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DEVELOPMENT OF CATALYSTS FOR NEUTRALIZING TOXIC NITROGEN OXIDES IN GAS EMISSIONS OF NITROGEN ACID PRODUCTION



Introduction. Reducing nitrogen oxides (NO_x) emissions from industrial plant is one of the most important environmental issues. Selective catalytic reduction (SCR) of NO_x is the main way to neutralize NO_x emissions, the effectiveness of which is determined by the activity of catalysts that need to be improved.

Problem Statement. SCR NO_x with ammonia using aluminum-vanadic catalyst (AVC-10) is the main method for neutralizing toxic NO_x in gas emissions from nitrogen industry plants. However, this catalyst contains toxic vanadium and does not meet present-day requirements for degree of purification from NO_x and decomposition of residual NH_3 . Therefore, it is very important to develop and to implement a technology for manufacturing vanadium-free catalysts to neutralize NO_x in gas emissions and for their further use in industry, which will help improve the environment condition.

Purpose. To develop and to implement technology fundamentals for producing a highly active aluminum-copper-zinc catalyst for SCR NO_x with ammonia to neutralize NO_x emissions in nitric acid production.

Materials and Methods. Aluminum-copper-zinc catalysts are prepared by impregnating $\gamma\text{-Al}_2\text{O}_3$ granules (grade A-1) with solutions of copper and zinc nitrates. The activity of catalysts is determined in a flow-bed reactor equipped with a gas analyzer.

Results. A technology for preparation of nanophase aluminum-copper-zinc catalysts with a crust structure of the active layer for selective reduction of nitrogen oxides in gas emissions of nitric acid production has been developed. The technology ensures the localization of copper oxide in the surface layer of carrier granules, which causes a high activity of catalysts based on this technology as compared with conventional catalysts.

Conclusions. The technological process of designed catalyst production has been worked out under conditions of Katalizator Additional Liability Company, Kamianske (Dnipro Oblast). Tests carried out using a pilot plant at operating unit for light nitric acid production at Ostchem have showed that the designed catalyst ensures reducing the amount of residual nitrogen oxides in purified gas down to 0.001–0.002 vol. % and removing almost all ammonia from the gas.

Keywords: nitrogen oxides, selective catalytic reduction, oxide aluminum-copper-zinc-containing catalyst, and copper oxide.

Reducing the atmospheric pollution with toxic emissions from industry and vehicles remains one of the most important environmental protection problems, as evidenced by the introduction of stringent requirements for emissions in the EU Member States and the European Economic Area (EEA). New atmospheric air pollu-

tion standards (EU Commission Implementing Decision 2017/1442) that have significantly tightened the harmful substance emission restraints should be implemented by 2021. To integrate into the European community, Ukraine shall tighten the requirements for toxic gas emissions into the atmosphere at the legislative level. The development of new generation domestic catalytic systems will ensure the necessary purification of in-

dustrial exhaust gases, harmonize them with the European standards and create knowledge-intensive production.

Nitric acid production is a multi-tonnage process of chemical industry, which encompasses the ammonia oxidation with air on a platinum catalyst to NO and its subsequent oxidation to NO₂ while cooling. The resulting technological gas is adsorbed with water in an oxygen-containing medium with the formation of nitric acid. Since one of the three NO₂ molecules involved in the formation of nitric acid is again reduced to NO, it is difficult to achieve a complete transformation of nitrogen oxides into acid, which results in the necessity to neutralize residual nitrogen oxides [1].

There are various techniques for purifying nitrous gases from nitrogen oxides, but in the industry, the widespread ones are absorption and catalytic methods. The absorption methods are based on the interaction of nitrogen oxides with aqueous solutions of alkalis. The formed nitrous oxide salts are used in industry and agriculture. The disadvantage of these methods is a low degree of gas purification, which does not meet the sanitary norms for emissions of nitrogen oxides into the atmosphere, the need for using large production equipment, as well as additional technological and transportation costs for processing the resulting solutions. Therefore, mainly the catalytic methods are used neutralizing nitrogen oxides on industrial scale. In practice, it is advisable to use reducing gases and catalysts with a lower ignition temperature. This enables to increase the oxygen content in the initial gas mixture and to carry out the process in one stage. The highest degree of reduction of nitrogen oxides to nitrogen is achieved in the absence of oxygen in the gas mixture reacting with reducing agent.

Selective catalytic reduction (SCR) of nitrogen oxides in the case of a high amount of excessive oxygen with the use of nitrogen-containing compounds (NH₃, (NH₂)₂CO) as reducing agents is an efficient and environmentally acceptable way of abating NO_x in gas emissions from nitrogen plants, trucks, and diesel-electric aggregates.

The peculiarity of this reaction is the addition of ammonia in amount that is close to stoichiometric value and sufficient for complete conversion of NO_x. The SCR process has been used for several decades to reduce the content of nitrogen oxides in emissions from industrial and power engineering plants [1].

Currently, in Ukraine, foreign-made block catalysts – the oxide (VWAl, VWTi, CeWTi, Mn-WTi) or the zeolite (copper, iron or cobalt-containing zeolites deposited on a cordierite matrix) ones – are used to reduce nitrogen oxides in diesel exhaust fumes [2]. The technology for producing these catalysts is the manufacturer intellectual property that has a significant share in the added value of their products.

Granulated aluminum-vanadium catalyst (AVC-10) that was designed and introduced into practice in the USSR has been used on industrial scale for purifying the emissions from nitric acid production by the SCR method with ammonia. Its disadvantage is the use of highly toxic, not easily available, and expensive vanadium compounds and insufficient catalytic activity for decomposing/combusting residual ammonia.

