeycomb catalyst was performed in 1996 in Berezniki. Table 5 shows the averaged operation data of thus arranged two-bed system. During the normal life time (3000 h) of gauzes, the ammonia conversion stays at the original level.

The platinum metal losses attained 0.1237 g/t of acid at a norm of 0.157 g, while neither activity nor mechanical properties of the monolith catalyst changed. Loaded in March 1996, the honeycomb catalyst worked without reloading for 1.5 years [13].

At present, the honeycomb catalyst is successfully operated in 10 high pressure converters in Berezniki, Cherepovets, Nevinnomyssk, Novgorod and other places in Russia.

7. Comments and future plans

Process economics improvement lies in the further reduction of the platinum metal weight via gauzes replacement by the honeycomb oxide catalyst. Keeping a high NO yields intact demands catalyst composition optimization and better geometry of monoliths. Though analysis of oxygen bonding to the oxide catalyst surface appears to be rather fruitful for experimental data systematization, the energy spectrum of the surface oxygen as a function of the surface morphology and defect structure is not yet studied enough. There is a lack of data on reaction kinetics under the industrial conditions. Though all these problems meet severe experimental difficulties, advanced methods designed to study reactions at millisecond contact times may provide a breakthrough in understanding the reaction mechanism.

Modified iron oxides and perovskites seems to be the most promising for the practical application. Further, optimization of their chemical composition and synthesis procedure will improve their selectivity and thermal stability.

Engineering problems relate to a more optimized arrangement of the two-bed system regarding monoliths (configuration and spatial disposition) as well as gauzes pack (their number and parameters).

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