

PERSPECTIVE CATALYSTS FOR N₂O DECOMPOSITION

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ABSTRACT

This work describes the experimental results of catalytic activity investigation of massive metallic and supported oxide catalysts in the reaction of N₂O decomposition, as a potential and perspective rocket fuel. Obtained results allowed us to formulate recommendations for choosing the active components of catalysts: supports, noble and transition metal ions, preparation methods, etc., which can be a basement for developing the most active and stable catalyst for N₂O decomposition.

1. INTRODUCTION

Nitric oxide N₂O attracts attention as a perspective, highly active and ecologically pure mono-component rocket fuel, which has some advantages in comparison with other analogous fuels [1-4]. As an example, N₂O can be stored in a space apparatus as a liquid with gasification just before input into the thruster. The catalytic decomposition of N₂O produces highly energetic products, which can be used in micro-engines for correction, as well as in the air-regeneration systems of space apparatus.

During the process of N₂O decomposition, temperature in the catalytic layer can achieve 1600°C. Therefore, it would be necessary to develop catalysts of two types for a micro-rocket engine or a gas-generator: a highly active catalysts with high dynamic characteristics for the upper part of the reactor, and a less active one for the second part, closer to the nozzle (metallic or granulated) provided the thruster work at a high temperature area.

This paper describes our results on the development of active catalytic systems for N₂O decomposition, which can be used in future as a basement for creation of practical systems for space-rocket technique.

2. MATERIALS AND METHODS

Thermodynamic and chemical properties of N₂O, as well as working conditions in rocket thrusters initiated our work [5]. Technical details of samples preparation were described in detail in [4]. Granulated catalysts were prepared with the use of standard carriers by the method of frequent impregnation [6].

Different supports: refractory oxides (highly porous carriers) such as α -Al₂O₃, (γ + θ + α)-Al₂O₃, Al₂O₃-AlN,

Al₂O₃-CaO, ZrO₂, Al₂O₃-ZrO₂, SiO₂-Al₂O₃, SiO₂ (siloxane), SiO₂ (quartz), were studied in the work. Parameters of (γ + θ + α)-Al₂O₃ granules were: specific surface area, $S = 110$ m²/g; specific volume of pores, $V_{\text{pore}} = 0.34$ cm³/g; average diameter of granules, $d = 0.8$ – 1.2 mm [7].

The following catalytically active components (AC) for N₂O decomposition were tested:

- compact metal catalysts prepared from wires and alloys of noble metals or Nickel and its Chromium alloys;
- catalysts based on metal oxides supported on (γ + θ + α)-Al₂O₃: CoO, CuO, NiO, Cr₂O₃, Fe₂O₃, ZrO₂, and MnO₂
- catalysts based on noble metals supported on (γ + θ + α)-Al₂O₃: Rh, Ru, Ir, Pt, Pd. In the case of Rhodium, other supports were also used.

Catalytic activity was tested in a flowing-type reactor till heat temperature 1100° and in a rocket thruster. The scheme of the laboratory reactor was reported in [4]. The lay out of N₂O was equal to 100 cm³/min. The catalyst volume in the reactor was 10 cm³. The heating rate, $W_t = 5$ grad/min up to $T_{\text{max}} = 1100^\circ\text{C}$.

Before testing, all samples were treated with heating in air at 600°C during 3 hours for equal conditions. It was shown that after heating, Platinum samples were not changed. Samples prepared from Nichrome wire have changed their colour: this revealed formation thin oxide film on the wire surface; the mass of catalysts stayed quite the same. Only catalyst granules based on Nickel, underwent sufficient changes: they became green, and their mass increased at 1.5 %. Oxidation of Nickel wire was confirmed by the X-ray spectroscopic analysis.

The lowest temperature T_{min} , at which the reaction started, was used as a parameter for catalytic activity characterization. The beginning of N₂O conversion was recorded by the appearance of chromatographically measured O₂.

Paramagnetic species in the samples before and after the reaction were recorded with a standard X-band Bruker ESR spectrometer at 298 and 77 K.