The world scientific community has been doing research to replace vanadium as main component of the catalysts for SCR of NO_x with ammonia in order to convert NO_x into other less toxic substances. The use of metal-containing zeolites, including, Cu, Fe-, and Co-VEA, is of particular interest [1, 3]. The activity, selectivity, and thermal stability of Fe- and Cu-exchange zeolites as commercial catalysts for neutralizing NO_x emissions of diesel engines have been widely studied [4]. However, the zeolite catalysts have both advantages (high activity, selectivity) and disadvantages (high cost, no production of VEA zeolite in Ukraine, peculiarities of the formation of massive catalysts and complexity of their use in the existing industrial plants) that have prevented their use at domestic enterprises.

Combinations of cerium, tungsten, iron, manganese, and other oxides are promising for practical application [4]. The cerium-based catalysts

can be an alternative to the conventional V_2O_5 - WO_3 (MoO_3)/ TiO_2 catalysts for purifying the emissions from stationary power stations due to their non-toxicity and high oxygen storage capacity in SCR of NO_x with ammonia [5, 6]. Among various cerium-based composite oxide catalysts, CeO_2 - WO_3 and CeO_2 - MoO_3 have better properties, including a high activity and selectivity (about 100% for N_2), a wider working temperature range (250–400 °C), and a higher resistance to the action of H_2O and SO_2 [7].

An important task is also to replace the high-temperature reduction of nitrogen oxides with methane, based on the palladium-containing catalyst APC-2 (that has been used so far for purifying the exhaust gases emitted by heavy-tonnage aggregates AK-72 at domestic nitric acid production enterprises) by the SCR with ammonia. In UKL-7 aggregates, nitrous oxides are abated by the selective reduction with ammonia, based on a vanadium-containing catalyst (AVC-10) (vanadium oxide: 12–15 wt%, manganese oxide on γ - Al_2O_3 : 1.0%). However, inasmuch as the AVC-10 is toxic and exhaust gas purification is inadequate, it should be replaced by an environmentally safe, cheaper and more effective catalyst.

Katalizator, ALC, has proposed to use an aluminum-copper-zinc (ACZ) catalyst that does not contain any highly toxic components, in the current production. However, a high degree of reduction of nitrogen oxides and oxidation of residual ammonia can be achieved only in the case of a high content of copper oxide (about 14 wt%), which significantly affects its cost and, consequently, competitiveness in the market.

The purpose of this research is to develop and to implement the technological principles for the production of CuO - ZnO/Al_2O_3 catalysts for the selective reduction of nitrogen oxides with ammonia, which are characterized by a higher activity, selectivity, and a lower content of high-value components, as compared with domestic and foreign analogs.

The aluminum-copper-zinc catalysts are prepared by impregnating aluminum oxide granules

γ - Al_2O_3 (grade A-1) with solutions of copper and zinc nitrates, based on the moisture content. The modified catalysts are made using solutions of iron, manganese, cerium nitrates or zirconium oxychloride. The crust-type ACZ catalysts are prepared by impregnating aluminum oxide granules with the mentioned solutions adding ammonia in amount required for hydrolyzing salts only in the near-surface layer of the carrier. The samples are kept at a room temperature, dried at 110–120 °C, and treated with heat at 400–750 °C. The content of the components in the catalysts is given in terms of oxides.

The phase composition of catalysts samples is determined by X-ray diffraction analysis (XRD). The diffraction patterns are obtained using *BRUKER AXS GmbH* D8 ADVANCE (Germany) diffractometer in monochromatic (nickel filtered) $CuK\alpha$ -radiation.

The microanalysis (semi-quantitative local determination of the chemical composition at points located at a 10 μm diameter circle) and mapping of the distribution of certain elements of the sample surface are made by the energy-dispersive X-ray spectroscopy (EDXS) method using an add-on (*Bruker*, Germany) to the *Tescan* high-emissivity scanning microscope (Czech Republic). The samples are prepared by applying a powdered catalyst to a carbon-based adhesive substrate.

The valence state of the catalyst active components is studied by the X-ray photoelectron spectroscopy (XPS) method. The source of monochromatic X-rays is $AlK\alpha$ (1486.6 eV), the internal standard is the energy of C 1s electron band (284.7 eV). The samples are prepared by applying a powdered catalyst to an indium foil with subsequent injection.

The catalytic properties have been studied in a flow-type quartz reactor in which 1.6 cm^3 catalyst (granules having a diameter of 2–3 mm) is loaded. The reaction mixture composition is as follows: 0.15% NO , 0.195% NH_3 , 5% O_2 , the rest is argon and nitrogen. The flow rate of the gas mixture is 400 cm^3/min , the volumetric flow rate is 15000 h^{-1} (the volumetric flow rate in the man-

ufacturing conditions is about 7500 h⁻¹). The initial mixture and the reaction products have been analyzed using a gas analyzer ANKAT-410 (*Analitpribor*, Russia) equipped with electrochemical cells to measure the content of nitrogen oxides (NO, NO₂, ppm) and ammonia (NH₃, mg/m³).

An industrial catalyst sample provides a 98% conversion of nitrogen oxides in the manufacturing conditions, at a volumetric flow rate of 7500 h⁻¹; when tested in the laboratory conditions, at a higher volumetric flow rate (15,000 h⁻¹), such indicators have not been reached because of a high-

er load. The studies under such conditions have enabled to expand the scale for assessing the differences in the activity of ACZ catalysts as compared with the commercial ones. The results of laboratory studies of the activity of ACZ catalyst used in industry and the catalysts designed while implementing the project are given in Table 1.

