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. Obtained results can be used in future as a basement for creating the most active and stable catalyst for N₂O decomposition.

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. 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.

RESULTS AND DISCUSSION
Fig. 1 shows typical curves of the important parameter, measured O₂.

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Rhodium, Ruthenium and Cobalt supported on \((\gamma+\theta+\alpha)\) \(\text{Al}_2\text{O}_3\). 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.

![Graph showing the dependence of specific surface area \(S\) on metal content in catalysts supported on \((\gamma+\theta+\alpha)\) \(\text{Al}_2\text{O}_3\): \(\text{Ir} (\bullet), \text{Rh} (\circ), \text{Ru} (\Delta), \text{Co} (\nabla)\)](image)

### Table 1. Specific surface area \(S\) and the packed density \(\rho\) of the supported catalysts

<table>
<thead>
<tr>
<th>Active component</th>
<th>(m), wt.%</th>
<th>(\rho), g/cm(^3)</th>
<th>(S), m(^2)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>4.7(^a)</td>
<td>1.03</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>6.2(^b)</td>
<td>1.04</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>9.9(^b)</td>
<td>1.06</td>
<td>95</td>
</tr>
<tr>
<td>Pt</td>
<td>5.5</td>
<td>1.05</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>9.8</td>
<td>1.13</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>13.1</td>
<td>1.18</td>
<td>105</td>
</tr>
<tr>
<td>NiO(^c)</td>
<td>6.4</td>
<td>1.02</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
<td>1.07</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>20.4</td>
<td>1.29</td>
<td>87</td>
</tr>
<tr>
<td>(\text{Fe}_2\text{O}_3)(^c)</td>
<td>19.0</td>
<td>1.35</td>
<td>110</td>
</tr>
<tr>
<td>(\text{MnO}_2)(^c)</td>
<td>15.5</td>
<td>1.12</td>
<td>109</td>
</tr>
<tr>
<td>CuO(^c)</td>
<td>18.6</td>
<td>1.21</td>
<td>110</td>
</tr>
<tr>
<td>Cr(_2)O(_3)(^c)</td>
<td>20.0</td>
<td>1.09</td>
<td>88</td>
</tr>
</tbody>
</table>

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

Typical dependences of \(\text{N}_2\text{O}\) decomposition degree with temperature for three samples: \(\text{Rh}_2\text{O}_3/\text{Al}_2\text{O}_3\), \(\text{ZrO}_2\), 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\(_{\text{max}}\)\) (at the degree of \(\text{N}_2\text{O}\) conversion equal 0.03–0.05); temperature \(T\(_{0.5}\)\) of 50% decomposition of \(\text{N}_2\text{O}\); or the temperature \(T\(_{\text{max}}\)\) for the complete conversion of \(\text{N}_2\text{O}\).

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\(_{\text{max}}\)\) value allowed us to assume the existence of some limitations for the diffusion of reagents and products inside the catalyst pores [9].

![Graph showing the dependence of \(\text{N}_2\text{O}\) decomposition degree on temperature for \(\text{Rh}/\text{Al}_2\text{O}_3\) (\(\bullet\)), \(\text{ZrO}_2\) (\(\bullet\)) and \(\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3\) (\(\Delta\)) catalysts](image)

### Table 2. Temperature of 50% decomposition of \(\text{N}_2\text{O}\), \(T\(_{0.5}\)\), in a laboratory catalytic reactor at different contents of the active component (AC) \(m\), supported on \(\text{Al}_2\text{O}_3\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(M), wt.%</th>
<th>(T(_{0.5})), °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>4(^a)</td>
<td>325</td>
</tr>
<tr>
<td></td>
<td>15(^b)</td>
<td>340</td>
</tr>
<tr>
<td>Pt</td>
<td>6(^c)</td>
<td>495</td>
</tr>
<tr>
<td></td>
<td>13(^d)</td>
<td>470</td>
</tr>
<tr>
<td>Pd</td>
<td>6(^d)</td>
<td>510</td>
</tr>
<tr>
<td></td>
<td>13(^d)</td>
<td>535</td>
</tr>
<tr>
<td></td>
<td>6(^d)</td>
<td>595</td>
</tr>
<tr>
<td>NiO</td>
<td>9(^e)</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>20(^f)</td>
<td>550</td>
</tr>
<tr>
<td>(\text{Fe}_2\text{O}_3)</td>
<td>19(^h)</td>
<td>555</td>
</tr>
<tr>
<td>(\text{CuO})</td>
<td>19(^i)</td>
<td>510</td>
</tr>
<tr>
<td>(\text{MnO}_2)</td>
<td>16(^i)</td>
<td>470</td>
</tr>
</tbody>
</table>

