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V.A. Vekshyn^a, *E.R. Grabovetskaya*^b**KINETICS OF SELECTIVE REDUCTION OF NITROGEN OXIDES ON A CELLULAR PLATINUM CATALYST**^a **Kharkiv National Medical University, Kharkiv, Ukraine**^b **V.N. Karazin Kharkiv National University, Kharkiv, Ukraine**

Kinetics of the selective reduction of nitrogen oxides by using ammonia on a supported cellular platinum catalyst is considered in the article. The calculations allowed determining the kinetic areas of these reactions on the catalysts concerned. The effects of temperature and volumetric flow rate on the efficiency of the purification process were investigated. The values of the rate constants for nitrogen oxides reduction and ammonia oxidation reactions were calculated on the basis of experimental studies with the use of mathematical modeling methods. The influence of monobasic organic acids, acetic and formic acids, on the activity of the catalysts of this type was determined. The samples of catalysts modified with formic acid showed the highest activity. This fact can be explained by a high rate of the main reactions of NO_x reduction compared to the rate of ammonia oxidation side reactions. The causes of a decrease in the activity of catalysts with change in temperature were established. The surplus of temperature results in a decrease in the concentration of ammonia below stoichiometry, which leads to the reduction in effectiveness of the process.

Keywords: oxides, carrier, catalyst, modifier, purification, kinetics.

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Introduction

Anthropogenic pollution of the environment with nitrogen oxides is mainly due to their release into the atmosphere as a result of fuel combustion by power plants, road transport, metallurgical enterprises, and emissions of waste gases from chemical industries. At the same time, nitric acid production accounts for about 5% of total NO_x emissions from chemical factories. Despite the relatively small contribution of these factories to the environmental situation, the main danger lies in the fact that atmospheric pollution is local in this case.

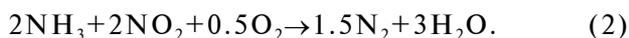
Harmful substances in the form of acidic oxides enter the atmosphere and react with water vapor under the action of solar radiation. Clouds containing drops of acid form acid rain which falls directly into rivers and lakes. Such atmospheric condensation changes the acidity level of the aquatic medium. On land, acids penetrate into the soil and dissolve calcium and potassium compounds and carry them away from the surface layer. Thus, plants become deprived of the main source of nutrition. Minerals dissolved in acidified water enter the water reservoirs along with groundwater, which leads to the death of all living

creatures. Only the simplest forms of life can survive in such reservoirs. Air pollution by acid gaseous oxides also causes significant harm to human health. It is associated with such diseases as upper respiratory catarrh, emphysema, angina, pharyngitis, pneumonia, bronchitis, and tuberculosis. Ever-growing incidence rate of oncological diseases in cities with developed motor transport is being detected.

The discussed problem forces the governments of industrialized countries to spend significant funds to eliminate the effects of air pollution. For instance, 72 billion euros is spent by Western Europe countries each year for control of gas emissions, 11 billion euros is spent for nitrogen oxide concentrations monitoring. Despite this, about 1 million people die each year from pulmonary diseases in the EU. In order to solve this problem, the European Union spends 380 billion euros every year [1]. In the US, more than \$ 60 billion a year is spent to support air quality which is more than medical and construction costs.

To solve this problem, modern nitric acid plants provide low-temperature catalytic purification of waste gases from nitrogen oxides using ammonia gas

as a reducing agent [2]. This purification scheme is based on the NO_x reduction with ammonia on the surface of a heterogeneous catalyst in the presence of oxygen. The low-temperature catalytic reduction process can be described by the following equations:



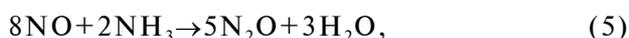
Selective catalytic reduction (SCR) of pure nitrogen oxides with ammonia is effective at 200–350°C [3]. Nitrogen monoxide (NO) and nitrogen dioxide (NO_2) react with ammonia at the same rate. Oxygen activates the nitrogen formation.

Lowering of the process temperature leads to decreasing of degree of NO_x reduction. This can be explained by a decrease in the reaction rate. Exceeding the temperature range also decreases the degree of purification, which is explained by the following side reactions:



Elevation of the process temperature also results in decreased adsorption capacity of the catalyst with respect to the reactants [4].

Depending on the type of a catalyst, the processes of reduction of NO_2 and NO to nitrous oxide (N_2O) and oxidation of ammonia with oxygen to N_2O are also possible:



The efficiency of low-temperature purification of exhaust gases from NO_x by means of ammonia depends on the concentration of reagents, their ratio, temperature, catalyst composition, activity, selectivity, and the time of contact. The time of contact is determined by the form of the catalyst, configuration of the catalytic reactor, and the gas flow rate. In nitric acid production, the catalytic reduction is mostly effective at the temperature of 300–450°C on industrial alumina vanadium catalysts AVC-10 and AVC-10 M, where vanadium oxide (V) acts as a catalytically active substance.

