
REVIEWS

Hydrogen Peroxide Decomposition Catalysts Used in Rocket Engines

Sh. L. Guseinov^a, S. G. Fedorov^{a,*}, V. A. Kosykh^a, and P. A. Storozhenko^a

^a State Research Institute of Chemistry and Technology of Organoelement Compounds, Moscow, 111123 Russia
*e-mail: stan-fed2011@yandex.ru

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Abstract—The results of the development and studies of heterogeneous catalysts for decomposition of highly concentrated hydrogen peroxide used as monopropellant and oxidant in rocket engines are summarized. Being nontoxic, hydrogen peroxide is an excellent alternative to highly toxic hydrazine and dinitrogen tetroxide used today in rocket engines and is only slightly inferior to them in the energy efficiency. Data on the influence of the catalyst active phase and support material and shape on the thruster operation conditions are discussed and summarized.

Keywords: hydrogen peroxide, decomposition catalysts, rocket engines, silver, platinum, manganese oxide

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INTRODUCTION

Hydrazine is used today as a high-performance rocket propellant in systems of orbital space engines on satellites and other spacecrafts. High levels of toxicity and corrosion action give rise to serious staff and environmental safety problems in storage and handling of hydrazine under earth conditions. Therefore, researchers in the field of rocket propellant pay growing attention to the development of environmentally safer, so-called “green” propellant. One of such rocket propellants is highly concentrated hydrogen peroxide (HP). Its catalytic decomposition results in large heat release and formation of a hot steam–gas mixture consisting of oxygen and water vapor.

Although hydrogen peroxide was discovered by Thénard as early as 1818 [1], its commercial production was mastered only in the late 1930s in many European countries, and also in the Soviet Union, Korea, Japan, the United States, and Australia. Today hydrogen peroxide is widely used in various branches of engineering. Its use as oxidant or monopropellant in rocket engines was started in the 1930s in the Soviet Union and Germany [2]. In the 1940–1950s, 80–85% hydrogen peroxide came into wide use in the world as an oxidant or single-component propellant in a number of rockets and

aviation engines: V-2, Redstone, Viking, Jupiter, Sea Slug, Natter, Blue Streak, Me-163, X-15, etc. [2–5]. Later (in the 1960–1980s), it was used as an oxidant in the liquid rocket engine of the first step of Diamant B rocket (France) in combination with unsymmetrical dimethylhydrazine and in the first step of the Black Knight rocket (the United Kingdom) in combination with kerosene [4].

Catalytic oxidation of 80–85% hydrogen peroxide was widely used in the Soviet Union as a source of the steam–gas mixture in turbo pump aggregates of rocket engines. Space carrier rockets Sputnik, Vostok, Molniya, Soyuz, etc., based on R-7 rocket, have been developed in the Soviet Union in the 1950–1960s and successfully launched. 85% hydrogen peroxide (or HP-85) is also successfully used in modern Russian space rockets in reactors of 11D511 and 11D512 engines [5–7].

The performance of propellants using hydrogen peroxide as oxidant and gas generator largely depends on its concentration, because both the available oxygen content and decomposition temperature of hydrogen peroxide increase with the concentration. The available oxygen content increases from 40.0 for 85% hydrogen peroxide to 46.1% for 98% hydrogen peroxide, and the decomposition temperature in the same concentration interval increases from 907 to 1125 K [8].

Low toxicity, well-mastered production process, commercial availability, and versatility of hydrogen peroxide (it can be both a monopropellant and an oxidant) confirm the possibility of developing a cheap and environmentally friendly propellant system. When used as a monopropellant, hydrogen peroxide ensures 11% lower specific impulse even when 98% hydrogen peroxide is used (98% is the highest commercially available concentration). It should be noted that, in going from 87.5% to 98% hydrogen peroxide, the theoretical specific impulse increases by 12 s (for hybrid engines) [9]. The specific impulse in the hydrazine–dinitrogen tetroxide binary system is 4% higher than the value that can be obtained using 98% hydrogen peroxide as an oxidant and JP-4 kerosene as a propellant. The pattern changes when the specific impulse is considered taking into account the density. Namely, the specific impulse for the JP-4–98% H₂O₂ system is higher at the oxidant to propellant weight ratio of 7 [10].

The interest in using hydrogen peroxide as monopropellant and oxidant for satellite thrusters, landers, gas generators [11], aircrafts, and submersible vehicles [12, 13], renewed in the past 25 years, led to the publication of numerous papers on the development of new, more effective (compared to those known previously) catalysts for hydrogen peroxide decomposition.

One of advantages of hydrogen peroxide is the possibility of initiating its catalytic decomposition without using an igniting (or initiating) device required in the case of other rocket propellants. This simplifies the design of the engine and allows also repeated or multiple engine startup.

As rocket engineering passes to the use of high-concentration (>92%) hydrogen peroxide, whose catalytic decomposition leads to the buildup of high temperatures, it becomes topical to develop highly heat-resistant high-performance catalysts and methods for testing them.

In this review, we analyze the characteristics of the existing catalysts and catalysts being developed for the decomposition of HP of different concentrations, consider the procedures for their preparation, and compare the catalytic activity and use of catalysts in thrusters being developed. Very brief data on the hydrogen peroxide decomposition catalysts are given in [14–18].

REQUIREMENTS TO HYDROGEN PEROXIDE DECOMPOSITION CATALYSTS

The catalyst choice is one of the most important problems in the development of engines based on hydrogen peroxide. The catalyst operation life is influenced by numerous factors: catalyst material, pressure in the decomposition chamber, hydrogen peroxide concentration, load of its flow on the catalyst, and operation mode. The total time of the catalyst operation in the working mode can exceed 1 h. If a catalytic bed operates in the pulse mode with alternating starts and stops, the thermal cycle will destroy the catalytic material. Modern types of catalysts can stand up to 5000 cycles and more [19].

Along with the main requirement that complete decomposition of concentrated hydrogen peroxide solutions should be ensured, the catalysts should meet the following requirements:

- High activity. The time in which hydrogen peroxide starts to decompose after the contact with the catalyst should be as short as possible (preferably 100 ms), and the reaction rate should be maximal.

