Catalytic decomposition of N_2O, contained in waste gases originating from HNO_3 production

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The object of the present investigations is a catalyst sample possessing a spinel-like structure, comprising copper, zinc and aluminum oxides in a ratio Cu:Zn:Al = 1:1:4. The conditions of co-precipitation of copper - zinc ammonia-carbonate solutions and a solution of aluminum nitrate ensure nano-size dimensions of the precursors and high dispersion degree after calcination of the contact masses at a temperature of 900^0C. This fact predetermines the high activity of the catalyst during the testing in kinetic and diffusion regime of operation at gaseous hourly space velocities of W = 8500 h^{-1} and 17000 h^{-1}, T = 830^0C and inlet N_2O concentration = 1100 ÷ 1400 ppm, i.e. under conditions analogous to those in the industrial process. The degree of decomposition (α) is higher than 0.9. The catalytic sample having the above indicated composition is highly active in the reaction of decomposition of N_2O into N_2 and O_2 in the case of production of HNO_3 based on the method of Ostwald as early as in the first steps of the process – catalytic oxidation of NH_3, i.e. "secondary in sequence".
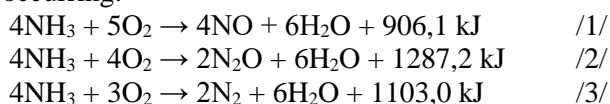
INTRODUCTION

In view of the increasing importance of the chemical branch in developing industry, the issue of monitoring harmful emissions, liberated into the atmosphere, is becoming a hot topic of the day. The problem of reducing „the hot house effect" is occupying one of the first positions among the top priorities, as a consequence of the global warming. The nitrous oxide N_2O is among the several hot house gases, having 300 times higher coefficient of the hot house effect compared to that of CO_2.

The total amount of N_2O emitted into the atmosphere has been evaluated to be 7.2×10^6 tons per year, and out of this amount the emissions during the production of HNO_3 are 0.4×10^6 t/y.

In the course of producing HNO_3 based on „Ostwald's process" the following reactions are occurring:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 906,1 \text{ kJ} \qquad /1/$$
$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O + 1287,2 \text{ kJ} \qquad /2/$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O + 1103,0 \text{ kJ} \qquad /3/$$

Among these three reactions it is only the reaction /1/, which is desirable. The purification of waste gases originating from the production of HNO_3 is accomplished by means of catalytic decomposition or reduction of the nitrogen oxides into elemental N_2. The current research and patent literature considers the problem of reducing the emissions of N_2O liberated in the production of HNO_3 through the „Ostwald's process" [1 - 4].

Some oxide catalysts have also been proposed for the decomposition of N_2O. Analyzing the available literature data it has been noted that the highest activity is manifested by the oxides of the transition metals belonging to Group VII (Rh, Ir, Co, Fe, Ni) and also by Group 1B – mainly Cu [5 - 9].

The authors of ref. [10] made a remark that the decomposition reaction of N_2O is sensitive with respect to the structure of the oxides. In some cases the oxygen vacancies are involved, while in other cases it is the coordinatively unsaturated transition metal ions that are taking part. High catalytic activity is displayed by zeolites of the Y – ZSM – 5 type (pentasil). In accordance with the mechanism of the reaction two classes of catalysts are being formed. The first ones are catalysts of the type Mn_2O_3, Fe_2O_3, NiO, $LaCoO_3$, Cu-ZSM-5, on which the decomposition is occurring on the oxygen vacancies / /:

$$N_2O + / \ /O_2 + N_2$$

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(O) + (O)O$_2$ + 2/ /

The catalysts of the second class/group are the zeolites, such as Fe-HZSM-5 and Co-HZSM-5, where the decomposition of N$_2$O involves the participation of isolated ions of the transition metals [Mn+]:

N$_2$O + [Mn+]N$_2$ + [Mn+]O

N$_2$O + [Mn+]ON$_2$ + O$_2$ + [Mn+]
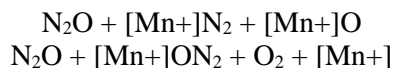
The catalytic properties of the catalysts of zeolite type are associated with the presence of α-sites, complexes of iron, stabilized in the matrix of the zeolite ZSM-5 [11, 12]. An iron oxide catalyst supported on Al$_2$O$_3$, prepared by the method of co-precipitation, manifested high catalytic activity and also mechanical stability during the reaction of N$_2$O conversion at T = 750^{0}C, in the presence of H$_2$O and NO [13]. Many oxide-supported catalysts for the above specified process contain oxides or spinels of Cu or Co as the active phase [6, 7, 9, 14]. Analyzing the variety of catalytic compositions it is stated that both the effect of the active spinel phase, as well as the influence of the nature of the support, should be taken into account [14 - 18].

The catalytic decomposition of N$_2$O using a model gas mixture analogous to that liberated in the production of HNO$_3$ is commented on in ref. [19, 20]. It is only a small number of the studied catalysts that have been tested under the actual industrial conditions in the N$_2$O decomposition reaction.

On the basis of the above presented survey of literature one can draw the conclusion that the most promising catalysts for N$_2$O decomposition are those based on oxides of the transition metals Rh, Ir, Co, Fe, Ni and copper oxide catalysts.

In this aspect the aim of our studies was to establish the optimal conditions for synthesizing a Cu-Zn-Al catalyst of spinel-type for decomposition of N$_2$O to N$_2$ and O$_2$, as an accessible and economically advantageous catalyst. The decomposition reaction is expected to occur at certain fixed values of the thermodynamic, kinetic and technological parameters, immediately after the contact mesh, in accordance with the industrial operation conditions.

EXPERIMENTAL

Preparation of the catalyst samples

The synthesis of the catalyst samples was described in the patent application [21]. The spinel-like structure is based on the oxides of Cu, Zn and Al at a ratio Cu:Zn:Al = 1:1:4, the phase composition comprising CuAl$_2$O$_4$ and ZnAl$_2$O$_4$. The initial precursors are in the form of solutions of dissolved (electrolytic) Cu, ZnO and metallic Al.

Copper and zinc are in the form of a copper-ammonia, respectively zinc-ammonia carbonate solution. Upon mixing the two solutions of Cu and Zn a copper-zinc ammonia-carbonate solution is obtained, which is the precipitating agent in the reaction system. The homogeneity of precipitation is achieved by a fixed set of conditions: pH factor – 5, 2÷7; temperature 60÷80^{0}C; time interval of precipitation 15÷30 min and aging time of the precipitate from 30 to 60 min. The so obtained system possesses a high degree of dispersion and the chemical and phase compositions are homogeneously distributed. The consecutive steps of the synthesis are trivial: filtering, washing until the absence of NO$_3^-$ ions, drying at T = 120 ÷ 150^{0}C, calcination at T = 350 ÷500^{0}C for 4 to 8 hours, forming of tablets or extruding the material, followed by calcination at a higher temperature T = 800 ÷ 1000^{0}C for 4 to 6 hours. This technological scheme ensures absence of any waste material and high catalytic activity and selectivity.

The catalyst sample **S** was prepared by the above described technology and then it was characterized after calcination at different temperatures. Another supported type of catalyst sample was synthesized for comparison. The support was α-Al$_2$O$_3$, while the supported phases were the oxides of Cu, Zn and Al at a ratio 1:1:4 (catalyst sample **S$_1$**).

Characterization of the catalyst samples

The structure and the phase composition of the catalyst samples were identified on a XRD apparatus Bruker Advance, using CuKα radiation and SolX Detector with 2θ ranging from 20^0 to 80^0 at a scan step of 0.04^0. The degree of dispersion of the phases was determined on the basis of the XRD analysis and in accordance with Scherrer′s rule L = k.λ/β.cos θ).