The catalysts used in industry are sufficiently active but they still have significant disadvantages typical of all granular catalysts: high resistance to gas flow, low strength, difficult regeneration, etc.

Nowadays, there is an increasing interest in design and investigation of block metal catalysts deprived of the indicated drawbacks.

The industrial block catalysts are advantageous because at a high gas feeding rates they provide low pressure difference before and after the catalytic system. At the same time, metal blocks are manufactured easier than ceramic ones, they also have higher mechanical strength, thermal conductivity and resistance to temperature difference.

The block catalysts are more promising due to simplicity of loading, absence of dust and possibility of regeneration. Block catalysts allow reaching the contact time at the level of several milliseconds and raising the system temperature from room temperature to 1000°C almost instantaneously [5]. The possibility of such rapid heating and cooling is extremely important for undesirable side reactions control. Block materials differ from granular because they have constant spatial position of the structural elements and high porosity. Displacement and damage of surface layer in block carriers are impossible, therefore they provide more efficient use of the surface. The mass of reactors with such carriers is much lower. Preparation of catalysts of this type combines homogeneous application of small amount of the active component with high activity of the final product.

Based on the given data, investigations were carried out which resulted in design of cellular metal catalyst for the exhaust gases purification from NO_x . The catalyst is highly active and possesses low hydraulic resistance.

Experimental

The catalyst is based on oxidized titanium plates with subsequent impregnation with platinum salts with or without modification of the support by monobasic organic acids [6]. Research and industrial tests performed in the laboratory at OAO «Severodonetskoye Ob'edineniye «Azot» allowed a full complex of physicochemical and kinetic calculations.

Determination of kinetic characteristics of chemical reactions occurring on a particular catalyst is one of the main steps of the catalytic reactor construction. Kinetic calculations for plate-type catalysts must take into account three main areas of catalytic processes: external diffusion, intradiffusion and kinetic ones. Depending on the overall reaction rate-determining step, different kinetic models are used. Based on the above, hydrodynamic calculations were carried out for precise determination of the working areas of the process.

The investigations were performed on a flow

type installation in a quartz glass reactor with the following process parameters: concentration of nitrogen oxides in the gas mixture $C(\text{NO}_x)=0.12-0.16$ vol.%, ($C(\text{NO}_x)/C(\text{NO}_2)=50/50$); concentration of ammonia $C(\text{NH}_3)=0.13-0.22$ vol.%; air concentration (carrier gas) $C_{\text{air}}=99.62$ vol.%; temperature range of 423–573 K; gas mixture volumetric flow rate of 5000–15000 h^{-1} .

Reynolds criterion was calculated according to the standard procedure [7] using the following initial data for laboratory conditions: gas flow rate $Q_g=4 \cdot 10^{-5}$ m^3/s (2.4 L/min); volumetric flow rate 15000 h^{-1} ; and cross-sectional area of the reactor $9.6 \cdot 10^{-5}$ m^2 .

Linear gas velocity was determined as its volume flow rate under flow conditions (temperature, pressure) through a unit of cross-section:

$$w = \frac{Q_g}{F} = \frac{4 \cdot 10^{-5}}{9.6 \cdot 10^{-6}} = 4.2 \text{ m/s}, \quad (7)$$

where Q_g is the gas volume flow rate under flow conditions, m^3/s ; F is the cross-section area of the flow (pipe), m^2 ; and w is the linear gas velocity in the gas pipeline, m/s .

Reynolds criterion was calculated taking into consideration the equivalent diameter of the reactor, d_e , through the rectangular cross section of the hardware units (the channels) in the reaction zone as follows:

$$d_e = \frac{2ab}{a+b} = \frac{2 \cdot 0.024 \cdot 0.004}{0.024 + 0.004} = 0.007 \text{ m}, \quad (8)$$

where a and b are the sides of the channels of the reactor units, m .

Reynolds criterion was determined by the formula:

$$\text{Re} = \frac{wd_e\rho}{\mu} = \frac{4.2 \cdot 0.007 \cdot 0.6758}{2.8 \cdot 10^{-5}} = 710. \quad (9)$$

The obtained value of the Reynolds criterion is characteristic for the laminar regime, which shows that process proceeds in the external diffusion area and is characteristic for catalysts of this type [8].