- Mechanical impact and thermal shock resistance. Hydrogen peroxide decomposition occurs at a high rate with large heat release; the adiabatic temperature of the steam–gas mixture formed is 632, 755, and 953°C for 85, 90, and 98% hydrogen peroxide, respectively [10]. An increase in the temperature leads also to an increase in the pressure of hydrogen peroxide decomposition products. The resistance to mechanical impact and thermal shock associated with the engine start/stop (ignition/stop of operation) is particularly important. The hydrogen peroxide decomposition is accompanied by large heat release in a very short time, with the heat-up rate of 200–300 deg s⁻¹; therefore, the majority of catalysts are destroyed after several thermal cycles.

- High activity and stability in a wide interval of the operation conditions in the liquid and vapor phases.

- In some cases, the maximal cycling of the engine in the start/stop mode should be ensured.

- Resistance to stabilizing agents added to hydrogen peroxide to enhance its long-term stability. These agents can degrade at higher temperatures, with the degradation products poisoning the catalyst.

- High resistance to overloads and transportations and low carry-over in the course of catalyst operation.

– Optimum ratio between the mechanical strength and specific surface area. In low-porous catalysts (with low specific surface area), the hydrogen peroxide decomposition occurs at a lower rate, which leads to its incomplete decomposition and to a decrease in the temperature of decomposition products and causes the catalyst drowning with the first portion of hydrogen peroxide, whereas in high-porosity catalysts (with high specific surface area) the thermal action causes the support disintegration, leading to excessively increased pressure drop in the catalyst bed [20].

One more important requirement to catalysts is resistance to high load on the catalyst (gravimetric flow rate of hydrogen peroxide through the cross section area of the catalyst bed). In a number of studies, it is in the range 117–280 kg m⁻² s⁻¹ [21]. The higher is the catalyst performance, the larger is the amount of hydrogen peroxide that can be passed through it in unit time; hence, the catalyst bed size and thus the engine volume and mass can be reduced. On the other hand, an increase in the load can lead to an increase in the rate of the catalyst erosion, decreasing the catalyst performance.

CATALYST SUPPORTS

Since the discovery of hydrogen peroxide, more than a hundred substances capable to catalytically initiate its decomposition have been discovered [22–24]. Silver, cobalt, and platinum group metals are most effective among metals; transition metal (Mn, Cu, Cr) oxides, among oxides; and alkali and alkaline earth metal permanganates, among salts.

As a rule, the specific surface area of a catalytic metal itself or of its compound is low. Therefore, if only their active phase is used, the hydrogen peroxide decomposition rate is insufficient for using these catalysts for hydrogen peroxide decomposition in a rocket engine. To increase the surface area of the active phase, it is applied as a thin layer onto a highly porous support. The physical properties of the catalyst support are an important factor largely influencing the mechanical and thermal properties of the catalyst, its operation life, and hydrogen peroxide decomposition rate.

Silver gauzes or granules with the active phase are widely used in rocket engines since the 1950s. However, in the past decade there has been growing interest in new forms of the support: structured or cellular, honeycomb supports made of a single block of the material and therefore named monoliths [10, 21–26].

Gauze catalysts. Gauze catalysts are made of noble metal wire (in this case, they cannot be named supports). 20 mesh silver gauzes with the wire diameter of 0.356 mm have the specific surface area of approximately 10.7 cm² g⁻¹ [18]. This is lower by several orders of magnitude than the specific surface area of ceramic pellets. To reduce the catalyst cost, silver or platinum is deposited onto gauzes made of stainless steel or nickel. Although more than 95% efficiency is reached on such gauze catalysts, they have certain drawbacks. High gauze density required to reach high specific surface area causes sharp pressure drop in the catalytic pack. This, in turn, requires high pressure in the feeding system. The gauzes are very heavy, because they consist of nickel and silver. The materials and the deposition procedure are very expensive. Problems in reaching high specific impulse by using hydrogen peroxide of >92% concentration on silver catalysts are associated with the relatively low melting point of silver (962°C), close to the temperature developed in the decomposition of 90% hydrogen peroxide. In turn, the gauzes undergo sintering, which decreases the specific surface area of the catalyst and thus the efficiency of the hydrogen peroxide decomposition [27].

Granulated supports. Beds of ceramic porous pellets and spherical granules with the active phase of various catalytic substances are widely used as an alternative to gauze catalysts. Several research groups have recently proved that this approach is promising [28–33].

Pelletized catalysts started to be used in rocket engines as early as the 1950s. They could be readily produced from available and relatively cheap materials and could be readily processed. Owing to relatively low cost, well-mastered technology, and availability, the development of such catalysts is still being continued.

Porous aluminum oxide is the most widely used support (due to its high specific surface area), and platinum metal and manganese oxides are the most widely active phases. These catalysts are usually prepared as pellets of various shapes and sizes with various specific surface areas to ensure the optimum design of the catalyst bed and engine. It should be noted that pellets also have certain drawbacks: The catalytic material can disintegrate owing to nonuniform packing and mutual friction of the pellets, to mechanical impact, and to thermal shock caused by extremely sharp increase in the pressure and temperature in the course of hydrogen peroxide decomposition. In addition,

structural problems can arise in catalyst beds in the course of starting and stopping the engine.

To replace silver catalysts, Rusek [34] suggested granulated catalysts on aluminum oxide support with the manganese oxide active phase. The catalysts are prepared by thermal decomposition of a mixture of various precursors such as hydroxides, carbonates, nitrates, and oxalates [35]. Manganese and cobalt oxide catalysts were prepared by this method [36]. Catalysts in the form of pellets or spherical granules can be prepared by impregnation of commercially available granulated supports with precursors of active compounds. For example, manganese oxide catalysts with the addition of lead oxide on aluminum oxide support were prepared by this procedure [37, 38].

The most frequently used materials for preparing granulated catalyst supports are γ -alumina because of its high specific surface area and α -alumina because of its high heat resistance. However, their use for preparing the catalyst depends on the concentration of the hydrogen peroxide used. γ - Al_2O_3 was found to be more sensitive to the thermal shock. When using 98% hydrogen peroxide, high temperature causes phase changes in γ - Al_2O_3 , leading to a decrease in the specific surface area. The specific surface area of the more heat-resistant α - Al_2O_3 is lower by two orders of magnitude than that of γ - Al_2O_3 , and the performance of catalysts based on it is somewhat lower [39].