The studies of ACZ catalysts with a copper content from 10 to 14 wt% (Table 1, samples 2–4) have shown that with an increase in the copper content, the conversion of ammonia increases from 87.7% to 98%, at 330 °C, although

Table 1

ACZ and CuO-ZnO/Al₂O₃ Catalyst Activity at a Volume Velocity of 15000 h⁻¹

No.	Catalyst	T, °C	Conversion	
			NO, %	NH ₃ , %
1	Commercial ACZ(14% CuO-4 %ZnO/Al ₂ O ₃)	300	91.3	83.6
		330	91.4	95.6
2	10 % CuO-5 % ZnO/Al ₂ O ₃ (650 °C) ¹	300	90.2	77.6
		330	91.6	87.7
3	12 % CuO-5 % ZnO/Al ₂ O ₃ (650 °C)	310	91.7	90.4
		330	92.3	92.3
4	14 % CuO-5 % ZnO/Al ₂ O ₃ (650 °C)	305	94.1	97.2
		330	92.0	98.0
5	10 % CuO-5 % ZnO/Al ₂ O ₃ (750 °C)	310	93.5	90.5
		330	94.4	95.3
6	14 % CuO-5 %ZnO/Al ₂ O ₃ (750 °C)	310	95.0	98.8
		330	92.0	98.0
7	14 % CuO-5 % ZnO/Al ₂ O ₃ (Al(OH) ₃ /750 °C)	310	97.0	86.7
		330	96.9	94.3
8	1 % Fe ₃ O ₄ /12 % CuO-5 % ZnO/Al ₂ O ₃ (650 °C)	300	95.9	84.7
		330	96.4	97.0
9	1 % Mn ₃ O ₄ /12 % CuO-5 % ZnO/Al ₂ O ₃ (650 °C)	300	95.4	85.6
		330	95.5	96.4
10	1 % CeO ₂ /12 % CuO-5 % ZnO/Al ₂ O ₃ (650 °C)	300	94.4	88.0
		330	94.4	97.5
11	1 % ZrO ₂ /12 % CuO-5 % ZnO/Al ₂ O ₃ (650 °C)	300	93.9	87.5
		330	93.7	98.1
12	10 % CuO-ZnO/Al ₂ O ₃ (0.5 wt% NH ₄ OH) ²	300	94.4	85.4
		330	94.5	97.4
13	10 % CuO-ZnO/Al ₂ O ₃ (1.0 wt% NH ₄ OH) ³	300	91.1	82.2
		330	91.8	93.7
14	10 % CuO-ZnO/Al ₂ O ₃ (1.2 wt% NH ₄ OH) ³	300	93.7	81.0
		330	94.0	94.5

¹ Catalyst heat treatment temperature. ² Simultaneous soaking with solutions of zinc and copper nitrates in the presence of ammonia hydrate. ³ Sequential soaking by zinc nitrate solution with further treatment with heat and copper nitrate solution in the presence of ammonia hydrate.

the degree of conversion of nitrogen oxides remains almost unchanged. The activity of ACZ catalysts has been established to significantly influence their heat treatment temperature at the stage of preparation. Thus, an increase in the heat treatment temperature from 400 °C to 750 °C contributes to growing catalyst activity: the conversion of NO at a temperature of 330 °C in the presence of a catalyst containing 10% CuO and 5% ZnO/Al₂O₃, which has been treated is 91.6%, at 650 °C, and 94.4%, at 750 °C; in the presence of a catalyst containing 14% CuO and 5% ZnO/Al₂O₃ treated at 400 °C, the conversion is 81% and 92%, at 650–750 °C.

Fig. 1 shows diffraction patterns of samples of catalysts containing 14% CuO and 5% ZnO/Al₂O₃, treated at different temperatures. As the heat treatment temperature increases, so does the degree of crystallinity of the components. The reflexes typical for CuO (35.4 °C, 38.7 °C) are observed only for the sample treated at 400 °C. The other reflexes typical for copper oxide have not been reported, whereas the intensity of the reflexes typical for copper and zinc aluminates increases. However, in the case of industrial catalyst, a significant amount of CuO (reflexes at 35.4 °C, 38.7 °C) has been observed, as some part of copper unevenly contacts the surface of aluminum oxide without the formation of copper aluminate.

According to the results of the catalyst surface composition analysis, which has been made by the EDXS method (Table 2), the catalyst consisting of 14% CuO and 5% ZnO-Al₂O₃ and the

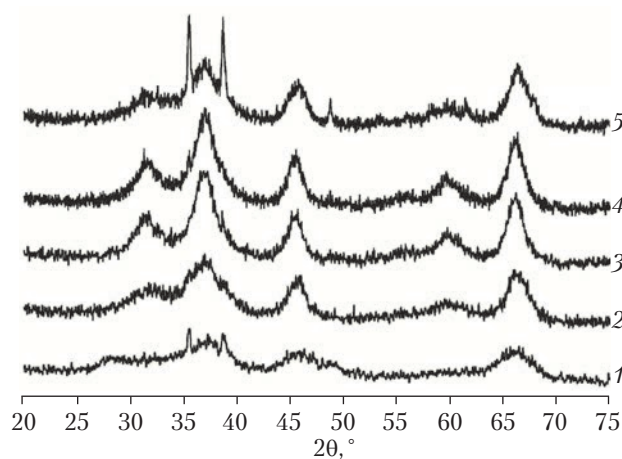


Fig. 1. Diffraction patterns of 14 % CuO-5 % ZnO/Al₂O₃, catalyst heated at different temperature (1 – 400 °C; 2 – 650 °C; 3 – 750 °C; 4 – 750 °C (2–3 mm fraction impregnated with Al₂O₃) and commercial catalyst (5), reheated at 650 °C)

industrial ACZ catalyst composed of 14% CuO and 4% ZnO-Al₂O₃ have the same content of the elements.