The specific surface area was determined based on the weight and X-ray adsorption analysis data on DRON-2: the size of the carrier plate was 2 cm×10 cm×0.2 cm, the plate weight was 6.6475 g, the amount of platinum deposited was 0.0055 g, and the size of platinum crystallites was 2 nm. The total specific surface area of platinum crystallites was determined with accounting that all crystals were

cubic and evenly distributed over the surface of the TiO_2 layer of the catalyst carrier. Calculations showed that the specific surface area of the catalyst was $S_a=0.003$ m^2/g . As indicated above, the process of the catalyst construction was accompanied by the investigation of the effect of monobasic organic acids, in particular formic and acetic acids, on the distribution of platinum crystallites on the carrier surface during impregnation.

Thus, for the following evaluation of kinetic characteristics of the SCR process, specific catalyst samples having the highest degree of reduction were selected: prepared by 3-fold impregnation of the carrier with hexachloroplatinic acid without treatment with modifiers (1); with a single impregnation with H_2PtCl_6 and preliminary treatment with acetic acid (2), and a sample that exhibited the highest catalytic activity was prepared by a single impregnation with H_2PtCl_6 accompanied by addition of formic acid (3). Figure 1 illustrates the average characteristic curves of degree of reduction versus temperature at a gas volumetric flow rate of 10000 h^{-1} .

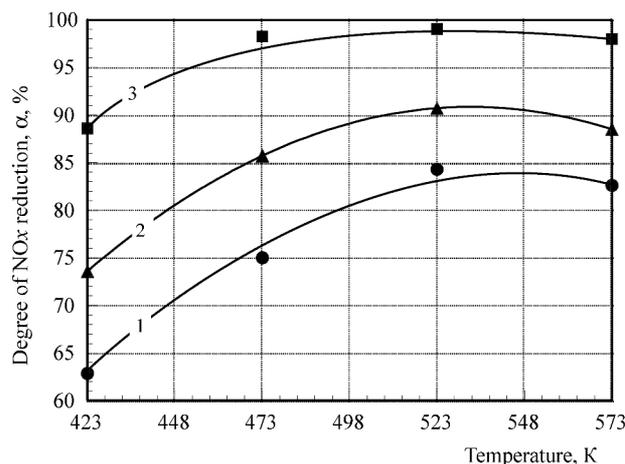


Fig. 1. Temperature dependences of the degree of reduction: 1 – sample treated with CH_3COOH ; 2 – sample without modifiers; 3 – sample treated with HCOOH

The average curves show that a maximum purification can be achieved at a temperature of 523 K, regardless of the preparation conditions, then the reduction degree α significantly reduces. The contact time for the reacting substances is an important technological characteristic of the catalytic process. Its finding allows determining not only the kinetic parameters, but also calculating all parameters of the industrial reactor, if necessary. The contact time was calculated by the following formula:

$$\tau = \frac{V_r \eta}{V_g}, \quad (10)$$

where V_r is the volume of the reaction zone, m^3 ; V_g is the gas flow rate, m^3/h ; η is the fraction of the free volume of the catalyst (according to the design of the reactor and the dimensions of the sample, $\eta=0.5$).

The results of the calculations are given in Table 1.

Table 1

Dependence of the contact time on the volumetric flow rate

Volumetric flow rate, h^{-1}	Contact time τ , s
5000	0.36
10000	0.18
15000	0.12

To determine the influence of the gas volumetric flow rate (contact time) on the efficiency of the NO_x reduction process at the optimum temperature, the corresponding graphs have been plotted (Fig. 2).

These graphs have a common exponential type. A detailed examination of the curves shows that after elevation of the volumetric flow rate above 10000 h^{-1} , the growth of NO_x degree of reduction diminishes. The sample 3 shows the most significant decrease in the growth.

The obtained data indicate that the degree of reduction appreciably decreases at a temperature

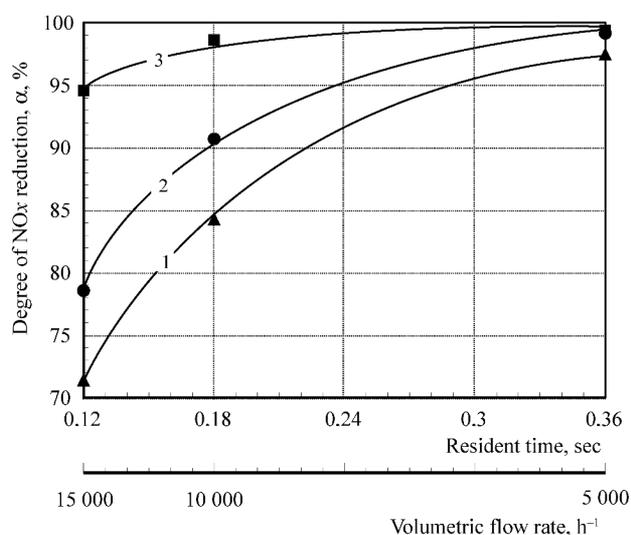
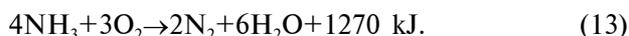
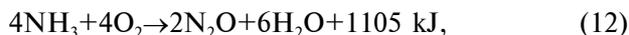
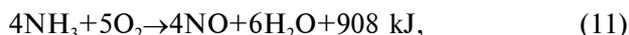