The heat resistance of aluminum oxide can be enhanced by its doping with silicon, lanthanum, or barium oxide [40, 41]. Barium and lanthanum hexaaluminates were suggested as heat-resistant supports preserving their properties, including the specific surface area, at temperatures higher than 1200°C [42, 43]. Barium hexaaluminate was used as a support for platinum metal and manganese oxide with the addition of lead oxide in a hybrid thruster in which a 50 : 50 mixture of hydrogen peroxide and ethanol was used as a propellant. The temperature reached in the course of combustion of such mixture exceeded 1000°C [42].

In supports with the addition of lanthanum hexaaluminate [28], the specific surface area at high temperatures is preserved better than in straight aluminum oxide. In addition, lanthanum hexaaluminate surpasses γ - Al_2O_3 in the bending strength and crack resistance.

The development of a high-performance monopropellant thruster with a 10 N thrust, operating on a hydrogen peroxide–ethanol mixture, required, as in [42],

a highly heat-resistant catalyst support. Baek et al. [44] prepared such support from silicon oxide doped γ -alumina (SiO_2 - Al_2O_3) with the manganese oxide active phase. The strength tests were performed for the following catalysts: SiO_2 - Al_2O_3 , lanthanum hexaaluminate, and γ - Al_2O_3 . The SiO_2 - Al_2O_3 support surpassed the other supports in the activity and heat resistance of the catalyst at a high temperature (1400°C). Similar results were obtained with aluminum oxide containing 13% silicon oxide used as a support [45].

Studies of granulated and pelletized platinum catalysts on a γ - Al_2O_3 support revealed higher performance of the former catalyst. It ensures fast and complete decomposition of hydrogen peroxide. The granule size strongly influences the hydrogen peroxide decomposition rate. For equal amounts of catalysts, the external surface area increases with a decrease in the granule size, leading to an increase in the catalytic activity [46, 47].

The results of numerous studies on the decomposition of concentrated hydrogen peroxide on catalysts using manganese oxide confirmed significant influence of the support type on the catalytic properties of the catalyst [48, 49].

Although pelletized catalysts are characterized by considerably lower pressure drop compared to powdered catalysts, large pressure drop and pressure oscillations are still observed on these catalysts at high flow rates of hydrogen peroxide and its decomposition products (the load can reach $10 \text{ g cm}^{-2} \text{ s}^{-1}$) [50].

Wear of the pellets in the course of operation and transportation leads to the formation of fragments and dust, which, in turn, can cause nonuniform distribution of the flow, increased pressure drop, and catalyst carry-over. The other drawbacks of the pelletized catalysts are restricted mass transfer and scaling problems in going from the laboratory to commercial production scale [50].

The above drawbacks of pelletized catalysts stimulated search for alternative types of catalyst supports and procedures for preparing them.

Monolithic supports for hydrogen peroxide decomposition catalysts. The number of papers on the development of new catalyst structures for the decomposition of concentrated hydrogen peroxide in rocket engines steadily increased in the past decade. These structures are based on cellular or honeycomb supports made of a single block of the material and

are therefore named monolithic [25, 26, 51, 52]. Metal foams are also considered as monolithic supports [53]. Catalysts on metal foams are seldom used for the hydrogen peroxide decomposition despite a number of advantages. Their surface area is considerably larger than that of gauzes, and the foams made of active metals do not require deposition of the active phase. One of the drawbacks is large pressure drop in the catalyst bed due to irregular structure [54].

Honeycomb monolithic catalysts are widely used in automobile industry for exhaust gas treatment. The production technology and large-scale production of such materials have been mastered on the commercial scale after 50 years of experiments in the field of catalysts for neutralization of automobile exhausts [55]. The honeycomb ceramic has numerous useful properties suitable for harsh conditions of the operation of a rocket engine on concentrated hydrogen peroxide. It is commercially available. Monolithic supports differing in the nature, shape, and channel density are produced industrially [52].

As compared to common gauze catalysts and granulated catalysts prepared by extrusion or sintering in the form of pellets or spherical granules, cellular monolithic catalysts have a number of advantages: (1) lower pressure drop in the catalyst bed; (2) higher resistance to thermal shock and wear resistance, compared to pellets; (3) uniform distribution of HP flow and better conditions for the mass and heat transfer; (4) shorter diffusion path length, because the catalyst is present in the form of a very thin layer [48].

All these properties allow such supports to be used under the conditions of rapid pressure and temperature changes in the catalyst bed. In addition, porous cellular or foamed monoliths with definite flow-through channels increase the active surface area, allowing the catalyst bed volume to be decreased. The channels can have square or triangular cross sections. The number of channels can range from 40 to 90 per 1 cm² [10].

Thus, monolithic catalysts are an attractive alternative to traditional systems, allowing the development of catalyst beds for microengines [25, 26, 51]. Such minerals as cordierite, mullite, and synthetic silicon carbide are used for fabricating monolithic catalysts most frequently [22, 52, 56]. Cellular supports based on yttria-stabilized zirconia with manganese oxide as an active phase were used in [27]. These catalysts were developed without using the wash-coat layer method

commonly used for increasing the active surface area of cellular catalysts.

Monolithic catalysts for hydrogen peroxide decomposition have been less studied than catalyst beds consisting of pellets and were under development in the United States and Europe only in the past decade. Honeycomb catalysts for automobile industry have been considered in reviews [55, 57].

To prepare catalysts, the cellular ceramic is first subjected to the wash-coat process (deposition of a thin porous layer on the internal surface of the channels), after which the porous layer is impregnated with an active phase [50].