The analysis of Cu 2*p* and Zn 2*p* XPS spectra of ACZ catalysts (Fig. 2) shows that copper and zinc in the catalyst are in the 2+ oxidation state, which coincides with other data [8–10]. Reducing the binding energy of O 1*s* and Al 2*p* electrons for the catalysts produced in laboratory conditions may indicate that copper and zinc aluminates are formed during the preparation of the catalyst [11].

Thus, the difference in the activity of the ACZ catalyst in the manufacturing and laboratory conditions may be explained by the fact that the larger part of copper is concentrated in the cata-

Chemical Analysis of Catalyst Surface by the EDXS Method

Table 2

Catalyst	Element	Component content		
		Unnormalized, wt%	Normalized, wt%	Normalized, % atom.
14 % CuO-5 % ZnO-Al ₂ O ₃	Cu	9.26	20.26	10.33
	Al	32.47	71.06	85.36
	Zn	3.97	8.68	4.30
Commercial ACZ catalyst (14 % CuO-4 % ZnO/Al ₂ O ₃)	Cu	9.38	20.14	10.25
	Al	33.26	71.38	85.56
	Zn	3.95	8.47	4.19

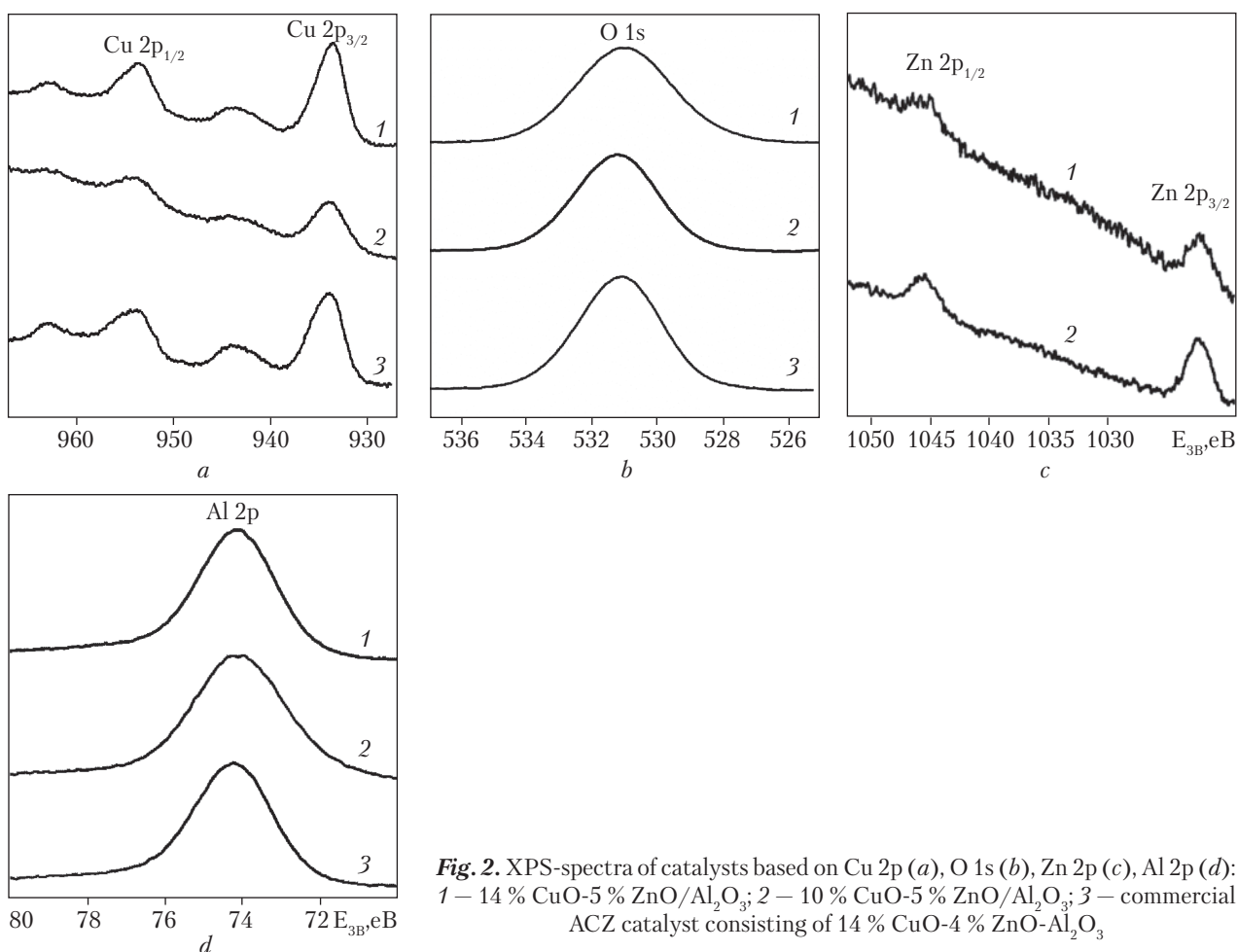


Fig. 2. XPS-spectra of catalysts based on Cu 2p (a), O 1s (b), Zn 2p (c), Al 2p (d): 1 – 14 % CuO-5 % ZnO/Al₂O₃; 2 – 10 % CuO-5 % ZnO/Al₂O₃; 3 – commercial ACZ catalyst consisting of 14 % CuO-4 % ZnO-Al₂O₃

lyst near-surface layer that is the most accessible in the course of the catalytic reaction.

If to prepare the catalysts the powdered aluminum hydroxide is used instead of A-1 (γ -Al₂O₃) carrier, the activity of the obtained samples is higher than in the case of the catalysts based on γ -Al₂O₃ extruded granules (Table 1, sample 7). This may be caused by a more even distribution of active components throughout the catalyst volume. A high activity of the sample prepared using Al(OH)₃ as an aluminum oxide source opens the way to simplify the manufacturing process of the ACZ catalysts, in particular, to reduce the number of heat treatment stages by avoiding the heat treatment of aluminum hydroxide to form the oxide, since in this case it is possible to extrude the hydroxide with active components.