3. RESULTS AND DISCUSSION

Fig. 1 shows typical curves of the important parameter, the specific surface area S , changes with the increase of the metal content in a catalyst in the case of Iridium,

Rhodium, Ruthenium and Cobalt supported on ($\gamma+\theta+\alpha$) Al_2O_3 . In all cases, S is decreased with enlarging of metal mass content although the degree of these changes is different. For other catalysts, their characteristics are presented in Tab. 1.

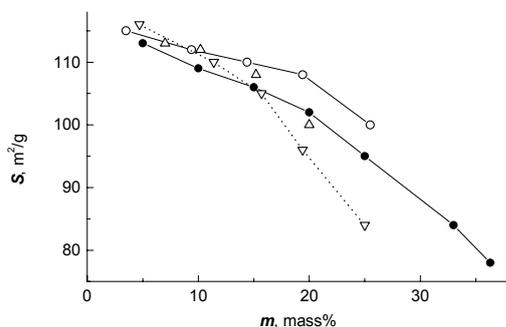


Figure 1. Dependence of specific surface area S on metal content in catalysts supported on ($\gamma+\theta+\alpha$) Al_2O_3 : Ir (\bullet), Rh (\circ), Ru (Δ), Co (∇)

Table 1. Specific surface area S and the packed density ρ of the supported catalysts

Active component	m , wt.%	ρ , g/cm ³	S , m ² /g
Pd	4,7 ^{a)}	1,03	115
	6,2 ^{b)}	1,04	110
	9,9 ^{b)}	1,06	95
Pt	5,5	1,05	114
	9,8	1,13	110
	13,1	1,18	105
NiO ^{c)}	6,4	1,02	112
	9,3	1,07	106
	20,4	1,29	87
Fe_2O_3 ^{c)}	19,0	1,35	110
MnO_2 ^{c)}	15,5	1,12	109
CuO ^{c)}	18,6	1,21	110
Cr_2O_3 ^{c)}	20,0	1,09	88

a) Prepared from $\text{Pd}(\text{NO}_3)_2$, and b) from PdCl_2 ; c) the content of AC calculated on the metal.

Typical dependences of N_2O decomposition degree with temperature for three samples: $\text{Rh}_2\text{O}_3/\text{Al}_2\text{O}_3$, ZrO_2 , and $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ are given in Fig. 2, from which one can see that temperature intervals of catalytic activity depend strongly on the metal nature in a catalyst. Noble metals, for example, Rhodium, were the most active. It should be also pointed out that the shape of such plots is typical for chemical and catalytic processes with the induction period, during which the auto-activation of the AC in the system occurs [8]. Three parameters one can use for characterization the activity of catalysts with such kinetics: the temperature of the beginning of the process T_{\min} (at the degree of N_2O conversion equal 0.03–0.05); temperature $T_{0.5}$ of 50% decomposition of N_2O ; or the temperature T_{\max} for the complete conversion of N_2O .

Also, it should be mentioned that in the case of low active supported catalysts with non-noble transition metals (e.g., $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, etc.), 100% conversion has not been usually achieved (Fig. 2), therefore the form of the curve and the T_{\max} value allowed us to assume the existence of some limitations for the diffusion of reagents and products inside the catalyst pores [9].

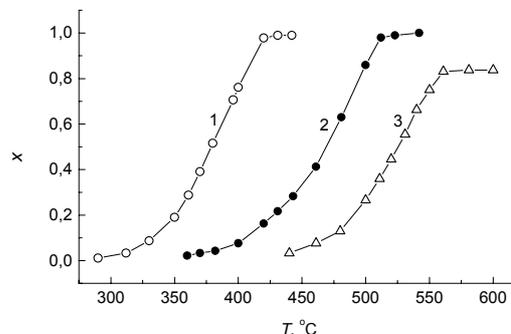


Figure 2. Dependence of N_2O decomposition degree on temperature for Rh/ Al_2O_3 (\circ), ZrO_2 (\bullet) and $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ (Δ) catalysts

For several investigated catalysts, parameters $T_{0.5}$ which can be measured with high accuracy, are listed in Tab. 2 for comparison. Experimental Arrhenius plots between the rate constant $\ln k$ and the reversed temperature T^{-1} allowed us to calculate the activation energies and the pre-exponential factors for all catalysts studied. They are given in Eqs. 1-3.