The express BET method was applied to measure the specific surface area, based on low-temperature adsorption of nitrogen – i.e. at the boiling temperature of liquid nitrogen 77K. The relative error of the method amounts to about 8%. The specific surface area and the pore size distribution of the two catalyst samples were measured on an automated apparatus NOVA Win/Nova Win – CFR Quantachrom – Gas Sorption System. The calculation of the surface area was done using the BET equation, whereupon the pore size distribution, as well as the average pore diameter were evaluated by DFT assuming a cylindrical model of the pores. The total pore volume was estimated in accordance with the rule of Gurvich ata relative pressure of 0.96.

The derivatographic analysis was realized using the STAPT 1600 TG-DTA/DSC apparatus, manufactured by LINSEIS Messgeräte GmbH, Germany; the monitored temperature interval was $20 \div 1550^0C$.

The catalytic activity testing was carried out in a three-channel integral isothermal reactor under kinetic control conditions. The space velocity was equivalent to 100 mm, respectively 200 mm height of the catalyst bed (i.e. $16\,000$ h^{-1}, respectively $32\,000$ h^{-1}). Under these hydrodynamic conditions the ratio H/D > 2 and D/dz > 3, the Peclet number was Pe > 120, i.e. conditions determining a plug flow reactor, which is most often occurring under industrial conditions of heterogeneous catalytic processes. In the ratio H/D and D/dz H is the height of the catalyst bed, D is the diameter of the reactor tube, while dz is the diameter of the catalyst granule. The concentration of N_2O was determined using a gas chromatograph equipped with a thermal conductivity detector (hot-wire detector HWD) and a packed-bed GC column of „Porapack Q" (the feed gaseous mixture was purified from NOx prior to the experiment). The catalytic activity was studied also on a pilot-plant scale reactor, under conditions analogous to those in the industrial process – catalyst grain size, catalyst loading (space velocity), height of the catalyst bed (100 mm and 200 mm), temperature 830^0C and pressure up to 100 mm H_2O column. The reaction mixture under consideration in this study, consisting of NOx, N_2O,

N_2 and O_2, was sampled out immediately after the contact meshes in the industrial installation.

RESULTS AND DISCUSSION

The process of the formation of the precursor, as well as the thermal transitions inside, are both of special importance in view of obtaining different structures and textures of the contact masses. Having this in mind we carried out differential thermal analysis (DTA), in order to trace the processes of phase transformations within a specific temperature interval. The phase transitions inside the S catalyst sample were observed within the T = $0 \div 1150^0C$ temperature interval. The selected parameters of precipitation – pH factor, time interval of precipitation and aging time of the residue predetermine the nature of the precipitate - mainly malachite and some isomorphous admixtures in the hydrozincite, $(Cu,Zn)_5(OH)_6(CO_3)_2$, established in our previous investigations [22]. The high percentage of Al_2O_3 content in the system and the initial lower pH value of precipitation pH = $6 \div 6.5$ – all these create conditions for precipitation of scarboite phase having composition $12Al(OH)_3 \cdot Al_2(CO_3)_3$, which is stable up to ~130^0C and passes over to metascarboite phase thereafter. The first observed endothermal effect in the course of the thermal analysis in the interval $150 \div 205^0C$ is an indication of the presence of this phase.
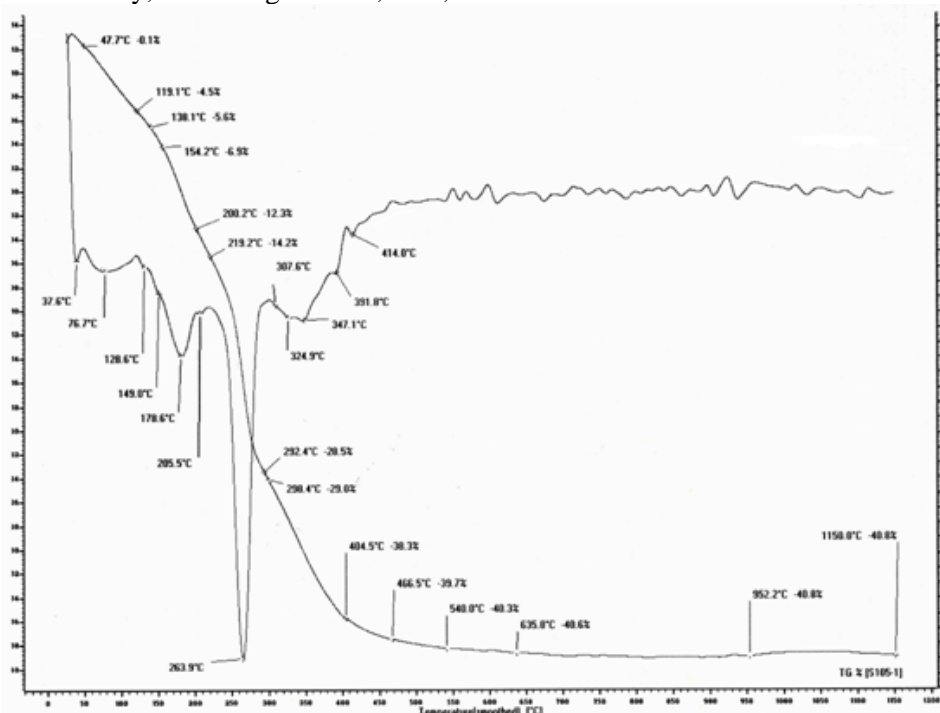

