

Introduction Ozone finds wide application in such important industrial processes like: purification of drinking water, bleaching of textiles, oxidation of sulfurous gas, complete oxidation of exhaust gases from production of nitric acid and production of many organic compounds [1]. Ozone in the atmosphere protects the Earth's surface against UV radiation, but on the ground level it is an air contaminant [1-3]. At this level ozone can be removed by adsorption, absorption, thermal and catalytic decomposition. The most effective catalysts for ozone decomposition are based on manganese oxide [4-7]. The main method for purification of waste gases containing residual ozone is the heterogeneous catalytic decomposition. Noble metals like Pt, Ag, Pd and transition metal oxides including Co, Cu, and Ni supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> also are effective catalysts in this reaction [8-14], as it can be mentioned for activated carbon fibers [15]. The decomposition of ozone is a thermodynamically favored process with a heat of reaction of  $\Delta H_{298}^0 = -138$  kJ/mol and free energy of reaction of  $\Delta G_{298}^0 = -163$  kJ/mol [16]. The ozone structure is resonance stabilized that is a reason for its relative stability. The coefficient of ozone decomposition  $g$  was used in other studies for investigation of NiO addition influence over cement-containing catalysts activity [17] and for study of thermal treatment influence over oxide catalyst activity [18]. The aim of present study is to apply mixed metal oxide catalyst for ozone decomposition, to investigate its behavior at different conditions and to determine its composition and surface properties using different physical methods for analysis.

Experimental The basic copper, manganese, nickel carbonates and clay-bearing cement are milled in advance, then carefully mixed, crushed and compressed under pressure 4 t/cm<sup>2</sup>. The resulting tablets were treated hydrothermally at temperature of 80°C for 6 hours, dried at 120°C for 6 hours and calcinated at 420°C for 6 hours. The metal oxide catalyst based on the mixture of manganese oxide (20 wt%), copper oxide (10 wt%), nickel oxide (30 wt%) and clay-bearing cement (40 wt%) was thermally modified at 500°C for 2 h and finally was applied in our investigation as catalyst for ozone decomposition in dry and water enriched gas flows. The catalyst was granulated and contained cylindrical grains with a diameter of about 5 mm and thickness of 3 mm. The reactor for kinetic measurements was a glass tube (6×150 mm) filled in with 0.08-0.12 g of catalyst. The kinetic measurements of ozone degradation were performed at flow rates ranging from 6.0 to 24 l h<sup>-1</sup> and ozone concentration - from 1.0 to 1.2 mM. Ozone was generated by passing dry oxygen through a high-voltage silent-discharge ozone generator. At 15-20 kV was achieved ozone concentration about 1 mM. The inlet and outlet ozone concentrations were monitored using an UV absorption-type ozone analyzer at 300 nm. The specific surface area of the catalyst (72 m<sup>2</sup>/g) was measured by N<sub>2</sub> adsorption-desorption isotherms at 77 K using BET method in a FlowSorb 2300 instrument (Micromeritics Instrument Corporation). Results and Discussion The catalytic activity was evaluated on the basis of the coefficient  $g$  [19] that is proportional to ozone decomposition rate and to catalyst efficiency. It has been already used in other studies [17, 18]: where  $w$  is the flow rate,  $V_t$ -specific heat

rate of ozone molecules,  $S$ -geometrical surface of catalyst sample and  $[O_3]_0$  and  $[O_3]$  - inlet and outlet ozone concentrations, respectively. In general, there is not exist precise estimation of  $g$  by solving the diffusion-kinetic equation. This is possible in some special cases, for example to find  $g$  using the approximate method of Frank-Kamenetsky (method of equally accessible surface) [20]. Equally accessible surface is that surface where in each section the molecules fall with equal probability. The rate of the chemical reaction on the surface is expressed by concentration of reacting molecules in the volume near the surface. For reactions of first order:  $ws = \kappa cs = \kappa c'$ . The parameters dimension is as follows:  $ws$  - (molecules/cm<sup>2</sup>.s),  $\kappa s$  и  $\kappa$  - (s<sup>-1</sup>) и (cm/s),  $cs$  и  $c'$  - (molecules/cm<sup>2</sup>) и (molecules/cm<sup>3</sup>). It has been suggested that the molecular flow from volume to surface does not depend on the reaction rate, and with approximation it is defined of the equation:  $j=b(c-c')$  where:  $b$  coefficient of mass transfer, having dimension as the rate constant  $k$ , equal to cm s<sup>-1</sup>,  $c$  and  $c'$ - concentration in the regions of the volume, where the flow is passing trough. The distance between the surface and the region with concentration  $c'$  the ozone molecules pass without collisions with average specific heat rate  $vT$ . The number of hits on unit of surface per unit of time  $z = vT c'$  and taking into account the definition of coefficient of ozone decomposition it has been found that: Thus the coefficient  $g$  is related to the rate constant  $k$ . Now we could consider the case when the surface, where the reaction takes place, is located in an unlimited volume of gas. In stationary conditions the molecular flow toward the surface is equal to the chemical reaction rate: where  $c$  - concentration of actives molecules standing to great distance from the catalytic surface. Thus the rate of reaction on the surface is expressed by the concentration in the volume and the effective rate constant that depends on the rate constant  $k$  and the coefficient of mass transfer  $b$ . Obviously: If  $b \gg k$ , then  $c'=c$  and  $k_{eff}=k$ : the total reaction rate is limited by the no hits stage with constant  $k$ . In this case the reaction proceeds in the kinetic region. If  $b$