The increase in ACZ catalyst activity can be achieved by introducing modifying additives, in particular, iron or manganese oxides (Table 1, samples 8–11). In the case of these catalysts, NO conversion is higher than in the case of the sample containing the same amount of copper and zinc oxides and even in the case of the sample containing 2% more CuO. In addition, the introduction of additives of iron, manganese, cerium, and zirconium oxides contributes to an increase in the ammonia conversion as compared with the sample having the same content of copper and zinc oxides.

Based on the studies of ACZ catalysts, one can conclude that the major part of the active catalyst component should be concentrated in the near-surface layer. Therefore, further research is

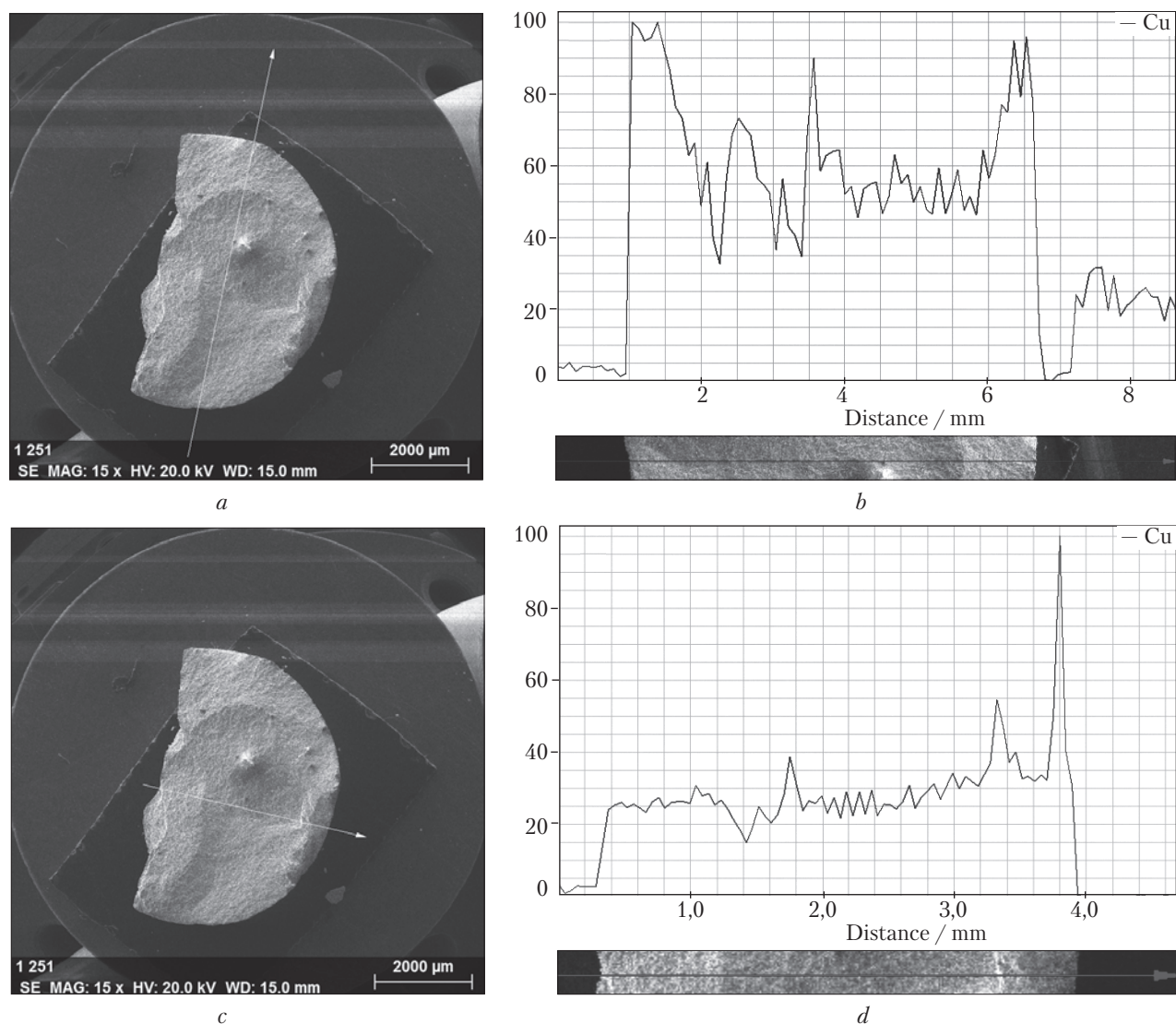


Fig. 3. Analysis of copper content in ACZ catalyst (10 % CuO-5 % ZnO/Al₂O₃), prepared with the use of impregnation solution containing 0.5 wt% ammonia hydrate (sample 12): *a, c* – microphotograph of crust-type granular catalyst; *b, d* – results of chemical analysis of granule depth by the EDXS method

focused on reducing the copper content in the catalyst by preparing a crust-type catalyst, in which the active component is concentrated on the outer surface of the granules. The results of studies of the crust-type catalysts in the process of selective catalytic reduction of NO with ammonia (Table 1) have shown that the addition of ammonia hydrate to the solution of zinc and copper salts contributes to the obtainment of more active catalysts (sample 12) as compared with

the samples impregnated with aqueous solutions (sample 6). It should be noted that an especial increase in the catalyst activity has been reported in relation to the ammonia conversion in the SCR process.