Fig.1. DTA and TG curves of the catalyst sample precursor S within the temperature interval T = $0 \div 1150^0C$

The hydroxyl-carbonate groups are decomposed upon increasing the temperature from 250^0C to 400^0C – this is the second endothermal effect with a maximum at $T = 264^0C$. In view of the combined process of co-precipitation of copper and zinc, it is most probable that there occurs isomorphous substitution in the hydrozincite - $(Zn,Cu)_5(OH)_6(CO_3)_2$ (Figure 1).

This substitution predetermines the nanometer-sized dimensions of the phases after calcination at considerably higher temperatures.

The phase composition, the particle sizes of the different phases and the pore size distribution in the system are factors of essential importance for the catalytic activity and for the stability of the composite catalyst sample. For this purpose we followed the changes occurring with the increase in the temperature and prolonging the duration of the calcination treatment of sample S in regard to the specific surface area variation and the degree of dispersion of the phases (Table 1, Figure 2). The dispersity was evaluated by the above indicated method.

Table 1. Specific surface area and degree of dispersion as functions of the calcination time interval and calcination temperature

Samples-τ(h)-T (^0C)	Specific surface area S (m^2g^{-1})	Dispersion, D (nm)
S – 4 - 400	203	3÷4
S – 2 - 830	112	7÷8
S – 4 - 830	102	12
S – 6 - 830	96	18
S – 8 - 1000	23	50

Figure 2 illustrates the XRD patterns of the catalyst sample **S** calcined at $T_{calc.}$ varying from 400 to 1000^0C and various time intervals of maintaining the calcination temperature. A characteristic feature, observable for this system, is that as early as $T = 400^0C$ spinel phases of Cu and Zn are appearing: 01-070-8181 (Gahnite – $ZnAl_2O_4$); 00-033-0448 ($CuAl_2O_4$). A limited presence of CuO phase max lines is observed. The high specific surface area of the catalyst sample is due not only to the homogenizing conditions of preparation during the precipitation of the precursor, but also to the content of Al_2O_3. The latter is the structure-forming and dispersing component in the system. This high surface area is preserved, in spite of the drastic increase in the temperature of calcination (up to 1000ºC) and the long time interval of maintaining such high temperature. Although spinel-phase formation is occurring at low temperatures the nanosize dimensions of the particles in the contact mass are preserved and this

