

TECHNICAL SCIENCES

LOW TEMPERATURE OXIDATION OF AMMONIA TO N₂O OVER MIXED OXIDE CATALYSTS

Bliznjuk O.
Ogurtsov A.
Masalitina N.

Abstract

The study is devoted to development of technology of catalytic ammonia oxidation to nitrogen(I) oxide. The process of low-temperature oxidation of ammonium on oxidizing catalysts has been investigated for production of nitrogen(I) oxide to be used for medical purposes and organic synthesis.

Mixed oxide catalysts under various technological parameters were investigated. Experimentally validated concepts became the basis for creation the technological process of ammonia oxidation. Technological scheme of nitrogen(I) oxide production for organic synthesis was developed. The developed technological process is proposed for industrial implementation and appropriate output data are provided for industrial design.

Keywords: technology of nitrogen(I) oxide, ammonia, mixed oxide catalysts, reaction zones, technological parameters.

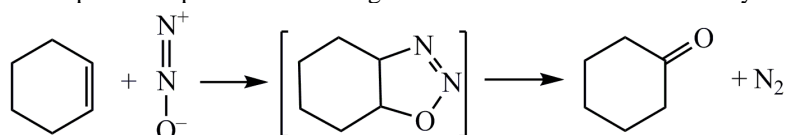
The process of low-temperature catalytical oxidation of ammonia has been investigated for production of nitrogen (I) oxide for medical purposes and organic synthesis. The investigation has been carried out by the stage separation approach with ammonia oxidation occurring in several reaction zones, which characterized by different catalytic conditions.

Introduction

Nitrogen (I) oxide applies as a soft anesthetic in medicine. In current medical practice it is used mainly in a mixture with other, more powerful inhalation narcotics [1]. Due to low toxicity and good solubility in lipophilic media N₂O is also used in the food industry, in particular, as a foaming gas [2]. Nitrogen (I) oxide is one of three interstellar space compounds containing

the N-O bond [3]. Within the last several decades the environmental effects of nitrogen (I) oxide have been a subject of constant interest of scientific ecologists. There is a clear connection of the "laughing gas" with destruction of the ozone layer. Research has shown that an average stability of N₂O in the lower atmosphere is about 120 years, since no necessary conditions for its chemical transformation are present in these atmospheric layers. Nitrogen (I) oxide diffuses from troposphere to stratosphere, where it is decomposed by direct photolytic dissociation [4].

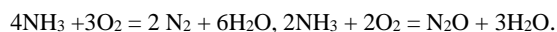
Potentially, N₂O is a powerful oxidizer. Recently the use of N₂O as an oxidizer under the heterogeneous catalysis conditions in reactions of selective oxidation of aliphatic and aromatic hydrocarbons and oxidizing condensation of the lowest alkynes are discussed [5, 6]:



For these applications the substantial attention is focused on the improvement of the nitrogen (I) oxide production technology [7-11]. Nitrogen (I) oxide is produced for medical purposes by thermal decomposition of ammoniac saltpeter. The reaction proceeds at temperature 530-550 K. In addition to the main reaction, a number of side reactions of formation of elementary nitrogen, NO, N₂O₄, N₂O₃ proceed in the specified temperature interval. Leaving the reactor, the gas mixture is purified from impurities and moisture. Then, the gas is compressed, and liquid nitrogen (I) oxide is poured out the steel cylinders of 10 l capacity. The hazards of the existing methodology of the thermal decomposition of ammonia nitrate involve the possibility of explosion of ammonia nitrate at heating and speeding up of the side reactions with increasing temperature.

The catalytic oxidation of ammonia to nitrogen (I) oxide at low temperatures (200–400°C) is a promising and more economically efficient technique. The cata-

lytic oxidation of ammonia by technical oxygen to nitrogen (I) oxide has been investigated by N.I. Il'chenko [13]. N₂ and N₂O are formed during low temperatures ammonia oxidation in reactions:



In the course of these reactions the formation of unstable intermediate particles (OH, ONH₃, ONH₂, NH₂, N, NH etc.) is also possible in parallel and sequential stages. In the present work we study different steps of the ammonia oxidation process and determine the influence of each step on the product yield. For this purpose, the ammonia oxidation reaction steps are carried out in separate reaction spaces, each having a different catalyst. To some extent, this approach avoids parallel reactions that may occur within a single reaction space and that are responsible for nitrogen unbounding. The influence of various technological parameters and various catalysts [14] on the ammonia oxidation process

and production of nitrogen (I) oxide can be investigated as well.