Table 2. Temperature of 50% decomposition of N_2O , $T_{0.5}$, in a laboratory catalytic reactor at different contents of the active component (AC) m , supported on Al_2O_3

Catalyst		$T_{0.5}$, °C
AC	M , wt.% ^{a)}	
Rh	4	325
	15	340
Pt	15 ^{b)}	295
	6	495
Pd	13	470
	5 ^{c)}	310
	6 ^{d)}	530
	13 ^{d)}	535
NiO	6	595
	9	590
Fe_2O_3	20	550
Cr_2O_3	19	555
CuO	20	510
MnO_2	19	510
	16	470

a) Calculated; b) washed in HNO_3 ; c) from PdCl_2 ; d) from $\text{Pd}(\text{NO}_3)_2$

Our experiments showed that all investigated catalysts of various types could be placed by their activity in the

reaction of N_2O conversion, by the reaction initiation temperature T_{min} , to the following ranges:

1. Metallic porous tablets made of metal wires (degree of conversion was equal to 0,05): Ni (510°C) > Pt, Pt-Rh, Pt-Ir (~560°C) > Ni-Cr (710°C)
2. Granulated catalysts based on highly porous oxides – supports (degree of conversion was equal to 0.2): ZrO_2 (430°C) > Al_2O_3 -CaO (505°C), Al_2O_3 - ZrO_2 (500°C) > $(\gamma+\theta+\alpha)$ - Al_2O_3 (510°C) > Al_2O_3 -AlN, SiO_2 - Al_2O_3 (565°C) > SiO_2 (600°C) > α - Al_2O_3 (610°C).
3. Granulated catalysts based on transition metals supported on $(\gamma+\theta+\alpha)$ - Al_2O_3 (degree of conversion was equal to 0.2): Co_3O_4 (415°C) > NiO (425°C) > MnO_2 (430°C) > CuO (440°C) > Cr_2O_3 (445°C) > Fe_2O_3 (465°C).
4. Granulated catalysts based on noble metals supported on $(\gamma+\theta+\alpha)$ - Al_2O_3 (degree of conversion was equal to 0.2): Rh (255°C) > Ru (320°) > Ir (330°) > Pt (430°) > Pd (490°C).

It was interesting to compare how the catalytic activity depends on the AC content. It was shown that such behavior differs much for various systems. Fig. 3 illustrates all types of possible changes.

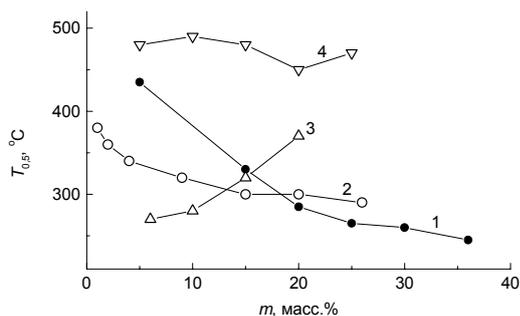


Figure 3. Changes of temperature $T_{0.5}$ of 50% N_2O conversion in a catalytic reactor vs. metal content of Ir (●), Rh (○), Ru (△), Co (▽) supported on $(\gamma+\theta+\alpha)$ Al_2O_3