fact is in correlation with the data reported in [23, 24]. It is probably the precursor of the studied catalyst that determines the high degree of dispersion of the phases. On the other side the presence of the two spinel phases of copper and zinc is the inhibiting factor causing the preservation of the nanosize crystallinity [25].
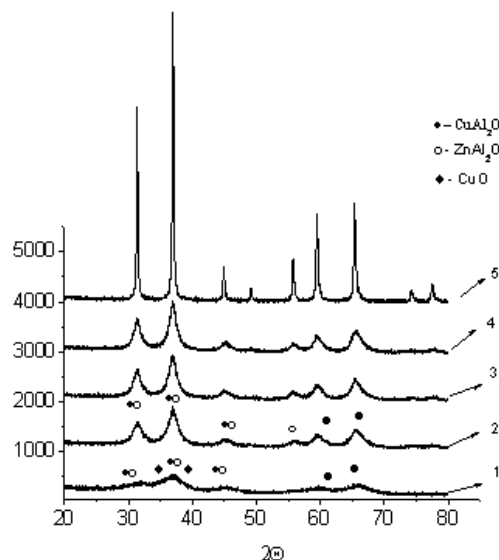

Fig.2. XRD patterns of the catalyst samples: 1 - S-4-400, 2 - S-2-830, 3 - S-4-830, 4 - S-6-830, 5 - S-8-1000

The adsorption isotherms of the samples S-4–400 and S-2–830 show the presence of mesopores. In the catalyst sample calcined at the lower temperature $T = 400^0C$, the system is monodisperse and the prevailing pore volume is within the interval 3 ÷ 9 nm. Upon increasing the temperature the appearance of bidispersity becomes observable, whereupon the peak at 4 ÷ 6 nm is comparatively narrow, while the second peak at 6 ÷ 14 nm demonstrates an increase in the relative share of pores of larger dimensions. The type of the adsorption isotherms can be classified as type IV, while the hysteresis loops belong to the type H2 according to the classification of IUPAC. There is very good coincidence between the calculated specific surface area, based on the isotherms, and that determined by the express method (Table 2, Figure 3).

The phase structural and physicochemical characteristics of the contact mass **S**, calcined at various temperatures and different time intervals of thermal treatment gave us the reason to expect a high catalytic activity in the reaction of N_2O decomposition in the reaction mixture NO_x, N_2O, N_2 and O_2, immediately after the contact meshes.

Table 2. Total pore volume and specific surface area of the catalyst samples

Samples	Specific surface area $S(m^2g^{-1})$	Total pore volume V_t (cm^3g^{-1})	Average pore diameter τ_{av} (nm)
S-4-400	213	$2.038.10^{-1}$	3.82396
S-2-830	111	$2.323.10^{-1}$	8.38132

The tabletted catalyst sample calcined at T = 900⁰C for 4 hours contains nanosize particles of diameter D ~ 25 nm and specific surface area S = 62 m²/g. The catalyst granules have dimensions D × d × h = 11 × 5 × 5 ± 1 mm. The degree of conversion of N_2O to N_2 and O_2 was taken as the measure of the catalytic activity and it was measured under the following conditions:

	Laboratory reactor	Pilot plant Reactor
Catalyst bed volume, ml	4	100
Size of granules, mm	0.63÷0.8 Kinetic regime	11 × 5 × 5 Diffusion regime
Catalyst bed temperature,(⁰C)	830	830
Pressure, bar	0.96	0.96
N_2O inlet conc., (ppm)	1100 ÷ 1400	
Space velocity, (W, h⁻¹)	8 500 17 000	8 500 17 000
Degree of decomposition, α_p	0.98 0.95	0.92 0.90

The gas mixture sample for this study was taken after the contact meshes of the industrial installation for the production of HNO_3 based on the method of Ostwald.