\(^a\) Calculated; \(^b\) washed in \(\text{HNO}_3\); \(^c\) from \(\text{PdCl}_2\); \(^d\) from \(\text{Pd(NO}_3\)\(_2\)); \(^e\) from \(\text{Pd(NO}_3\)\(_2\)); \(^f\) from \(\text{Pd(NO}_3\)\(_2\)); \(^g\) from \(\text{Pd(NO}_3\)\(_2\)); \(^h\) from \(\text{Pd(NO}_3\)\(_2\)); \(^i\) from \(\text{Pd(NO}_3\)\(_2\));

Our experiments showed that all investigated catalysts of various types could be placed by their activity in the
reaction of N₂O 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): ZrO₂ (430 °C) > Al₂O₃-CaO (505 °C), Al₂O₃-ZrO₂ (500 °C) > (γ+θ+α)-Al₂O₃ (510 °C) > Al₂O₃-AlN, SiO₂-Al₂O₃ (565 °C) > SiO₂ (600 °C) > α-Al₂O₃ (610 °C).

3. Granulated catalysts based on transition metals supported on (γ+θ+α)-Al₂O₃ (degree of conversion was equal to 0.2): Co₃O₄ (415 °C) > NiO (425 °C) > MnO₂ (430 °C) > CuO (440 °C) > Cr₂O₃ (445 °C) > Fe₂O₃ (465 °C).

4. Granulated catalysts based on noble metals supported on (γ+θ+α)-Al₂O₃ (degree of conversion was equal to 0.2): Rh (255 °C) > Ru (320 °C) > Ir (330 °C) > Pt (430 °C) > Pd (490 °C).

It was also very important to study what degrees of N₂O 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/ZrO₂ (USA), Rh/(γ+θ+α)-Al₂O₃, and Rh/Al₂O₃-AlN > Rh/Al₂O₃-ZrO₂ (320 °C) > Rh/SiO₂ (Surrey, GB) (340 °C) > Rh/SiO₂-Al₂O₃ (460 °C). These results should be taken into consideration for constructing the thrusters for N₂O 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 N₂O 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 spectrosopically 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/(γ+θ+α)-Al₂O₃ catalysts. Paramagnetic Rhodium species have not been observed.

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 N₂O decomposition in model reactors and thrusters showed that the amount of paramagnetic species was noticeably changed in samples. In Cobalt catalysts, the content of Fe³⁺ ions has decreased, while in Rhodium catalysts supported on Al₂O₃ carriers it practically did not change, and in Rhodium catalysts supported on ZrO₂, content of Fe³⁺ 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 N₂O 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 N₂O decomposition will be continued for better understanding of the mechanisms of processes occur in such systems.

Mathematic modeling of N₂O decomposition process in a thruster has been studied for the 19 wt.% Rh catalyst supported on (γ+θ+α)-Al₂O₃. It was found that kinetics of the reaction rate at temperatures lower 350°C can be described by one of the following three equations, depending on conditions of the reaction realization:

\[
W_1 = 2.27 \cdot \exp(-150/RT) \cdot C_{N_2O} \\
W_2 = 0.27 \cdot \exp(-150/RT) \cdot C_{N_2O}/C_{O_2}^{0.25} \\
W_3 = 0.035 \cdot \exp(-150/RT) \cdot C_{N_2O}/C_{O_2}^{0.5}
\]

One can see from Fig. 6 and Eqs. 1-3 that the reaction order by N₂O (in temperature and concentration range used) is equal to 1, while the order by O₂ 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 N₂O decomposition rate constants ln k for three kinetic equations: ○ (1), ● (2) and △ (3)](image)

These changes of the reaction order by oxygen can be explained by different degree of covering the catalytic surface with O₂, which depends on concentration of reagents and on temperature. Equal values of activation energy in various equations allowed us to suggest that N₂O 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°C was O₂, produced two peaks: one at 600°C, and another, much more intensive, at temperatures higher 800°C. At the same time, for Rhodium catalyst, which was not treated with N₂O, only one thermodesorptive peak at 870°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 N₂O 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 N₂O decomposition for rocket thrusters can be recommended 19% Rh/(γ+θ+α)-Al₂O₃ and 12% Rh/ZrO₂.
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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References