Experimental

The measurements have been carried out in a reactor with two spatially separated catalysts (Fig. 1a). This allowed us to investigate individual stages of ammonia oxidation and the influence of various stages on

the product yield as well as to avoid the parallel reactions that can occur in same reaction space and result in unbounding of nitrogen. The influence of technological parameters on the process of ammonia oxidation to nitrogen (I) oxide is studied for a variety of catalysts.

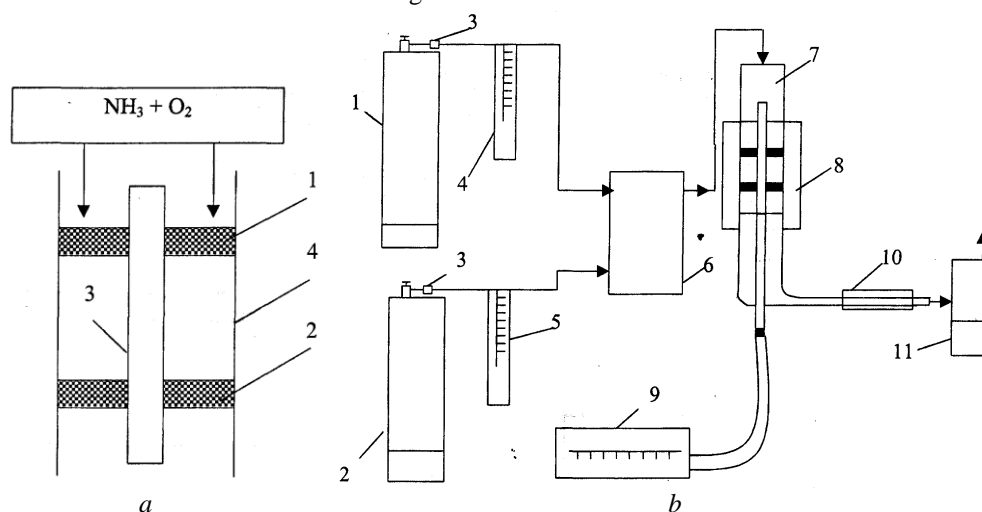


Fig. 1. The laboratory setup for the N_2O production. a – The catalysts arrangement in the reactor: 1, 2 – catalysts, 3 – thermocouple, 4 – reactor body. b – The laboratory installation: 1, 2 – cylinders with ammonia and oxygen, 3 – reducer, 4, 5 – rheometers, 6 – amalgamator of gases, 7 – reactor, 8 – heater, 9 – thermometer, 10 – refrigerator, 11 – condensate collector.

The catalysts for ammonia oxidation were prepared from oxides of bismuth, manganese, cobalt, aluminum and zirconium as well as from nitrates of these metals. Metal oxides of platinum and palladium generated from H_2PtCl_6 and $PdCl_2$ were applied as additives. Cordierite having the $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ structure was used as a catalyst carrier. Upon mixing of the metal oxides with the activators, the active phase was deposited on cordierite. Before ammonia oxidation the catalysts were heated to 473 K for two hours at the presence of an oxygen flow. The basic characteristics of the catalysts are summarized in Table 1.

A layer of catalyst 2 was stacked on the quartz grid of the reactor. A layer of broken quartz glass with particle sizes from 3 to 4 mm was located above the catalyst layer. A layer of catalyst 1 was stacked on top of the broken quartz glass layer. The design of the device allowed us to vary the distance between the catalysts up to 55 mm. The experiments show that in the system containing two separate catalyst layers, the N_2O yield can be sharply increased by 7 to 15 percent depending on the separation distance between layers. However, the some negative phenomena were observed in parallel with increase of the yield. If the catalyst 1 begins to work in an autonomous thermal mode, the ammonia oxidation process takes place solely on catalyst 1, and the temperature of this catalyst sharply increases. As a

result the temperature of catalyst 2 decreases below the ignition temperature and catalyst 2 stops working. If the catalyst 2 is heated externally, then catalyst 2 switch on and dominates in the catalysis. As a result catalyst 2 uncontrollably heats up and catalyst 1 stops working as soon as its temperature decreases below the ignition temperature.

In order to eliminate the mutual influence of the catalysts and provide the more stable working conditions a series of experiments have been carried out in a quartz reactor ($d = 20$ mm). The design of reactor allowed us to increase the distance between the catalysts up to 90 mm. In this way, the temperature of one of catalysts was fixed in the range 200–225°C, while the temperature of the other catalyst was slowly changed. The outlet nitrous gases were tested for the content of nitrogen (I) oxide by gas chromatography method.