Along with significant advantages, monolithic catalysts have a number of drawbacks. As shown in [27, 58], the temperature in a catalyst bed at a low load (less than 10 kg m⁻² s⁻¹) increases relatively slowly. The load is considerably lower than for the bed of pellets, for which the load can exceed 900 kg m⁻² s⁻¹ [59], although usual loads are in the interval 50–100 kg m⁻² s⁻¹. Low load requires considerably larger diameter of the catalyst bed, which leads to an increase in the thruster volume. In addition, the monolithic support has very low specific surface area (<<1 m² g⁻¹) requiring additional application of a thin layer with a developed surface, bound to the support (wash-coat process), followed by impregnation with an active phase. The wash-coat technology is labor-consuming.

HYDROGEN PEROXIDE DECOMPOSITION CATALYSTS FOR ROCKET ENGINES

Hydrogen peroxide decomposition can occur as a thermal or catalytic process. Catalysts considerably reduce the activation energy required for the hydrogen peroxide decomposition. As we found, the activation energy of the thermal decomposition is 188–230 kJ mol⁻¹ [60], and the activation energy of the catalytic decomposition is in the interval 40–50 kJ mol⁻¹ [61]. The hydrogen peroxide decomposition occurs under the action of both factors.

Koopmans [62] distinguished seven steps in the catalytic decomposition process, of which the most important are adsorption and decomposition of hydrogen peroxide on the catalyst surface. The reaction rate depends on the choice of the active phase. The adsorption depends on the number of active sites accessible to hydrogen peroxide.

The main catalysts used in rocket engines are those based on silver metal, platinum metal, and manganese oxides.

Silver-based catalysts. Despite high cost and the development of new catalysts for hydrogen peroxide decomposition, silver catalysts are still widely used in the existing and newly developed thrusters. Many presently used thrusters contain packs of silver gauze pieces or silver deposited onto metal gauze or ceramic supports [21, 31, 63–73]. The main advantages of silver catalysts are high efficiency of hydrogen peroxide decomposition, small size, relatively easy fabrication, and availability of numerous shapes [21]. Silver gauze packs are traditionally used as a hydrogen peroxide decomposition catalyst, e.g., in Gamma 201 and Gamma 301 engines [71].

According to a number of studies, silver gauzes should be activated prior to use by keeping in a 10% samarium nitrate solution [16] or in a 10–15% nitric acid solution [16, 21, 66, 68, 74–76], followed by heat treatment at 900 K; nitric acid treatment should be preferred [16, 75]. The melting point of silver is relatively low and close to the temperature of the decomposition products of 98% hydrogen peroxide. Therefore, the concentration of hydrogen peroxide used in decomposition chambers containing silver or silver-coated steel or nickel gauze as an active phase should not exceed 90–92%.

To enhance the heat resistance and strength of the silver gauze catalytic pack in operation with highly concentrated hydrogen peroxide, silver gauzes was combined with stainless steel or nickel gauzes [21, 66, 77]. Such catalyst was successfully used for the decomposition of 92% hydrogen peroxide with the degree of decomposition higher than 95%. This may be due to the fact that the heat is partially absorbed by the steel gauze; in addition, the “volumetric concentration” of silver decreases. Furthermore, partitions of gauzes of other metals allow elimination of through channels in the catalytic pack and thus ensure uniform flow of hydrogen peroxide. However, large weight is a drawback of such catalyst packs.

To enhance the heat resistance of a silver catalyst, instead of using gauze, Chan et al. [78] suggested using alternating beds of pellets of silver-coated and uncoated ceramic material. This allowed the temperature in the combustion chamber to be reduced, probably owing to partial absorption of the released heat.

The results of the trials demonstrated high decomposition efficiency, decreased catalyst carry-

over, and decreased pressure drop in the catalyst bed [78]. However, the assembling of such bed is labor-consuming.

Instead of the commonly used pack of gauzes, a pack of thin silver plates with holes of different size in them was suggested. The pack has large surface area. Such design, compared to the gauze pack, was claimed to reduce the pressure drop in the pack during engine operation and to increase the operation life. The catalyst showed high performance in the decomposition of 90% hydrogen peroxide at a load of $40 \text{ g m}^{-2} \text{ s}^{-1}$ in a wide pressure interval during 900-s operation [16]. No data on the gauze sintering were reported. A composite silver catalyst prepared by adding a ceramic material (in the form of balls or pellets) was suggested recently [78, 79]. The catalyst showed good characteristics in the decomposition of 98% hydrogen peroxide with the efficiency close to 100%; the reaction delay time was less than 50 ms (for the hot start). The decomposition delay time increases to 100 ms for the cold start. The authors also determined the optimum silver content and showed that excess silver in the active phase can cause sintering, i.e., degradation of the working bed due to changes in the catalytic surface. The specific impulse was 104 s at the cold start and 114.9 s at the hot start.

Interesting data were obtained by Blank et al. [19], who studied the state of silver gauzes in the course of decomposition of 90% hydrogen peroxide at very high pressures (from 69 to 276 bar) and the axial load (gravimetric flow rate of hydrogen peroxide per unit cross section area of the catalytic pack) exceeding the common nominal values ($0.03 \text{ kg m}^{-2} \text{ s}^{-1}$) by a factor of 3. The efficiency exceeded 90%. The advantages of increasing the surface area of supports with the deposited active phase were considered using as example silver on Al_2O_3 support, compared to pure silver [14]. Bramanti et al. [23] have found that a part of silver is carried over with time in the course of its operation as a hydrogen peroxide decomposition catalyst. This reduces the catalyst operation life. Another drawback of the silver catalyst is the weight loss after several engine startup cycles, which is proportional to the catalyst bed area squared. However, the major advantage of silver is its sensitivity to poisoning of the active surface with stabilizers present in hydrogen peroxide. Because the hydrogen peroxide decomposition on silver is a heterogeneous process, the accurate reaction mechanism is still unknown. It may be based on the radical mechanism [73].

In addition, there are some other drawbacks such as large pressure drop in the catalyst pack, the decomposition delay increasing with time in several cycles of starting the process, and the need for the catalyst preheating. Despite high cost and certain drawbacks of silver gauzes, studies on their use for catalyzing the hydrogen peroxide decomposition are being continued. The development of a novel hybrid rocket engine equipped with a decomposition chamber with silver gauzes was reported recently [80]. The chamber allows passing 1 kg s^{-1} 87.5% hydrogen peroxide and ensures simple and reliable ignition of the propellant based on metalated polybutadiene with terminal hydroxy groups (propellant–binder, HTPB) in its contact with hydrogen peroxide decomposition products. The system is capable of repeated startup [80].