Fig. 2. Dependence of the degree of reduction of NO_x on the gas volumetric flow rate (average data at the optimum temperature 523 K): 1 – sample treated with CH_3COOH ; 2 – sample without modifiers; 3 – sample treated with HCOOH

higher than 523 K. Based on the literature data [9], a decrease in the NO_x degree of reduction at a temperature higher than 523 K can be explained by the side reactions of ammonia oxidation with the formation of elemental nitrogen and its oxides according to the following reactions:



At the same time, according to literature data [10], reactions with the formation of nitrous oxide are typical of the processes of purification from NO_x on a platinum catalysts. According to data [11], reactions of ammonia oxidation on platinum catalysts begin at 420 K and proceed predominantly with the formation of N_2 . Elevation of temperature leads to an increase in the NO content and a decrease in the N_2 concentration. The latter reaction is thermodynamically most probable but the probability of the second reaction increases with increasing temperature.

In order to elucidate the possibility of the reactions described above, experimental studies were carried out under the conditions of the «blank experiment», that is, without the addition of nitrogen oxides. Only ammonia with initial concentration of 0.17% was supplied to the reactor. For accuracy of the experiment, the studies were performed under the same conditions as for the NO_x reduction reaction. In order to elucidate the possibility of NH_3 oxidation to NO , the temperature interval was extended to 423–623 K. Studies showed a rather low degree of ammonia conversion in the temperature range of 423–473 K and its significant increase within the temperature range of 573–623 K. At the same time, the formation of nitrogen oxides NO and NO_2 was not detected in the experiment. This allows excluding the first reaction of NO_x formation from the subsequent calculations, and only the reactions with the formation of nitrous oxide and N_2 are further considered.

Elevation of the process temperature above the optimum contributes to an increase in the rate of side reactions but does not lead to the formation of NO_x . It results in an undesirable reaction of ammonia conversion, which slowly leads to a decrease in its concentration below the stoichiometric minimum. It is the lack of NH_3 that causes lowering of the degree of reduction of nitrogen oxides. The experimental (apparent) reaction rate constant was

calculated based on the first-order equation according to certain concentrations of NO_x :

$$k_{\text{app}} = \frac{1}{\tau} \ln \frac{C_{\text{NO}_x}^o}{C_{\text{NO}_x}^f}, \quad (14)$$

where $C_{\text{NO}_x}^o$ is the initial concentration of nitrogen oxides, vol.%; $C_{\text{NO}_x}^f$ is the final concentration of nitrogen oxides, vol.%; and τ is the contact time, s.

Based on the obtained values of the apparent constant, temperature dependences of k_{exp} were used for further determination of a true rate constant. The true rate constant was calculated by linearization the function k_{exp} vs. T . Taking into account that all dependencies k_{exp} vs. T in the range of 423–523 K correspond to an exponential function, the linearization was performed by the inverse function $\ln k_{\text{exp}}$ vs. $1/T$. To determine the effect of the side reactions of ammonia oxidation, the calculations of their rate constants were done.

The experimental data of the «blank» experiment at a gas volumetric flow rate of 10000 h^{-1} are taken as the basis. The reduction reaction rate was calculated by the following equation:

$$-\frac{dC_{\text{NO}_x}}{\tau} = k_{\text{NO}_x} \left(C_{\text{NO}_x(n)} - C_{\text{NO}_x}^* \right), \quad (15)$$

where $\left(-\frac{dC_{\text{NO}_x}}{\tau} \right)$ is the rate of the NO_x reduction reaction, s^{-1} ; k_{NO_x} is the reaction rate constant of NO_x reduction, s^{-1} ; $C_{\text{NO}_x(n)}$ is the initial NO_x concentration, vol.%; and $C_{\text{NO}_x(n)}^*$ is the equilibrium concentration of NO_x , vol.%.

The rate of ammonia oxidation was calculated similarly:

$$-\frac{dC_{\text{NH}_3}}{\tau} = k_{\text{NH}_3} \left(C_{\text{NH}_3(n)} - C_{\text{NH}_3}^* \right) \quad (16)$$

where $\left(-\frac{dC_{\text{NH}_3}}{\tau} \right)$ is the rate of the NH_3 oxidation reaction, s^{-1} ; k_{NH_3} is the reaction rate constant of NH_3 oxidation, s^{-1} ; $C_{\text{NH}_3(n)}$ is the initial NH_3 concentration, vol.%; and $C_{\text{NH}_3(n)}^*$ is the equilibrium concentration of NH_3 , vol.%.