The catalyst sample **S₁** was studied under analogous conditions - this is the supported type of sample, which was tabletted into dimensions d × h = 12 × 12 mm and respectively its activity, taken as degree of decomposition of N_2O, is as follows:

- kinetic regime

    W = 16 000 h⁻¹

    α_p = 0.83

- diffusion regime

    W = 8 000 h⁻¹   W = 16 000 h⁻¹

    α_p = 0.62 α_p = 0.46

The drastic difference in the activities of the two contact masses shows the importance of the method of preparation of the synthesized precursor, as well as the effect of the genesis of different phases (phase formation) and the formation of different structures. The investigation proves that the low-temperature spinel formation process in the early stage of phase formation predetermines the high

dispersion degree of the phases, respectively the high specific surface area. Moreover, the isomorphous precursor phases of the synthesis by the method of co-precipitation of the composites are leading to Cu, Zn spinel phase formation, whereupon the alumina is the stabilizing component, which also causes dispersion and formation of specific structure.
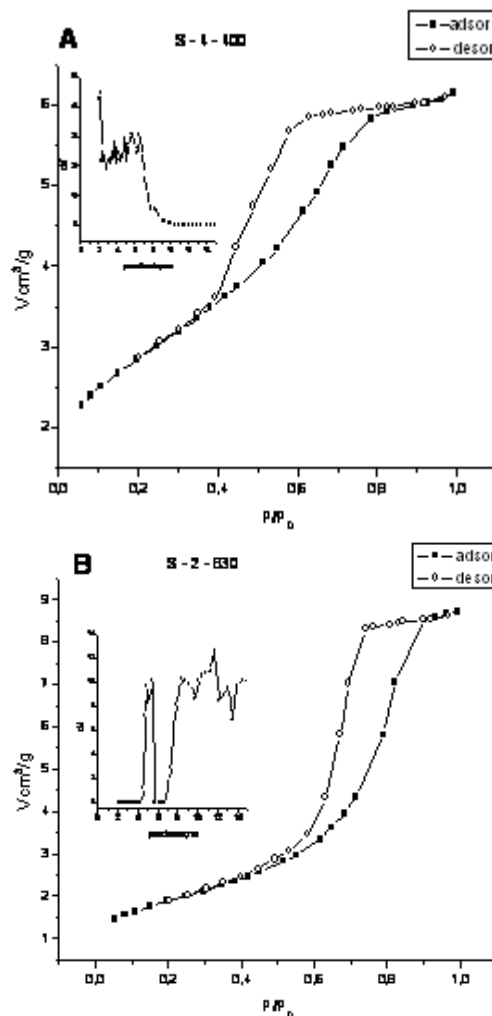

Fig.3. Adsorption isotherms and pore size distribution of catalyst samples: **A** – S-4-400 and **B**- S-2-830.

CONCLUSION

This gives us the reason to draw the following conclusions:

The catalyst composition having the ratio Cu : Zn : Al = 1 : 1 : 4, prepared by the method of co-precipitation from copper-zinc-ammonia carbonate solution and aluminum nitrate is a highly active catalyst for the decomposition of N_2O to N_2 and O_2, under industrial operation conditions from the production of HNO_3 by the method of Ostwald, as early as in the first stage – the catalytic oxidation of NH_3, i.e. "secondary in sequence".

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КАТАЛИТИЧНО ДЕКОМПОЗИРАНЕ НА N₂О ОТ ОТПАДНИ ГАЗОВЕ ПРИ ПРОИЗВОДСТВОТО НА HNO₃

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(Резюме)

Обект на изследванията е катализатор с шпинелоподобна структура на мед, цинк, алуминиеви оксиди в съотношение Cu:Zn:Al = 1:1:4. Условията на съутаяване от мед, цинк амонячно-карбонатни разтвори и разтвор от алуминиев нитрат осигуряват наноразмерност на прекурсорите и висока дисперсност след накаляване на контактните маси при температура 900⁰С. Това предопределя високата активност на катализатора при изследване в кинетичен и дифузионен режим при обемни скорости, W = 8500, 17000h⁻¹, T = 830⁰С и N₂O на вход = 1100 ÷ 1400ppm т.е. условия аналогични на промишлените. Степента на разлагане (α) е по-голяма от 0.9. Каталитичната композиция с посочения състав е високоактивен катализатор за декомпозиране на N₂O до N₂ и О₂ при производството на HNO₃ по метод Освалд още в първия стадий – каталитично окисление на NH₃, т.е. "secondary".