Results and Discussions

A low-temperature oxidation of ammonia exhibits several unusual feature. At low temperatures the reaction mainly proceeds to N_2 and N_2O , while at high temperatures NO is produced much more efficiently. Formation of unstable intermediate products, such as O , OH , ONH_2 , NH_2 , N , NH , HNO etc., is also possible at low temperatures. The dependence of the N_2O yield on the temperature differences between the two catalysts is illustrated in Fig. 2.

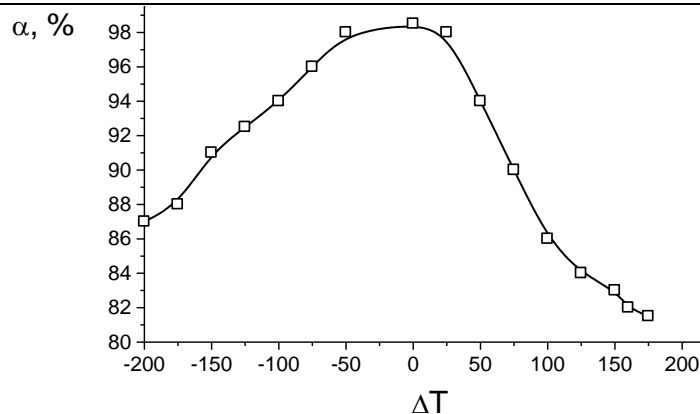


Fig. 2. The dependence of degree of ammonia oxidation into N_2O on temperature difference.

The data were obtained with manganese-bismuth-aluminum [14] as catalyst 1 and manganese (II) oxide promoted by palladium [15] as catalyst 2. Fig. 2 shows the maximum yield at $\Delta T = 0$. The temperature dependences of the nitrogen (I) oxide yield at various gas flow

rate are shown in Figs. 3, 4. The data show that at optimum temperatures and low concentrations of ammonia in the gas mixture the N_2O yield can reach 98–99%.

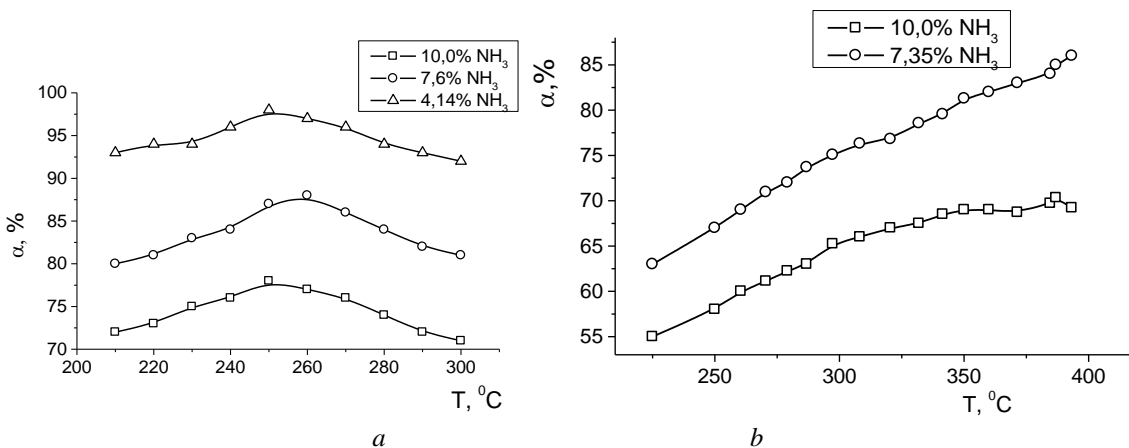


Fig. 3. Temperature dependence of ammonia oxidation degree to N_2O at catalyst $V_2O_5 + 0.1\%Pt$:
 $a - v = 0.005 \text{ m/s}$, $b - v = 0.015 \text{ m/s}$

At high ammonia concentration the N_2O yield can be decreased considerably. The N_2O yield reaches 80–82% for a given catalyst at the linear gas flow rate $v = 0.005 \text{ m/s}$ (see Fig. 3a) and ammonia concentration of 10%. Under these conditions an optimal temperature of the process is in the range 210–270°C. The N_2O yield

reaches 98–99% at optimal temperature and 4.14% ammonia concentration in gas mixture. It is necessary to note that the competing side reactions leading to the formation of nitrogen do not take place at the optimal temperature. At temperatures below 200°C the reaction rate is decreased considerably and ammonia remains in the gas mixture even after passing through the catalyst.