The equilibrium concentrations of nitrogen oxides were calculated according to the equilibrium constants presented elsewhere [12]. The results of calculations are given in Table 2.

Table 2
Temperature dependence of equilibrium concentrations of nitrogen oxides in reduction reactions and ammonia in oxidation reactions

Temperature, K	Equilibrium concentrations of nitrogen oxides $C_{\text{NO}_x}^*$, %	Equilibrium concentrations of ammonia $C_{\text{NH}_3}^*$, %
423	0.000143	0.008420413
473	0.000348	0.008695027
523	0.0008316	0.008936967
573	0.001904	0.009155697
623	–	0.00935684

Initial concentrations of NH_3 and NO_x were selected based on experimental studies and then averaged. Detailed models of the reactions rates were obtained by the combination of the general equations for rates of main and side reactions with regressive models of the constants k on the investigated samples at a volumetric flow rate of 10000 h^{-1} (Table 3).

The rates of the main reactions of NO_x

Table 3

Mathematical models of the dependence of reaction rate on temperature and determination factor on the investigated catalysts

Sample	Model	Determination factor R^2 , %
Modification with CH_3COOH	$-\frac{dC_{\text{NO}_x}}{\tau} = 266.72e^{-\frac{12893}{RT}} \left(C_{\text{NO}_x(n)} - C_{\text{NO}_x}^* \right)$	99.87
Unmodified	$-\frac{dC_{\text{NO}_x}}{\tau} = 134.29e^{-\frac{11245.9}{RT}} \left(C_{\text{NO}_x(n)} - C_{\text{NO}_x}^* \right)$	99.98
Modification with HCOOH	$-\frac{dC_{\text{NO}_x}}{\tau} = 741.74e^{-\frac{14272.43}{RT}} \left(C_{\text{NO}_x(n)} - C_{\text{NO}_x}^* \right)$	99.93
NH_3 oxidation	$-\frac{dC_{\text{NH}_3}}{\tau} = 2558.3e^{-\frac{24951.606}{RT}} \left(C_{\text{NH}_3(n)} - C_{\text{NH}_3}^* \right)$	99.56

Table 4

Rate of NO_x reduction reactions (–dc/dt) and NH₃ oxidation reactions as a function of process temperature and initial concentration at a gas volumetric flow rate of 10000 h⁻¹

Temperature, K	Sample treated with CH ₃ COOH		Sample without modifiers		Sample treated with HCOOH		Oxidation of NH ₃	
	C _{NO_x(n)} , vol.%	–dc/dτ, vol.%/s	C _{NO_x(n)} , vol.%	–dc/dτ, vol. %/s	C _{NO_x(n)} , vol.%	–dc/dτ, vol.%/s	C _{NH₃(n)} , vol.%	–dc/dτ, vol.%/s
423	0.14	0.952	0.12	0.657	0.14	1.789	0.15	0.320
473	0.13	1.401	0.14	0.919	0.14	2.783	0.14	0.588
523	0.14	1.911	0.13	1.203	0.13	4.332	0.14	1.242
573	0.14	2.456	0.14	1.495	0.14	5.730	0.14	3.130

reduction and the side reaction of NH₃ oxidation were calculated based on the dependences obtained. The results of the studies are given in Table 4.

The data given in Table 2 show that the equilibrium concentrations of nitrogen oxides and ammonia vary depending on the temperature.

Calculations using regression analysis were carried out in order to introduce equilibrium concentrations into the general kinetic model. The following exponential dependences were obtained:

– for NO_x reduction:

$$-\frac{dC_{\text{NO}_x}}{d\tau} = k_0 e^{-\frac{E_a}{R T}} \cdot \left(C_{\text{NO}_x(n)} - e^{-16.1462 + 0.01728 \cdot T} \right); \quad (17)$$

– for NH₃ oxidation:

$$-\frac{dC_{\text{NH}_3}}{d\tau} = k_0 e^{-\frac{E_a}{R T}} \cdot \left(C_{\text{NH}_3(n)} - e^{-4.4587 - \frac{135.0}{T}} \right). \quad (18)$$

Checking calculations of the rate constant according to the above models showed that the discrepancy between these data and the data of models presented in Table 3 does not exceed ±1.5%. This fact confirms high accuracy of the obtained data and the possibility of their use in further investigations.

Results and discussion

The results of kinetic calculations show that the rate constant increases in proportion to the temperature and almost does not depend on the contact time. Based on the experimental data given above and the data of previous kinetic studies, it can be concluded that the catalyst produced by the modification with HCOOH at the optimum parameters reveals the highest efficiency. The optimum parameters are shown to be as follows: contacting time τ=0.18 s (10000 h⁻¹) and temperature 523 K.