The 0.5wt% ammonia hydrate (NH₃ · H₂O) added to the solution for simultaneous impregnation with zinc and copper salts is the maximum permissible amount. An increase in the content of the substance in the solution leads to the setting

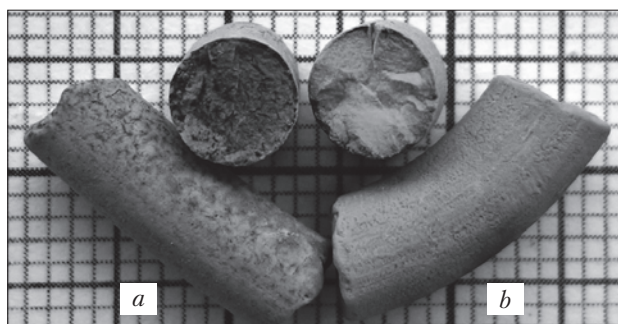


Fig. 4. Photographs of extruded granules of the commercial catalyst (a) and the designed crust-type ACZ catalyst (b)

of zinc hydroxide. For the sequential impregnation (firstly, with a solution of zinc salts (without ammonia), and then with a solution of copper nitrate), the ammonia content in the solution may increase to 1.2 wt% (sample 14). Any further increase leads to the setting of copper hydroxide. The complete conversion of copper hydroxide into a solution of copper ammonia is achieved only by adding a significant amount of ammonia water, resulting in a significant (or several times) decrease in the copper concentration in the solution. However, it should be noted that only increasing ammonia content from 1.0% to 1.2% (samples 13 and 14) leads to a significant increase in the catalyst activity.

The simultaneous impregnation of aluminum oxide with zinc and copper salts enables obtaining a more active catalyst (sample 12). This may be explained by synergistic interaction of copper and zinc compounds, which is achieved at the simultaneous uniform formation of common oxides.

Table 3

Chemical Analysis of ACZ Surface Layer Prepared with an Ammonia Hydrate Content of 0.5 wt% in the Solution for Impregnation by the EDXS Method

Element	Content		
	Unnormalized, wt%	Normalized, wt%	Normalized, % atom.
Cu	9.85	21.73	11.06
Al	32.35	71.42	85.56
Zn	3.10	6.85	3.38

Fig. 3 illustrates the results of the study of distribution of active components on the diameter of the crust-type catalyst pellet prepared with an ammonia hydrate content of 0.5 wt% in the solution for impregnation. Proceeding from the above data, it can be concluded that copper is found mainly in the near-surface layer of catalyst pellets.

The results of analysis of a 1 mm thick surface layer of ACZ catalyst prepared with a content of ammonia hydrate of 0.5 wt% in a solution for impregnation (sample 12) by the EDXS method are presented in Table 3. One can see that when applying the salts of active components on aluminum oxide granules from ammonia solutions it is possible to localize the active component mainly in the near-surface layer.

Thus, the use of technique for preparing ACZ catalysts by impregnating aluminum oxide granules with zinc and copper salts in the presence of ammonia hydrate enables to obtain samples having activity that are comparable to that of the catalysts containing 40% more copper oxide. This result is achieved due to the active components, in particular, copper oxide, localized in the near-surface layer, which form a crust-type catalyst (Fig. 4).

Table 4 shows the results of laboratory studies of a pilot batch of crust-type catalyst containing 10% CuO-4% ZnO-Al₂O₃ prepared using the proposed method. This catalyst has a high activity, ensures both an adequate level of NO purification and decomposition of residual ammonia, in industrial conditions (volumetric rate is 7500 h⁻¹, NO content is 0.1%). In addition, its activity exceeds that of an analog containing 14% CuO. It should be noted that the ratio NH₃/NO = 1:1.2 the NO conversion goes beyond 99%. The further increase in the excessive amount of ammonia does not lead to any growth in this indicator. Consequently, the use of developed technique for manufacturing ACZ catalyst enables reducing the content of copper in its composition and the excessive amount of ammonia for effective selective catalytic reduction of nitrogen oxides.

The technique developed in the laboratory for the production of structured aluminum-copper-zinc catalyst with an adjustable thickness of the active layer has been elaborated and tested in industrial conditions.

To test the trial batch of the catalyst, a reactor prototype has been manufactured based on the terms of reference for the design a pilot plant for testing a granular and structured ACZ catalyst on the exhaust gases of a nitric acid production unit. *Diia* Research & Innovation Corporation, LLC (Kamianske, Ukraine) has elaborated the technical and the design specifications. For manufacturing a pilot batch of crust-type catalyst for selective catalytic reduction of ammonia nitrogen oxides, *Catalysis and Ecology* Enterprise of the Pysarzhevskiy Institute of Physical Chemistry of the NAS of Ukraine has developed technological regulations and an ad hoc procedure for preparing a trial batch of granulated and structured aluminum-copper-zinc (ACZ) catalysts. The technology for the production of structured ACZ catalyst has been finalized at the facilities of *Katalizator* Company and approved for the future practical use, which has been certified by the relevant document.

The developed catalyst has been tested in commercial conditions using a pilot plant installed on an operating unit for manufacturing light nitric acid, at one of *Ostchem* companies. The catalyst is loaded into a reactor prototype, and the charac-

teristics of exhaust gas purification from nitrogen oxides and residual ammonia conversion have been studied under conditions identical to the operating parameters of the purification unit of nitric acid plant, namely:

- ✦ volumetric rate of gas flow through the catalyst bed: 7000–8000 h⁻¹;
- ✦ temperature of the gas mixture before the catalyst bed: 320–350 °C;
- ✦ NH₃/NO ratio in the gas mixture before the catalyst: 1:1.2–1.3;
- ✦ thickness of the catalyst bed: 800 mm.