Platinum catalysts. Platinum on various supports, e.g., on a ceramic–steel sieve support [49], is relatively widely used as a catalyst. Such structure exhibits high mechanical strength, but the catalyst performance at cold start was unsatisfactory. Platinum catalysts on cordierite and silicon carbide supports have been described [22]. Other noble metals (Pd, Au [23, 79, 81]) and some platinum group metals, e.g., iridium on a γ -alumina support [82], were also considered as catalysts.

Pt/Al₂O₃ catalysts. The results of numerous studies show that platinum is a very promising catalyst for hydrogen peroxide decomposition [9, 28, 30, 63, 73, 83–88]. On the other hand, platinum catalysts with a support based on aluminum oxide pellets showed high heat resistance and mechanical strength in thruster tests [31, 67, 89–91].

The development of an engine with a 200 N thrust on a two-component propellant and the determination of its activity should be noted as one of the most interesting results [28]. 87.5% hydrogen peroxide and various low-toxic hydrocarbon propellants were used in the engine. A bed of Pt–Al₂O₃ catalyst pellets ensured almost 100% decomposition of 21 kg of hydrogen peroxide without any degradation of the catalyst.

High-performance platinum catalysts were prepared by impregnation of porous aluminum oxide pellets with a platinum precursor, H₂PtCl₆, followed by firing and formation of platinum metal on the pellet surface [31, 67, 85]. The impregnation–firing cycles are repeated until the required platinum concentration is reached. The completeness of the decomposition of 87.5–90% hydrogen peroxide was 90–94%. No data are available on the catalyst operation life.

Similar catalysts with platinum on aluminum oxide particles of various sizes (from 1.18 to 2.00 mm) were tested for a hybrid engine in which polyethylene served as a propellant and 98% hydrogen peroxide, as an oxidant [9].

Good results were obtained with the Pt/Al₂O₃ catalyst in the form of pellets with the Pt content on the Al₂O₃ surface as low as 0.5%. The pellets were 3.2 mm in diameter and 3.5–4 mm long [73, 84, 92]. The pellets with platinum were found to surpass silver gauze in the catalytic properties. The hydrogen peroxide decomposition efficiency under the testing conditions was 95% for the pellets and 74% for the silver gauze; the highest degree of decomposition was reached at a shorter bed length even after the action of an almost triple amount of hydrogen peroxide [73]. However, as noted in [89], the pellets, in contrast to spherical granules, disintegrate upon thermal shock with gradual plugging of the catalyst bed during trials of the Pt/ γ -Al₂O₃ catalyst in a thruster prototype with a 5 N thrust. On the other hand, Dolci et al. [93] reported on the development of a Pt/ γ -alumina catalyst exhibiting high heat resistance and mechanical strength in decomposition of 98% hydrogen peroxide. The catalyst was capable to decompose 1 L of 98% hydrogen peroxide with more than 95% efficiency without pellet damage or decrease in the catalytic activity.

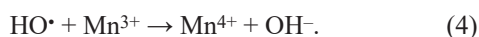
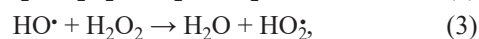
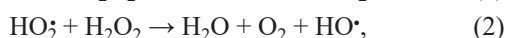
According to the experimental data [63], aluminum oxide pellets with medium content of the low-porosity α -phase, which are resistant to thermal shock in decomposition of hydrogen peroxide, are suitable for small rocket engines. Catalysts based on spherical Al₂O₃ granules coated with a thin layer of a mixture of cerium and zirconium oxides (Ce_xZr_{1-x}O₂), which is known to stabilize noble metal particles, have been developed to enhance the durability of the aluminum oxide support and stabilize the active metal phase. The content of the active phase, platinum, was 6–10% [94]. The authors revealed no changes in the crystal structure and morphology of the catalysts after the contact with 30% hydrogen peroxide.

Among platinum catalysts on other supports, a 1 N thrust two-component thruster with monolithic Pt/cordierite catalyst showed satisfactory performance. Kerosene or ethanol was used as a propellant [51].

Catalysts based on manganese oxides. Many transition metal oxides catalyze the hydrogen peroxide decomposition. Nevertheless, the majority of researchers

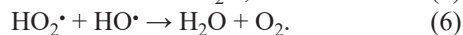
consider catalysts based on manganese oxides as the most promising for practical use [14, 48, 84, 95–98]. The MnO₂ activity was reported to increase on adding promoters such as Zn, Ni, Cu, Bi, Ce, and Pb, PbO [24, 37, 38, 47, 99, 100], and also samarium and lanthanum oxides [15, 101].

The hydrogen peroxide decomposition on manganese oxide is a more complex process than its decomposition on noble metals. Jildeh et al. [17] summarized the results of previous studies by different authors and suggested the following scheme of reactions of hydrogen peroxide on manganese oxide:

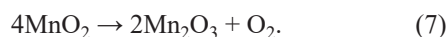


Equations (1)–(4) describe the steps of the catalytic decomposition of hydrogen peroxide. After the adsorption of a hydrogen peroxide molecule on active sites of the catalyst, the reaction starts with the electron exchange [reaction (1)] between H₂O₂ and MnO₂ with the formation of perhydroxyl radical (HO₂[·]). The subsequent steps involve the chain propagation with the generation of the HO[·] [Eq. (2)] and HO₂[·] [Eq. (3)] radicals. In the final step, the catalyst returns to the initial state [Eq. (4)].