Fig. 3 illustrates the temperature dependences of the rate of reduction reactions of nitrogen oxides on various catalysts and the ammonia oxidation in

the absence of NO_x. The analysis of the presented curves shows that below 473 K the tendencies of the main NO_x reduction reactions for unmodified samples and modified with CH₃COOH as well as ammonia oxidation side reaction are the same. The lines are almost parallel. In the temperature range of 473–548 K, the dependence 1 corresponding to the NH₃ oxidation reaction begins to rapidly approach the dependences 2 and 3, and finally crosses them at a temperature of 510 K and 550 K for the sample modified with CH₃COOH and for the unmodified sample, respectively. This shows a sharp increase in the rate of the NH₃ oxidation reaction, which eventually begins to predominate over the rate of the main reactions. This leads to a shortage of ammonia in the gas mixture and reduces the degree of purification.

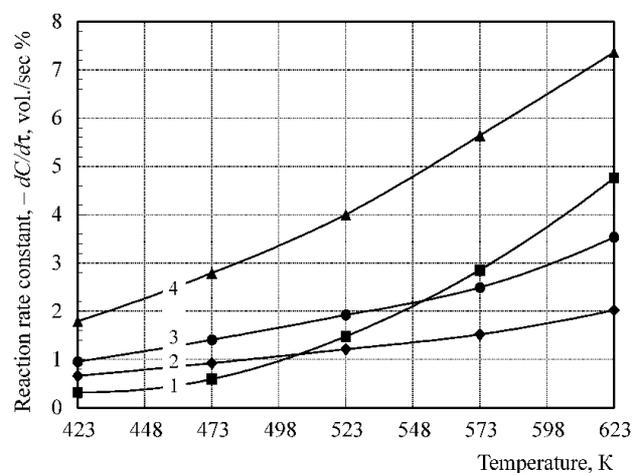


Fig. 3. Temperature dependences of the reaction rate: 1 – ammonia conversions; 2 – NO_x conversions on a sample modified with CH₃COOH; 3 – NO_x conversions on an unmodified sample; 4 – NO_x conversions on a sample modified with HCOOH

The dependence 4 has another form. It corresponds to the sample modified with HCOOH.

The comparison of dependences 1 and 4 shows that there is no intersection point within this temperature range, i.e. the rate of the main reactions always prevails over the rate of the NH_3 oxidation reaction. A significant increase in the growth of ammonia oxidation reaction rate at a temperature higher than 510 K may indicate the existence of an extreme temperature at which the rate of ammonia oxidation begins to predominate, but in this case its value is beyond the temperature range of the purification process. The dependence of α on temperature depicted in Fig. 1 shows that the degree of reduction on this sample is quite high in the temperature range of 473–573 K. A slight decrease in the degree of purification at 573 K can be explained by a shift in equilibrium of the main reactions to the left.

Thus, the maximum activity is exhibited by a sample modified with formic acid. The maximum degree of reduction is achieved at a temperature of 523 K and, unlike other samples, practically does not decrease up to 573 K. The NO_x reduction reactions proceed at a high rate on this catalyst. The advantages of the side reaction of NH_3 oxidation over the main one are not observed in this temperature range. These facts allow us to conclude that formic acid as a modifier has beneficial effect on the impregnation stage in the course of preparation of catalysts of this type.

Conclusions

Our findings showed that temperature significantly affects the rate of catalytic reduction of nitrogen oxides with ammonia. The effect of temperature can be explained by an increase in the reaction rate constant in proportion to temperature according to the Arrhenius law. The influence of the gas volumetric flow rate is insignificant.

Appearance of a temperature optimum in case of both unmodified samples and those treated with CH_3COOH can be explained by the predominance of the side reaction of ammonia oxidation rate over the main reaction of NO_x reduction at a temperature higher than 523 K. An extremum in case of a sample modified by HCOOH can be associated with a shift in equilibrium towards the reactants. The dependences of the degree of reduction on the volumetric flow rate are also extremal, although they are not as pronounced as for the temperature. After elevation of the volumetric flow rate above 10000 h^{-1} , the growth of α diminishes. This fact can be explained by a decrease in the duration of the contact. Thus, the given volumetric rate can be treated as the optimal one.

The main reactions of nitrogen oxides reduction are accompanied by ammonia oxidation reactions.

They affect the main reactions almost over the entire temperature range but within the limits of 510–550 K the rate of these reactions becomes sufficient to prevail over the rate of the main reactions. At the same time, NO is not produced and the degree of reduction decreases due to a shortage of ammonia according to stoichiometry.