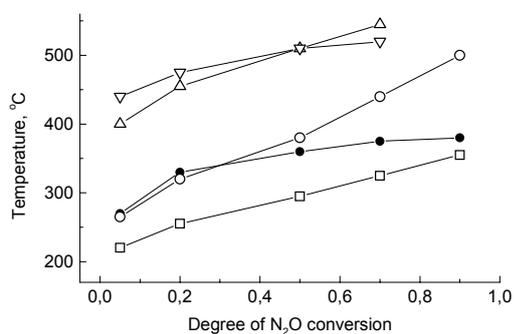


Figure 4. Temperature $T^\circ C$ at different degrees of N_2O decomposition for Ir (●), Rh (□), Ru (○), Co_2O_3 (△) and CuO (▽) catalysts at 15-20% metal content

It was also very important to study what degrees of N_2O decomposition could be reached at various temperatures in the reactor. This question has been clarified with the experiments for Ir, Rh, Ru, Co and Cu systems, which are presented in Fig. 4. It is evident that the most active catalyst among all were those based on Rhodium.

Activity of Rh catalysts (at ~10 wt.% Rh) supported on different carriers has been specially measured: Rh/ ZrO_2 (USA), Rh/ $(\gamma+\theta+\alpha)$ - Al_2O_3 , and Rh/ Al_2O_3 -AlN (300°C) > Rh/ Al_2O_3 - ZrO_2 (320°C) > Rh/ SiO_2 (Surrey, GB) (340°C) > Rh/ SiO_2 - Al_2O_3 (460°C). These results should be taken into consideration for constructing the thrusters for N_2O decomposition.

Investigation of catalysts after testing (two cycles by 2 h each till 800°C) showed that Platinum samples did not change, but there was 0.1% lose of mass. For Nichrome samples, the oxidation of the wire surface was observed. The most changes were observed for Ni samples: their mass increased at 4.5%, thus, there was oxidation of the Ni wire. Catalytically active in the last case for N_2O decomposition is Nickel oxide, as it is also known from literature. Therefore, Pt catalysts can be recommended as catalysts of the second layer for thrusters.

Changes of catalysts before and after testing in the thruster were also noticed spectroscopically with the use of ESR and XPS technique. In detail, these results will be reported elsewhere. As an example, Fig. 5 presents some typical changes have been observed in ESR spectra for Rh/ $(\gamma+\theta+\alpha)$ - Al_2O_3 catalysts. Paramagnetic Rhodium species have not been observed.

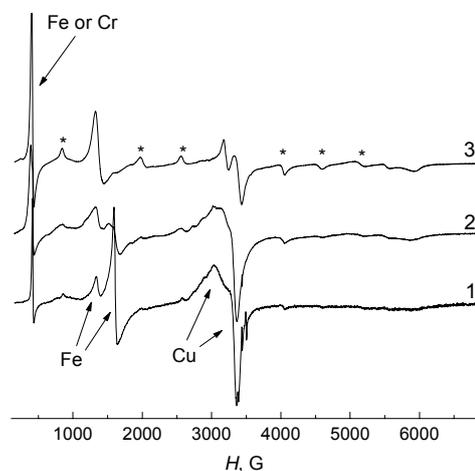


Figure 5. ESR spectra at 77K of Rh/ $(\gamma+\theta+\alpha)$ - Al_2O_3 catalysts: initial (1), after 1 h heating in air at 1100°C (2), and after 10 h testing in a thruster (3)

Comparing our experimental results with the published data for metal oxides and paramagnetic centers of metal ions [10-14], we could characterize the catalysts, which always contained some paramagnetic species, and also changes in their composition and structure:

– Long-time testing (up to 10-11 h) of the catalysts in the reaction of N_2O decomposition in model reactors and thrusters showed that the amount of paramagnetic species was noticeably changed in samples. In Cobalt catalysts, the content of Fe^{3+} ions has decreased, while in Rhodium catalysts supported on Al_2O_3 carriers it practically did not change, and in Rhodium catalysts supported on ZrO_2 , content of Fe^{3+} has even increased. The amount of impurities in the catalysts has also changed under processing.

– Chemical type and valence state of paramagnetic species differed before and after catalytic reaction of N_2O conversion. This allowed us to conclude that the matrix of the catalysts has been changed, including spatial distribution of paramagnetic centers.