Then, the water molecule is formed as a product of the reaction between hydroxide ion and hydrogen ion [Eq. (5)]. An alternative pathway is the reaction between HO₂[·] and HO[·] [Eq. (6)]:



Thus, the manganese(III) oxide formed in these reactions is converted back to the initial manganese dioxide. However, another reaction should not also be ruled out. It is known that manganese dioxide (MnO₂) decomposes at a relatively low temperature (525°C), losing an oxygen molecule and transforming [reaction (7)] into manganese(III) oxide [102]; on the other hand, the decomposition temperature of ≥85% hydrogen peroxide is considerably higher. Therefore, it can be expected that the decomposition of highly concentrated hydrogen peroxide on a manganese catalyst will lead to the formation of Mn₂O₃:



However, the transformation of MnO₂ into Mn₂O₃ leads to a decrease in the catalytic activity [17]. This can be attributed to a change in the activation energy of the hydrogen peroxide decomposition on Mn₂O₃, which is 77.1 kJ mol⁻¹ [17]. The activation energy of the decomposition of hydrogen peroxide on MnO₂ is about 50 kJ mol⁻¹ [103].

Because the decomposition temperature of ≥85% hydrogen peroxide is relatively high (≥750°C), the transformation of MnO₂ by reaction (7) with a decrease in the catalytic performance is highly probable. On the other hand, in the case of the decomposition of 30% hydrogen peroxide, when the decomposition temperature does not exceed 500°C, Mn₂O₃ surpasses MnO₂ in the catalytic activity [23].

Many researchers believe that a mixture of manganese oxides of the formula Mn_xO_y is formed when preparing manganese catalysts.

Granulated catalytic systems based on manganese oxides can be prepared both from a mixture of oxides of manganese and other metals and by impregnation of porous supports with precursors in the form of manganese hydroxides, carbonates, nitrates, and oxalates with the subsequent conversion to oxides [35, 104, 105]. For example, coprecipitation from a solution of Co, Mn, and Al nitrates in an Na₂CO₃ solution by adding an NaOH solution yielded a precipitate from which granules of mixed Co, Mn, and Al oxides were obtained by extrusion followed by heat treatment at 900°C [36]. The Co : Mn : Al molar ratio was 4 : 1 : 1. The final product for the catalytic pack had the shape of cylinders 2 mm in diameter and 3 mm long. The catalyst was capable of decomposing hydrogen peroxide at a cold start. The granulated catalysts based on mixed oxides, prepared in that study, had high mechanical strength and relatively low specific surface area (~6 m² g⁻¹) due to high calcination temperature. The catalyst carry-over in the course of trials in a microengine was insignificant. In addition, the pressure drop in the catalyst bed was minimal.

A high-performance solid porous catalyst for the decomposition of 85% hydrogen peroxide was prepared by deposition of manganese oxides onto a porous support [106]. The support was prepared by calcination of a charge consisting of carbonyl iron, sodium nitrate, and sodium carbonate at 490–525°C, followed by the cake crushing. Then, potassium permanganate and sodium carbonate were applied onto the obtained granules by

impregnation, after which the active phase of manganese oxides was obtained at 270–300°C. The catalyst trials showed that it allowed repeated starts with both long (350 or 411 s in each cycle, 3–4 starts) and short (8.5 s in each cycle, 10 starts one after another) operation. The temperature at the reactor outlet was 490–520°C, and the gravimetric carry-over of the catalyst was 0.42–1.5%. No signs of the catalyst disintegration were revealed [106].

To increase the degree and rate of the hydrogen peroxide decomposition, experiments were performed with nanocomposites of iron and manganese oxides, prepared by coprecipitation, sol–gel method, and mechanochemical activation using as starting compounds $\text{Fe}(\text{NO}_3)_3$, FeSO_4 , and $\text{Mn}(\text{NO}_3)_2$. The nanocomposites were deposited onto various supports. The catalytic activity of the sample obtained by coprecipitation was higher than the activity of the samples prepared by other methods. The use of sodium metasilicate as a support ensures high specific surface area and high activity [107].

Numerous studies deal with catalysts with the manganese oxide active phase on Al_2O_3 [15, 37, 56, 100], TiO_2 [108, 109], CoO [36], ZrO_2 [8, 22, 57, 110–113], cordierite [22, 114], and SiC [22] supports.

As shown by Kang et al. [41], doping of manganese oxides with lanthanum enhances the mechanical strength of the $\text{MnO}_x/\text{La}/\text{Al}_2\text{O}_3$ catalyst by almost 58% relative to the $\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst. Thus, it can be expected that the $\text{MnO}_x/\text{La}/\text{Al}_2\text{O}_3$ catalyst can minimize the wear of catalyst pellets in the catalyst bed in the course of the engine operation. In addition, it is reported that the support, lanthanum-doped alumina, is more resistant to thermal shock owing to decreased porosity.

Nanocomposite catalysts based on mixed manganese, yttrium, and zirconium oxides with 5, 15, and 30% Mn content were prepared by sol–gel synthesis. Their catalytic activity was higher than that of Mn/Zr oxide catalysts prepared by impregnation. However, the catalyst activity considerably decreased in the course of operation [95]. Almost 100% efficiency was noted for the $\text{MnO}_2/\text{ZrO}_2$ catalyst [81].

Bonifacio et al. [27] estimated the capability of a monolithic catalyst with the manganese oxide active phase to decompose hydrogen peroxide starting from the liquid phase at ambient temperature. This characteristic of the catalyst is an important prerequisite for accident prevention. The process was performed

using a reactor with a constant hydrogen peroxide volume with a preset amount of the catalyst; constant temperature was maintained. The reaction progress was monitored using various qualitative and quantitative methods [23, 53, 108]. The capability of the catalyst to decompose hydrogen peroxide in the vapor phase was also evaluated. Computation modeling and simulation of the catalyst operation have shown [27] that, under the operation conditions typical for an engine with hydrogen peroxide, the majority of catalysts will operate with hydrogen peroxide in the vapor phase. Unfortunately, published data mainly concern the conditions of the decomposition of liquid hydrogen peroxide. Data on the vapor phase are extremely scarce. A reactor operating under isothermal conditions was fabricated for studying the hydrogen peroxide decomposition in the vapor phase [25].

COMPARATIVE EVALUATION OF THE PERFORMANCE OF CATALYST ACTIVE PHASES

Literature survey shows that the conditions of trials on hydrogen peroxide decomposition in different studies appreciably differ from each other depending on the goals of the study, which strongly complicates comparative evaluation of the performance of hydrogen peroxide decomposition catalysts. The main parameters characterizing the catalyst performance are the degree and rate of hydrogen peroxide decomposition, time in which the steady-state operation mode is reached after the contact of hydrogen peroxide with the catalyst, rate and extent of the pressure buildup, temperature of decomposition products, and rate of outflow of the decomposition products from the combustion chamber nozzle.