The kinetic calculations showed that a sample modified with HCOOH is the most active catalyst. Its application provides a significant increase in the rate of the main reactions of NO_x reduction relative to the rate of ammonia oxidation side reactions. This allows expansion of the temperature range for the purification process and makes this catalyst most suitable for industrial application under the following optimum conditions: temperature of 473–573 K and volumetric rate of 10000 h^{-1} . Other investigated catalysts have significantly inferior properties and do not allow achieving the required MAC under the given conditions of a process.

REFERENCES

1. Lung health in Europe – facts and figures. – European Lung Foundation. – 2014. – P.16-17.
2. Bradford M., Grover R., Paul P. Controlling NO_x emissions. Part 2 // Chem. Eng. Progr. – 2002. – No. 3. – P.38-42.
3. Yan H., Qu H., Bai H., Zhong Q. Property, active species and reaction mechanism of NO and NH_3 over mesoporous Fe-Al-SBA-15 via microwave assisted synthesis for NH_3 -SCR // J. Mol. Catal. A. – 2015. – Vol. 403. – P.1-9.
4. Watson J.M., Ozkan U.S. Role of NH_3 as an intermediate in reduction of NO with CH_4 over sol-gel Pd catalysts on TiO_2 // J. Mol. Catal. A. – 2002. – Vol.192. – P.79-91.
5. Yokoyama C., Bharadwaj S.S., Schmidt L.D. Platinum-tin and platinum-copper catalysts for autothermal oxidative dehydrogenation of ethane to ethylene // Catal. Lett. – 1996. – Vol.38. – P.181-188.
6. *Issledovanie vliyaniya tekhnologii prigotovleniya katalizatora na raspredelenie kataliticheski aktivnogo veshchestva po poverhnosti nositelya* / Loboyko A., Vekshin V., Markova N., Vorozbiyan M., Shapareva L. // Suchasni Problemy Tekhnologii Neorganichnykh Rechovyn. – 2008. – No. 2(10). – P.59-62.
7. *Observations of asymmetrical flow behaviour in transitional pipe flow of yield-stress and other shear-thinning liquids* / Escudier M.P., Poole R.J., Presti F., Dales C., Nouar C., Desaubry C., Graham L., Pullum L. // J. Non-Newtonian Fluid Mech. – 2005. – Vol.127. – P.143-155.
8. *Tekhnologiya katalizatorov* / I. Mukhlenov, E. Dobkina, V. Deryuzhkina, V. Soroko. – L.: Khimiya, 1989.
9. *Kolesnikov V., Mihaylichenko A., Peshkova L. Osobennosti kataliticheskoi ochistki «khvostovykh» gazov ot oksidov azota v proizvodstve azotnoi kisloty* // Khimicheskaya Tekhnologiya. – 2005. – No. 6. – P.17-19.

10. *Catalysis in Diesel engine NOx aftertreatment: a review* / M. Piumetti, S. Bensaid, D. Fino, N. Russo // *Catal. Struct. React.* – 2015. – Vol.1. – No. 4. – P.155-173.

11. Orlik S.N., Mironyuk T.V., Boichuk T.M. Structural functional design of catalysts for conversion of nitrogen (I, II) oxides // *Theor. Exp. Chem.* – 2012. – Vol.48. – No. 2. – P.73-97.

12. Lunev N. Ochistka gazovykh vybrosov ot oksidov azota metodom kataliticheskogo vosstanovleniya // *Rol' Khimii v Okhrane Okruzhayushei Sredy.* – 1983. – P.15-28.

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КІНЕТИЧНІ ЗАКОНОМІРНОСТІ ПРОЦЕСУ СЕЛЕКТИВНОГО ВІДНОВЛЕННЯ ОКСИДІВ НІТРОГЕНУ НА ПЛАТИНОВОМУ КАТАЛІЗАТОРІ СТІЛЬНИКОВОЇ СТРУКТУРИ

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В наведеній роботі розглянуто кінетичні закономірності процесу селективного відновлення оксидів нітрогену за допомогою аміаку на нанесеному платиновому каталізаторі стільникової структури. За даними розрахунків визначено область протікання даних реакцій на каталізаторах такого типу. Досліджено вплив температури та об'ємної швидкості на ефективність процесу очищення. На основі експериментальних досліджень та із застосуванням методів математичного моделювання отримані результати розрахунків констант швидкостей для реакцій відновлення оксидів нітрогену та окислення аміаку. Визначений вплив додавання одноосновних органічних кислот – оцтової та мурашиної – на активність каталізаторів даного типу. Показано, що найбільшу активність проявляють зразки каталізаторів, які були модифіковані мурашиною кислотою через те, що швидкість основних реакцій відновлення NO_x на ньому значно перевищує швидкість побічних реакцій окислення аміаку. Досліджено причини зниження активності каталізаторів при зміні температурного режиму. Показано, що перевищення температурного інтервалу сприяє зменшенню концентрації аміаку нижче стехіометрії, що призводить до зниження ефективності процесу.