The results of ACZ catalyst tests on the exhaust gases from the industrial plant are given in Table 5.

From the given data it is possible to make a clear conclusion that the developed catalyst significantly improves the indicators of catalytic reduction of nitrogen oxides as compared with both domestic and foreign analogs. Also, an essential advantage of the proposed catalyst, as compared with all known analogs, is the almost complete absence of reactive ammonia in the purified gas. This is explained by the fact that for the effective implementation of the process on the developed catalyst, the NH₃/NO ratio in the reaction medium, which ensures the concentration of nitrogen oxides in the purified gas being lower than the sanitary norms (0.001–0.002 vol.%), is less than in the case of other catalysts. Ammonia that has not reacted in the target process is al-

Table 4

Specifications of the Pilot Batch of 10 % CuO-4 % ZnO/Al₂O₃ Catalyst (volumetric rate = 7500 h⁻¹)

Conditions				Conversion, %		Residual content, ppm	
NO, vol. %	NH ₃ , vol. %	NH ₃ /NO	T, °C	NO	NH ₃	NO	NH ₃
0.15	0.195	1.3	300	99.7	90.6	4	85
			315	99.6	97.2	6	26
			330	99.4	100	9	0
0.15	0.18	1.2	300	99.6	95	5	44
			315	99.6	100	5	0
			330	99.6	100	5	0
0.10	0.12	1.2	300	99.9	100	2	0

Conditions and Analytical Results of the ACZ Catalyst Trial Batch Tests on a Prototype Plant with the Use of Exhaust Gases from a Nitric Acid Production Plant

Exhaust gas consumption, nm ³ /h	Volumetric rate, h ⁻¹	Ammonia consumption, nm ³ /h	Temperature in the reactor, °C			Pressure in the system, kg s/cm ²		Gas mixture composition, vol.%					Purification from NO _x , %
			<i>t</i> _{input}	<i>t</i> _{output}	Δt	Before the reactor	After the reactor	Before the reactor		NH ₃ /NO _x ratio	After the reactor		
								NH ₃	NO _x		NH ₃	NO _x	
420	6700	240	315	335	20	8.2	8.1	0.133	0.102	1.30	0.00	0.0013	98.7
420	6700	250	316	335	19	8.2	8.1	0.139	0.110	1.26	0.00	0.0012	98.9
430	6900	245	317	337	20	8.2	8.1	0.136	0.100	1.24	0.00	0.0010	99.0
450	7200	260	320	340	20	8.2	8.1	0.144	0.120	1.20	0.00	0.0011	99.0
440	7100	255	322	342	20	8.2	8.1	0.142	0.110	1.29	0.00	0.0010	99.0
440	7100	255	320	340	20	8.2	8.1	0.142	0.112	1.27	0.00	0.0011	99.0
430	6900	255	323	344	21	8.2	8.1	0.142	0.110	1.29	0.00	0.0018	98.4
425	6800	258	322	342	20	8.2	8.1	0.143	0.120	1.19	0.00	0.0015	98.7
420	6700	260	320	340	20	8.2	8.1	0.144	0.125	1.20	0.00	0.0020	98.1
450	7200	258	320	340	20	8.2	8.1	0.143	0.118	1.22	0.00	0.0018	98.5
450	7200	258	319	339	20	8.2	8.1	0.143	0.115	1.24	0.00	0.0020	98.3
435	7000	250	321	341	20	8.2	8.1	0.139	0.110	1.26	0.00	0.0018	98.4

most completely decomposed in the case of this catalyst.

Hence, implementing the catalytic reduction of nitrogen oxides by ammonia on the developed catalyst enables to solve the following problems at once:

- ✦ to halve the concentration of nitrogen oxides in gas emissions, as compared with the known domestic and foreign analogs;
- ✦ to reduce ammonia consumption for purifying the exhaust gases by 8–10%;
- ✦ to minimize (to remove almost completely) the content of ammonia residue in the purified gas.

The mentioned above allows us to recommend the developed catalyst and the new technology for the purification of gas emissions for a wide introduction. First of all, this applies to nitric acid production plants, where the problem of purifying the exhaust gases from nitrogen oxides is particularly important as the content of harmful impurities after purification by the previously known methods exceeds the permissible standards.

Thus, in the course of the project implementation, the composition and method for the preparation of ACZ oxide catalyst to be used in selective catalytic reduction of nitrogen oxides with ammonia have been optimized, which ensures a proper purification from nitrogen oxides and further decomposition of residual ammonia.

The activity of ACZ catalyst has been established to depend predominantly on the content of copper oxide in its composition. A high activity is ensured by 10 wt% content. The highest conversion of nitrogen oxides has been found to be achieved by simultaneously impregnating the aluminum oxide carrier with copper and zinc salts, which, according to the results of physical and chemical studies, is caused by the formation of complex oxide compositions heating the catalyst mass.

A technique for preparing the crust-type structured nanophase ACZ catalysts for selective reduction of nitrogen oxides in gas emissions from nitric acid production plants has been developed. It ensures the localization of copper oxide in the

near-surface layer of granular carrier, which results in a higher activity of the catalyst prepared by the proposed method, as compared with the conventional catalysts.

The new technology enables to reduce the content of CuO in the ACZ catalyst from 14% to 10% without any loss of the reagent activity. When using the developed catalyst to ensure a proper purification from nitrogen oxides, the ratio $\text{NH}_3/\text{NO} = 1:1.2$ is optimal. It is lower as compared with that for the known commercial catalysts. This enables to reduce the ammonia consumption for purifying the exhaust gases in the nitric acid production industry. The introduction of additive promoter (iron, manganese, cerium or zirconium oxides) to the catalyst can increase its activity.

