

# KINETIC MODELING OF THE CATALYTIC AMMONIA OXIDATION TO N<sub>2</sub>O

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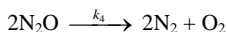
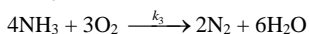
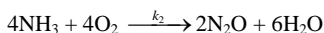
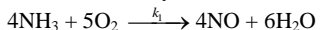
The process of low-temperature catalytical oxidation of NH<sub>3</sub> has been investigated for production of N<sub>2</sub>O for organic synthesis. In the recent years, nitrous oxide has become used as a mild oxidizer for partial oxidation of hydrocarbons, for example, oxidation of benzene to phenol. The catalytic oxidation of ammonia to N<sub>2</sub>O at low temperatures (200–400°C) is a promising and more economically efficient technique. Therefore the process of direct ammonia oxidation is of interest to numerous researchers [1–4].

A mathematical model of the process of ammonia oxidation on the oxide catalyst has been developed.

The studies [4–5] confirm the assumption about the mechanism of the ammonia catalytic oxidation on the oxide catalyst, give a kinetic model of the reaction, and allow us to determine the conditions of maximum N<sub>2</sub>O-output. As the analysis of the bibliography and our experimental research has shown, to ensure the maximum N<sub>2</sub>O-selectivity and high intensity of the process it is necessary to maintain external diffusion conditions. At low NH<sub>3</sub> concentration on the catalyst surface, which is typical for external diffusion conditions, the rate of its oxidation to NO и N<sub>2</sub> decreases dramatically and NH<sub>3</sub> selective oxidation to N<sub>2</sub>O takes place.

To create a mathematical model of the ammonia oxidation to N<sub>2</sub>O with due consideration of N<sub>2</sub>- and NO-synthesis, a complex of physicochemical, kinetic and technological research has been done. The analysis of the data shows that along with a high maximum N<sub>2</sub>O output, a simultaneous oxidation of ammonia to NO and N<sub>2</sub> is observed, though the rate of these processes is low. At the same time the conversion of NO into N<sub>2</sub> was revealed.

Stoichiometric basis of ammonia oxidation reaction routes, taking into account the formation of nitrogen I oxide for oxide catalyst, has the following form:



Modeling of the process is reduced to obtain the mathematical description of the process in the catalyst bed taking into account the assumed reaction mechanism. Oxygen on the catalyst surface at a high temperature is mainly in the dissociated state. The ammonia adsorption, as well as its dissociation and formation of intermediates interacting with each other, which leads to the formation of N<sub>2</sub>O, NO, N<sub>2</sub>, H<sub>2</sub>O, and being released at 350-360°C, take place on the free catalyst surface.

In the process of catalysis ammonia acts as an electron-donor, and oxygen as an electron-acceptor. Having adsorbed, O<sub>2</sub> molecules attach electrons from the catalyst surface and turn into oxygen surface atoms (step 1). On step 2 NH<sub>3</sub> molecule donates electrons from the catalyst surface which is not covered with oxygen, N-H bonds are thus weakening and the imido-particles are being formed. On the catalyst surface coated with oxygen, ammonia forms particles of the imide-type (step 3), which are then recombining to form nitrogen (step 7). Further addition of oxygen to the imide (steps 4, 5) leads to the formation of N<sub>2</sub>O. Steps 6, 8, and 9 are connected with N<sub>2</sub>O, N<sub>2</sub> and H<sub>2</sub>O formation.

The proposed detailed mechanism of the process has been used for deriving kinetic equations, which describe the reactions on the catalyst surface and relate to the formation of O, N<sub>2</sub>O, N<sub>2</sub>.

The system of equations, representing the rates of the certain steps and excluding the concentration of intermediates, form a kinetic model of the reaction. The rates on the routes I–IV are:  $r_1 = k_1 P_{\text{NH}_3} \cdot P_{\text{O}_2}^{0.5}$ ;  $r_2 = k_2 P_{\text{NH}_3} \cdot P_{\text{O}_2}$ ;  $r_3 = k_3 P_{\text{NH}_3}$ ;  $r_4 = k_4 P_{\text{N}_2\text{O}}^2$ , where:  $k_1, k_2, k_3, k_4$  – kinetic constants. The kinetic model of the reaction connected with the ammonia expenditure and N<sub>2</sub>O

formation has the following form:

$$r_{\text{NH}_3} = -k_1 P_{\text{NH}_3} \cdot P_{\text{O}_2}^{0.5} - k_2 P_{\text{NH}_3} \cdot P_{\text{O}_2} - k_3 P_{\text{NH}_3}$$
$$r_{\text{N}_2\text{O}} = k_1 P_{\text{NH}_3} \cdot P_{\text{O}_2}^{0.5} - k_4 P_{\text{N}_2\text{O}}^2$$

The process in the catalyst bed for external diffusion condition is characterized by a large temperature gradient. At small distance – a few centimeters in front of the catalyst – the gas is heated by the amount of the adiabatic heat-up of the reaction mixture from 200 to 360°C. This can lead to significant longitudinal heat and mass transfer. However, the effective coefficients of longitudinal diffusion and thermal conductivity of the gas phase are small and longitudinal heat transfer is carried out mainly along the solid skeleton of the catalyst bed. When describing the process the influence of the flows, arising in non-isothermal boundary layer of multi-component mixture (Stefan flow), thermal diffusion, as well as diffusion thermal conductivity, can be neglected, since the volume of the reaction mixture does not vary by more than 10%, and it is highly diluted with inert gas N<sub>2</sub>, molecular weights of components and, thus, their diffusion coefficients differ little [6]. The temperature of the catalyst in the bed of the oxide catalyst is assumed to be constant and is determined by the adiabatic heating of the coming reaction mixture. On this basis, to describe the process a model of plug-flow for the gas phase with the use of material balance equations for each component is accepted.

The degree of NH<sub>3</sub>-oxidation on oxide catalysts was calculated according to the developed mathematical model. For calculating this process it is necessary to know the coefficients of heat and mass transfer from the gas flow to the catalyst, as well as the physical and chemical properties of the mixture, depending on the temperature, pressure and composition of the mixture.

On solving the inverse problem of chemical kinetics, using the experimental data, we determined reactions rates constants connected with the formation of N<sub>2</sub>O (*k*<sub>1</sub>), NO (*k*<sub>2</sub>), N<sub>2</sub> (*k*<sub>3</sub>) and N<sub>2</sub>, resulting from the nitrogen oxide decomposition (*k*<sub>4</sub>), and the concentrations of the substances on the catalyst surface.

The comparison of calculating and experimental conversion coefficients shows good coincidence, the difference is not more than 1–3%.

A mathematical model of the oxidation process of NH<sub>3</sub>, considering the physical and chemical properties of the ammonia-air mixture and nitrous gas, has been developed; the rate constants and their temperature dependence have been determined. This will allow determining the optimal process conditions of NH<sub>3</sub> oxidation on the oxide catalyst at different pressures in a wide range of process parameters. On the basis of the developed model, a program for calculating the NH<sub>3</sub> oxidation reactor using the oxide catalyst has been created. During the operation process, the volume and the surface of the catalyst are changed. The mathematical model referring the rates of ammonia oxidation steps to a mass unit of the oxide catalyst has been derived in the research.

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