Ключові слова: оксиди, носій, каталізатор, модифікатори, очищення, кінетика.

KINETICS OF SELECTIVE REDUCTION OF NITROGEN OXIDES ON A CELLULAR PLATINUM CATALYST

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Kinetics of the selective reduction of nitrogen oxides by using ammonia on a supported cellular platinum catalyst is considered in the article. The calculations allowed determining the kinetic areas of these reactions on the catalysts concerned. The effects of temperature and volumetric flow rate on the efficiency of the purification process were investigated. The values of the rate constants for nitrogen oxides reduction and ammonia oxidation reactions were calculated on the basis of experimental studies with the use of mathematical modeling methods. The influence of monobasic organic acids, acetic and formic acids, on the activity of the catalysts of this type was determined. The samples of catalysts modified with formic acid showed the highest

activity. This fact can be explained by a high rate of the main reactions of NO_x reduction compared to the rate of ammonia oxidation side reactions. The causes of a decrease in the activity of catalysts with change in temperature were established. The surplus of temperature results in a decrease in the concentration of ammonia below stoichiometry, which leads to the reduction in effectiveness of the process.

Keywords: oxides; carrier; catalyst; modifier; purification; kinetics.

REFERENCES

1. *Lung health in Europe – facts and figures.* European Lung Foundation, 2014.

2. Bradford M., Grover R., Paul P. Controlling NOx emissions. Part 2. *Chemical Engineering Progress*, 2002, vol. 98, no. 4, pp. 38-42.

3. Yan H., Qu H., Bai H., Zhong Q. Property, active species and reaction mechanism of NO and NH_3 over mesoporous Fe-Al-SBA-15 via microwave assisted synthesis for NH_3 -SCR. *Journal of Molecular Catalysis A: Chemical*, 2015, vol. 403, pp. 1-9.

4. Watson J.M., Ozkan U.S. Role of NH_3 as an intermediate in reduction of NO with CH_4 over sol-gel Pd catalysts on TiO_2 . *Journal of Molecular Catalysis A: Chemical*, 2002, vol. 192, pp. 79-91.

5. Yokoyama C., Bharadwaj S.S., Schmidt L.D. Platinum-tin and platinum-copper catalysts for autothermal oxidative dehydrogenation of ethane to ethylene. *Catalysis Letters*, 1996, vol. 38, pp. 181-188.

6. Loboyko A., Vekshin V., Markova N., Vorozbiiyan M., Shapareva L. Issledovanie vliyaniya tekhnologii prigotovleniya katalizatora na raspredelenie kataliticheski aktivnogo veschestva po poverkhnosti nositelya [Investigation on the effect of preparation technology on the distribution of catalytic substances over the carrier surface]. *Suchasni Problemy Tekhnologii Neorganichnykh Rechovyh*, 2008, no. 2(10), pp. 59-62. (in Russian).

7. Escudier M.P., Poole R.J., Presti F., Dales C., Nouar C., Desaubry C., Graham L., Pullum L. Observations of asymmetrical flow behaviour in transitional pipe flow of yield-stress and other shear-thinning liquids. *Journal of Non-Newtonian Fluid Mechanics*, 2005, vol. 127, pp. 143-155.

8. Mukhlenov I., Dobkina E., Deryuzhkina V., Soroko V., *Tekhnologiya katalizatorov* [Technology of catalysts]. Khimiya, Leningrad, 1989. (in Russian).

9. Kolesnikov V., Mihaylichenko A., Peshkova L. Osobennosti kataliticheskoi ochistki «khvostovykh» gazov ot oksidov azota v proizvodstve azotnoi kisloty [The features of the catalytic purification of end gases from nitrogen oxides in the production of nitric acid]. *Khimicheskaya Tekhnologiya*, 2005, no. 6, pp. 17-19. (in Russian).

10. Piumetti M., Bensaid S., Fino D., Russo N. Catalysis in Diesel engine NOx aftertreatment: a review. *Catalysis, Structure & Reactivity*, 2015, vol. 1, no. 4, pp. 155-173.

11. Orlik S.N., Mironyuk T.V., Boichuk T.M. Structural functional design of catalysts for conversion of nitrogen(I, II) oxides. *Theoretical and Experimental Chemistry*, 2012, vol. 48, pp. 73-97.

12. Lunev N. Ochistka gazovykh vybrosov ot oksidov azota metodom kataliticheskogo vosstanovleniya [Purification of gaseous emissions from nitrogen oxides by means of catalytic reduction]. *Rol' Khimii v Okhrane Okruzhayushei Sredy*, 1983, pp. 15-28. (in Russian).