Studies of the catalytic activity of powders of various manganese oxides and silver in contact with 30% hydrogen peroxide have shown that Mn_2O_3 is the most effective catalytic material, silver and MnO_2 are less effective (they show approximately equal performance), and MnO is the least active [23]. Mn_2O_3 considerably surpasses the other materials in the performance. Silver oxide is one of the least active catalysts of hydrogen peroxide decomposition. Visual tests on metal wires have shown that, among metal catalysts, silver probably shows the highest performance; platinum, palladium, and gold are ranked next [23]. The catalyst activity series can change in going from powdered to supported catalysts.

The performance of hydrogen peroxide decomposition catalysts was compared in several papers; the results are often contradictory. For example, Pirault-Roy et al. [14] studied the catalytic activity of silver, platinum, and manganese dioxide in hydrogen peroxide decomposition and found that the catalysts could be ranked in the following order: $\text{Ag} > \text{MnO}_2 > \text{Pt} > \text{Ir}$ and Sn-doped Pt

Amrousse et al. [113] studied the catalytic activity exhibited in decomposition of 30% HP by manganese oxide and platinum deposited onto porous metal foam based on Fe, Cr, and Al with a $\gamma\text{-Al}_2\text{O}_3$ coating. They also showed that manganese oxide was more active than platinum.

Data on the decomposition of hydrogen peroxide on the Ag_2O , RuO_2 , MnO_2 , Mn_2O_3 , PbO , and V_2O_5 active phases deposited onto Al_2O_3 ($S_{\text{sp}} \sim 200 \text{ m}^2 \text{ g}^{-1}$), zeolite molecular sieves ($S_{\text{sp}} \sim 900 \text{ m}^2 \text{ g}^{-1}$), and silicon oxide ($S_{\text{sp}} \sim 300\text{--}500 \text{ m}^2 \text{ g}^{-1}$) show that the catalysts can be ranked in the following order with respect to the decomposition rate of 70% hydrogen peroxide: $\text{Mn}_x\text{O}_y > \text{RuO}_2 > \text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{V}_2\text{O}_5 > \text{Ag}_2\text{O} > \text{PbO}$ [18].

Romeo et al. [63] compared the performance of two types of catalysts on ceramic supports with the Pd, Pt, Ag, Mn_xO_y , Ru, or Ru_xO_y active phase. Spherical granules of Al_2O_3 0.6 mm in diameter ($S_{\text{sp}} = 170 \text{ m}^2 \text{ g}^{-1}$) and $\text{Al}_2\text{O}_3\text{-SiO}_2$ (70 : 30) 0.6 mm in diameter ($S_{\text{sp}} = 401 \text{ m}^2 \text{ g}^{-1}$) were used as supports. The catalyst performance was evaluated by their reaction with 30% hydrogen peroxide. The following activity series was obtained: $\text{Pt} > \text{Ag} > \text{Ru} > \text{Mn}_x\text{O}_y > \text{Pd} > \text{Ru}_x\text{O}_y$. The performance of silver was equal to that of platinum; however, after 15 runs the performance suddenly sharply decreased. It was found that silver was washed out from the aluminum oxide surface because of its weak adhesion to aluminum oxide.

Surmacz [49] presented published data on the experimental qualitative evaluation of the activity exhibited in the decomposition of 30% hydrogen peroxide by some types of catalysts with the Mn_xO_y , Pt, Ru, and Pd active phase deposited onto $\gamma\text{-Al}_2\text{O}_3$ by impregnation. The catalysts can be ranked in the following order with respect to the catalytic activity: $\text{Pt}/\text{Al}_2\text{O}_3 > \text{RuO}_2/\text{Al}_2\text{O}_3 > \text{Pd}/\text{Al}_2\text{O}_3 > \text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$. However, according to [36], granulated catalysts based on manganese, cobalt, and aluminum oxides surpass in performance silver gauze and platinum on aluminum oxide. On the other hand, in [115] pellets of a platinum catalyst on an aluminum oxide support surpassed in performance

pellets of manganese oxide on the same support; however, the experiments were performed with a mixture of hydrogen peroxide with ethanol. The above data show that manganese oxide and platinum catalysts exhibit the highest performance irrespective of the support.

INFLUENCE OF THE MATERIAL, SHAPE, AND SPECIFIC SURFACE AREA OF THE SUPPORT ON THE CATALYST BED PERFORMANCE

Several types of structured supports have been studied: gauzes [21, 64, 66, 116], beds of metal oxide pellets [31], fine granules, porous foamed metallic materials [113, 117, 118], or honeycomb (cellular) monoliths with definite flow-through channels [22, 29, 57, 119]. These structures were suggested for increasing the active surface area, but too large catalyst volume should be avoided in this case. Despite high porosity, the catalyst should exhibit high mechanical strength and ensure stable contact of hydrogen peroxide with the active phase. Another important characteristic of the structured catalyst is the uniformity of the flow-through channels, allowing the pressure drop in the catalyst bed, caused by too rapid decomposition of hydrogen peroxide, to be reduced or avoided.

Studies of the granulated and pelletized platinum catalysts on a $\gamma\text{-Al}_2\text{O}_3$ support have shown that the catalyst in the form of grains is more active than the pelletized catalyst. On the other hand, the catalyst grain size also significantly influences the hydrogen peroxide decomposition rate. For equal amounts of the catalysts, the external surface area increases with a decrease in the grain size, leading to higher catalytic activity [63].

A study of the catalytic decomposition of hydrogen peroxide in the vapor phase at 200°C on cylindrical and honeycomb monolithic catalysts prepared by deposition of the MnO_x active phase onto a zirconium dioxide support has shown that the honeycomb shape allows higher degree of hydrogen peroxide decomposition to be reached at lower content of the active phase and shorter length of the catalytic bed, compared to the cylindrical support [29].

Some experiments on the decomposition of concentrated HP on catalysts with manganese oxide have shown that not only the shape but also the composition of the support influences the catalytic properties [117, 120].