– Investigations of the metal-supported catalysts in the reaction of N_2O decomposition will be continued for better understanding of the mechanisms of processes occur in such systems.

Mathematic modeling of N_2O decomposition process in a thruster has been studied for the 19 wt.% Rh catalyst supported on $(\gamma+\theta+\alpha)-Al_2O_3$. It was found that kinetics of the reaction rate at temperatures lower $350^\circ C$ can be described by one of the following three equations, depending on conditions of the reaction realization:

$$W_1 = 2.27 \cdot \exp(-150/RT) \cdot C_{N_2O} \quad (1)$$

$$W_2 = 0.27 \cdot \exp(-150/RT) \cdot C_{N_2O}/C_{O_2}^{0.25} \quad (2)$$

$$W_3 = 0.035 \cdot \exp(-150/RT) \cdot C_{N_2O}/C_{O_2}^{0.5} \quad (3)$$

One can see from Fig. 6 and Eqs. 1-3 that the reaction order by N_2O (in temperature and concentration range used) is equal to 1, while the order by O_2 was fractional, and is changing from 0 till $-1/2$, depended on reaction conditions. The effective activation energy was equal to 150 ± 15 kJ/mol, did not depend on the scheme, but the pre-exponent value depended strongly on the equation.

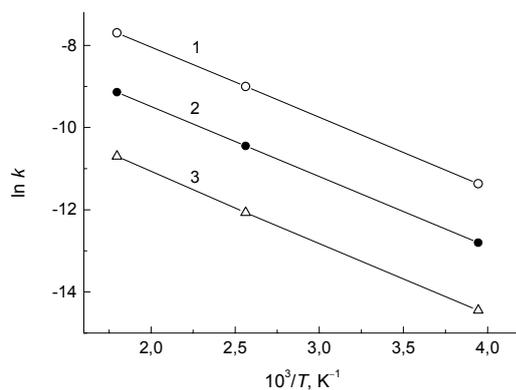


Figure 6. Arrhenius plots of N_2O decomposition rate constants $\ln k$ for three kinetic equations: \circ (1), \bullet (2) and Δ (3)

These changes of the reaction order by oxygen can be explained by different degree of covering the catalytic surface with O_2 , which depends on concentration of reagents and on temperature. Equal values of activation energy in various equations allowed us to suggest that N_2O decomposition at the used conditions occurs at the same catalytically active centers. Different values of the pre-exponent observed, seems, are connected with the inhibiting action of oxygen. This is confirmed by the recovery of the catalyst activity after thermal treatment in Helium atmosphere between kinetic measurements. Oxygen was also found in the pumped gas during this heating and could be measured chromatographically. Two types of the absorbed oxygen were observed at the desorption experiments: the main desorptive product from the surface at temperatures higher $350^\circ C$ was O_2 , produced two peaks: one at $600^\circ C$, and another, much more intensive, at temperatures higher $800^\circ C$. At the same time, for Rhodium catalyst, which was not treated with N_2O , only one thermodesorptive peak at $870^\circ C$ has been observed. So, there are two different forms of the adsorbed oxygen on the surface of the Rhodium catalyst in action.

4. CONCLUSIONS

From the results obtained one can conclude that in the reaction of N_2O decomposition:

1. Compact noble metal catalysts prepared from wires are noticeably less active in comparison with supported noble metal catalysts.
2. Among supported catalysts, prepared of noble metals are more active than the rest transition metals. Rhodium is the most active one.
3. Increasing of noble metal concentration has resulted in noticeable prolongation of the working resource of the model thruster.
4. The obtained results showed that as the most perspective catalysts of N_2O decomposition for rocket thrusters can be recommended 19% Rh/ $(\gamma+\theta+\alpha)-Al_2O_3$ and 12% Rh/ ZrO_2 .
5. The long-term catalysts testing results in a thruster confirmed that the laboratory cycling reactor modeled well catalytic behaviour.
6. Working capacity of catalysts depends not only on their physical-chemical properties but also on evaporation of the active component from the system.

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