Technological regulations have been developed, a technological process has been elaborated, and a trial batch of crust-type structured catalysts for selective reduction of nitrogen oxides

has been manufactured. The developed catalyst has been tested on a pilot plant installed on an operating unit of light nitric acid production plant at one of *Ostchem* companies. The tests have shown that the performance of proposed catalyst in terms of catalytic reduction of nitrogen oxides significantly exceeds that for both domestic and foreign analogs, as this catalyst provides reducing the content of residual nitrogen oxides in purified gas down to 0.001–0.002 vol.%.

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РОЗРОБКА КАТАЛІЗАТОРІВ ДЛЯ ЗНЕШКОДЖЕННЯ ТОКСИЧНИХ ОКСИДІВ АЗОТУ В ГАЗОВИХ ВИКИДАХ ВИРОБНИЦТВА АЗОТНОЇ КИСЛОТИ

Вступ. Зниження рівня викидів оксидів азоту (NO_x) промисловими підприємствами залишається однією з важливих проблем захисту навколишнього середовища. Основним способом знешкодження викидів NO_x є процес селективного каталітичного відновлення (СКВ), ефективність якого визначається активністю каталізаторів, які потребують вдосконалення.

Проблематика. СКВ NO_x амоніаком з використанням каталізатора АВК-10 є основним способом знешкодження токсичних сполук NO_x у газових викидах підприємств азотної промисловості. Зазначений каталізатор містить в своєму складі токсичний ванадій і за рівнем очистки від NO_x та розкладанням залишкового NH_3 не відповідає сучасним санітарним вимогам. Отже, важливим є розроблення та апробація технології виготовлення безванадієвих каталізаторів для даного процесу.

Мета. Розробка та впровадження технологічних засад виготовлення високоактивного алюмо-мідно-цинкового (АМЦ) каталізатора СКВ NO_x для знешкодження викидів у виробництві азотної кислоти.

Матеріали й методи. АМЦ каталізатори готували шляхом просочення гранул $\gamma\text{-Al}_2\text{O}_3$ (марки А-1) розчинами нітратів міді та цинку. Активність каталізаторів визначали в оснащених газоаналізатором установці проточного типу.

Результати. Розроблено технологію приготування нанофазних АМЦ каталізаторів із «скоринкову» структурою активного шару для СКВ NO_x в газових викидах виробництва азотної кислоти, яка забезпечує локалізацію оксиду міді в приповерхневому шарі гранули-носія, що обумовлює вищу активність, порівняно з існуючими каталізаторами.

Висновки. Відпрацьовано технологічний процес виготовлення розробленого АМЦ каталізатора в умовах Товариство з додатковою відповідальністю «Каталізатор», м. Кам'янське (Дніпропетровська обл.). Випробування на дослідно-промисловій установці на діючому агрегаті неконцентрованої азотної кислоти холдингу «Ostchem» показали, що розроблений каталізатор забезпечує зниження залишкових оксидів азоту в очищеному газі до рівня 0,001–0,002 % об. і практично повну відсутність амоніаку.

Ключові слова: оксиди азоту, селективне каталітичне відновлення, оксидний алюмо-мідно-цинковий каталізатор, оксид міді.

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РАЗРАБОТКА КАТАЛИЗАТОРОВ ДЛЯ ОБЕЗВРЕЖИВАНИЯ ТОКСИЧЕСКИХ ОКСИДОВ АЗОТА В ГАЗОВЫХ ВЫБРОСАХ ПРОИЗВОДСТВА АЗОТНОЙ КИСЛОТЫ

Введение. Снижение уровня выбросов оксидов азота (NO_x) промышленными предприятиями остается одной из важных проблем защиты окружающей среды. Основным способом обезвреживания выбросов NO_x является процесс селективного каталитического восстановления (СКВ), эффективность которого определяется активностью каталитаторов, которые нуждаются в совершенствовании.

Проблематика. СКВ NO_x аммиаком с использованием каталитатора АВК-10 является основным способом обезвреживания токсичных NO_x в газовых выбросах предприятий азотной промышленности. Указанный каталитатор содержит в своем составе токсичный ванадий и по уровню очистки от NO_x и разложением остаточного NH_3 не соответствует современным требованиям. Следовательно, важным является разработка и апробация технологии изготовления безванадиевых каталитаторов для данного процесса.

Цель. Разработка и внедрение технологических основ изготовления высокоактивного алюмо-меди-цинкового каталитатора селективного восстановления оксидов азота аммиаком для нейтрализации выбросов NO_x в производстве азотной кислоты

Материалы и методы. АМЦ катализаторы готовили путем пропитки гранул $\gamma\text{-Al}_2\text{O}_3$ (марки А-1) растворами нитратов меди и цинка. Активность катализаторов определяли в установке проточного типа оснащенную газоанализатором.

Результаты. Разработана технология приготовления нанофазных АМЦ катализаторов с «корочковой» структурой активного слоя для СКВ NO_x в газовых выбросах производства азотной кислоты, которая обеспечивает локализацию оксида меди в приповерхностном слое гранулы-носителя, что обуславливает высокую активность по сравнению с существующими катализаторами.

Выводы. Отработано технологический процесс изготовления разработанного АМЦ катализатора в условиях общества с дополнительной ответственностью «Катализатор», г. Каменское (Днепропетровская обл.). Испытания на опытно-промышленной установке на действующем агрегате производства неконцентрированной азотной кислоты холдинга «Ostchem» показали, что разработанный катализатор обеспечивает снижение остаточных оксидов азота в очищенном газе до уровня 0,001–0,002 % об. и практически полное отсутствие аммиака.

Ключевые слова: оксиды азота, селективное каталитическое восстановление, оксидный алюмо-медно-цинковый катализатор, оксид меди.