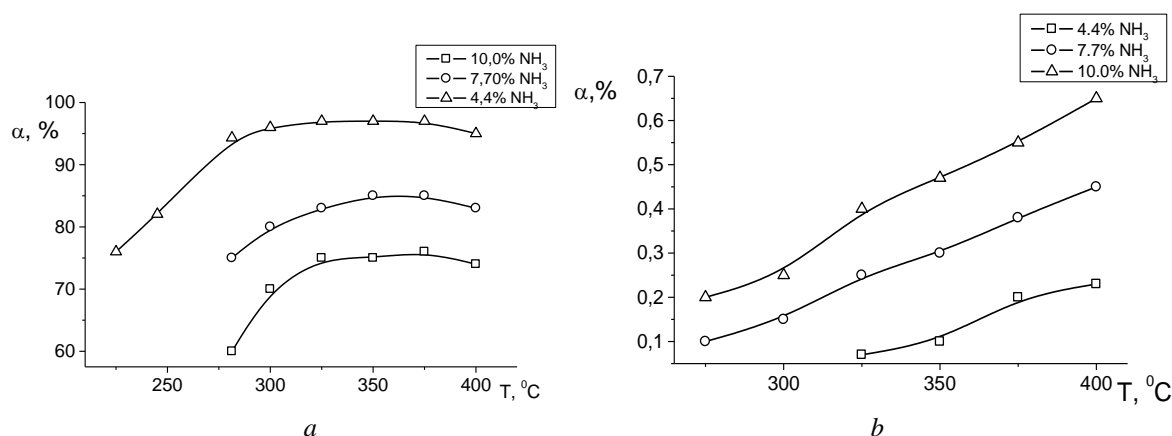


Fig. 4. Temperature dependence of ammonia oxidation degree: $a - \text{to } N_2O$, $b - \text{to } NO$. Catalyst $V_2O_5 + 0.1\%Pt$,
 $v = 0.025 \text{ m/s}$.

Figure 3b shows the results of investigation of the transformation of ammonia to nitrogen (I) oxide at various temperatures and the linear gas flow rate $v = 0.015$ m/s. Figures 4 (a,b) shows the temperature dependence of the degree of transformation of NH_3 to N_2O and the yield of the higher oxides of nitrogen. The data indicate that an optimal temperature of transformation of NH_3 to N_2O at the ammonia concentration of 10% can be found in the range 340–480°C, while at the ammonia concentration of 7.7% it is situated in the range 330–370°C. With the ammonia concentration 4.4% the degree of transformation of ammonia into nitrogen (I) oxide is very close to 98–99% at temperatures above 340°C. For the ammonia concentrations 10%, 7.7% and 4.4% the parallel side reactions occur at temperatures above 250, 290 and 330°C, accordingly.

Comparison of the N_2O yields at various levels of ammonia specific loading on the catalyst and at various ammonia concentrations gives the following results. With the specific ammonia loading on the catalyst 11.76 kg/m² and ammonia concentration of 7.7%, the N_2O yields 75% at 280°C that avoids formation of the higher nitrogen oxides. The same yield was obtained at the specific ammonia loading on the catalyst 11.4033 kg/m². At the 10% ammonia concentration in gas mixture and the specific ammonia loading on the catalyst 15.27 kg/m², the N_2O yield at 280°C was 57%. Thus, at the ammonia concentration of 10% the N_2O yield is lower than at the ammonia concentration of 7.7%. Moreover, the higher nitrogen oxides can be formed at 280°C and ammonia concentration of 10%. A pure nitrogen (I) oxide without the higher oxides is formed at

the ammonia concentration of 10% only if temperature is decreased to 250°C. However, at this temperature the degree of ammonia transformation is 40% and the N_2O yield is only 7.9 kg/m². At the ammonia concentration in the initial gas mixture equal 4.4% and the specific loading on the catalyst equal 6.7 kg/m², N_2O yield is as low as at the ammonia concentration of 7.7%. The concentration of ammonia in gas mixture is a more valuable parameter in the oxidation process than the catalyst specific loading.

An increase of catalyst specific loading at the ammonia concentration of 10% results in a sharp decrease in the degree of transformation of ammonia into nitrogen (I) oxide (Table 1). The N_2O outlet sharply decreases as well. For example, the growth of catalyst specific loading by factor of 5 increases the N_2O yield only by factor of 2.45. At the same time with the ammonia concentration of 7.5% a factor of 5 growth of the catalyst specific loading increases the N_2O yield in 4.44 times. With a further decrease of the ammonia concentration to 4.1–4.4%, the N_2O yield is increased 5.2 times at 5.3 times growth of the catalyst specific loading. With a simultaneous decrease of the ammonia concentration and increase of the catalyst specific loading, the N_2O yield is increased as well. The temperature interval within which the N_2O yield is near 98–99% is reduced. For example, if the gas flow rate is 0.005 m/s and ammonia concentration in gas mixture is 7.6%, the width of the favorable temperature interval is about 140°C. If the gas flow rate is increased to 0.025 m/s, the width of the favorable temperature interval decreases to 60°C.

Table 1

Parameters of the oxidation of ammonia to nitrogen (I) oxide

Linear gas rate, m/s	Catalyst capacity, kg NH_3 /m ²	NH_3 (inlet), %	Degree of NH_3 conversion, %	N_2O yield, kg /m ²	Catalyst temperature range, °C	Contacting time with catalyst, s
0.005	3.04	10.00	82	3.23	200-300	2.22
	2.31	7.60	86	2.57	200-340	
	1.26	4.14	99	1.61	200-350	
0.015	9.85	10.70	60	5.91	210-240	0.806
	6.77	7.35	75	5.08	210-290	
0.025	15.27	10.00	40	7.9	225-245	0.483
	11.76	7.70	75	11.41	220-280	
	6.72	4.40	97	8.4	220-320	

Conclusions

The results of the investigation of the low-temperature ammonia oxidation process using two catalysts located in separate reaction zones allows us to control and optimize the yield of nitrogen (I) oxide. The proposed design of the reaction chamber provides the increase of the N_2O yield by 7–15% under autothermally conditions of ammonia oxidation. The degree of ammonia oxidation into nitrogen (I) oxide is increased without any detectable nitrogen unbounding. The results of the investigation of the ammonia oxidation process using several catalysts and a variety of gas mixture flow rates, temperatures and catalyst specific loadings show that under optimal conditions a practically complete transformation of ammonia into nitrogen (I) oxide is possible.

REFERENCES:

1. J. O'CONNOR, Can. J. Anst., **37**, 603, 1990.
2. A.V. LEONT'EV, O.A. FOMICHEVA, M.V. PROSKINA, N.S. ZEFIROV, Usp. Khimii, **70**, 107, 2001.
3. L.M. ZIURYIS, A.J. APPONI, J.M. HOLLEIS, L.E. SNYDER, Astrophys. J., **436**, 187, 1994.
4. S.S. PRASAD, Geophys. Res., Sect. D, Atoms, **102**, 21527, 1997.
5. A.S. KHARITONOV, V.I. SOBOLEV, G.I. PANOV, Usp. Khimii, **61**, 2062, 1991.
6. A. REITZMANN, M. HAFELE, G. EMIG, Trends Chem. Eng., **3**, 63, 1996.
7. M. DEBOER, H.M. HUISMAN, R.J.M. MOS, R.G. LELIVED, A.J. VANDILLEN, J.M. GEUS, Catalysis Today, **17**, 189, 1993.

- 8.R. UKROPEC, B.F.M. KUSTER, J.C. SCHOUTEN, R.A. VAN SANTEN, *Appl. Catalysis B*, 23, 45, 1999.
- 9.T. CURTIN, F. O'REGAN, C. DECONICK, N. KNUTTLE, B.K. HODNETT, *Catalysis Today*, 55, 189, 2000.
10. J. LEPPAELAHTI, T. KOLJONEN, M. HUPA, P. KIPLINEN, *Energy and Fuels*, 11, 39, 1997.
11. G. BAGNASCO, L. BENES, P. GALLI, M.A. MASSUCCI, P. PATRONO, G. RUSSO, M. TURCO, *Stud. Surf. Sci. and Catalysis*, 119, 653, 1998.
12. V.F. POSTNIKOV, L.L. KUZ'MIN, N.K. TSAL'M, *Zh. Khim. Prom.*, 13, 1348, 1936 (Rus).
13. N.F. IL'CHENKO, *Usp. Khim.*, 45, 2168, 1976.
14. N.F. IL'CHENKO, D. Techn. Sci. Thesis, Technical University, Kiev 1982.
15. V.I. ATROSHCHENKO, A.S. SAVENKOV, A.P. ZASORIN, *Khim. Tekhnolog.*, 3, 23, 1971 (Rus).