Krejci et al. [120] studied a large amount of catalyst samples with the active phase of manganese oxides and platinum, deposited onto various types of cellular supports with different channel geometry. Other catalyst shapes such as pellets and foam were also considered for comparison.

In the first series of trials (22 kinds of catalysts), all the catalysts were of the monolithic type with the same size (20 mm long, 12.2 mm in diameter). Platinum metal and manganese oxides were used as an active phase. Attention was paid to comparison of support materials: cordierite and silicon carbide (SiC), and also to differences in the channel density and geometry (square and triangular channels). In addition, two methods for the active phase deposition with the deposition of intermediate thin layer of high specific surface area (wash-coating method) were compared. The channel density was 62–93 channels per 1 cm². Trials were performed in a flow-through reactor similar to a rocket engine.

Despite large data scatter in the trial results, the catalysts showed satisfactory characteristics. The pressure in the chamber increased to 90% of the required pressure within 350–500 ms after the injection of hydrogen peroxide. No less than 3.28 s is required to reach a temperature of 500°C after a cold start (the temperature threshold $T = 500^\circ\text{C}$ was chosen because, as shown in [121, 122], self-ignition of the propellant with hydrogen peroxide decomposition products in a two-component engine requires the temperature higher than 450°C.)

In the second series, various shapes of catalyst supports, including monoliths and foams of various lengths, and pelletized catalysts were studied. Qualitative comparison of different catalyst types was performed on the same test reactor.

It was found that the time of reaching the steady-state operation mode varied from 6 to 21 s for monolithic catalysts and from 6 to 12 s for pelletized catalysts. The preferable catalysts are MnO_x/cordierite monolithic catalysts and MnO_x/γ-Al₂O₃ pellets with high specific surface area and tetrapetal cross section.

The influence of the load on the catalyst characteristic in the transient period was studied. The positive effect of the increased flow mass was noted. A study of the lifetime of monolithic catalysts 20 and 10 mm long has shown that the total hydrogen peroxide load before the catalyst operation stops is 17.7 and 4.15 kg, respectively [120].

Wide assortment of catalysts used in that study demonstrate satisfactory characteristics (mean efficiency

95–99%), but the scatter of the results in many cases is larger than the difference between the results obtained on different catalyst configurations. Nevertheless, the results obtained allow the general way to improve the catalyst performance to be outlined. The above-noted MnO_x/cordierite monolithic catalyst and MnO_x/γ-Al₂O₃ pelletized catalyst and, in addition, Pt/γ-Al₂O₃ exhibit also the highest mean performance evaluated by the maximum temperature reached.

Surmacz [49] studied the activity exhibited toward 98% hydrogen peroxide by catalyst beds based on manganese oxides deposited on aluminum oxide pellets as supports. The pellets differed in the size, specific surface area, and aluminum oxide phases. Trials were performed on an installation simulating a monopropellant rocket engine. The catalyst activity was judged from the maximal temperature of the products. The highest performance was reached with pellets of high specific surface area irrespective of the active phase content, whereas spherical particles of low specific surface area, including zeolites, showed the lowest performance.

As judged from the maximum reached temperature, pellets of the catalyst with γ-alumina support of high specific surface area show the highest performance.

Along with comparison of the active phase performance and with the influence exerted on the catalyst performance by the kind of support, procedures for active phase deposition, and catalyst bed structure, the influence of other parameters was also studied. For example, Bonifacio [10] performed a comparative study of the influence of such parameters as the ratio of the catalyst bed length to its diameter, axial load on the catalyst, and volumetric load (defined as the gravimetric flow rate of hydrogen peroxide divided by the catalyst volume).

In most cases, high performance of both pelletized and monolithic catalysts can be noted, but it is difficult to estimate unambiguously the effect of the geometric size.

Despite the above-noted advantages of monolithic catalyst supports, in some cases they are inferior in certain parameters to catalysts on pelletized supports. Comparative trials of pelletized and monolithic catalysts with the Na_{0.2}MnO₄ active phase, used for the decomposition of 90% hydrogen peroxide, were performed with a 10 N thruster; the temperature of hydrogen peroxide decomposition products and pressure in the chamber were higher in the case of the pelletized catalyst [123].

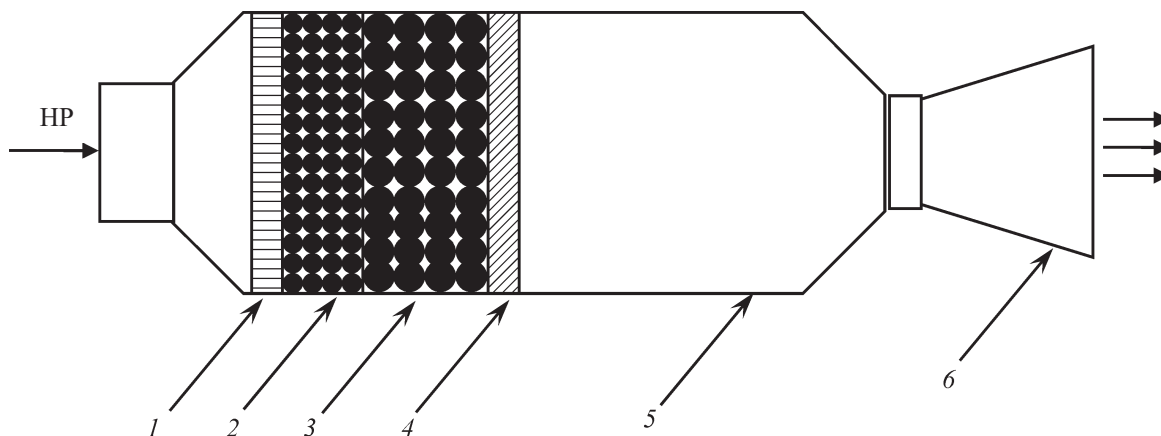


Fig. 1. Schematic of a thruster with doubled bed: (1) injectors, (2) bed of 1.18–2.00 mm granules, (3) bed of 3.175 mm granules, (4) disperser, (5) combustion chamber, and (6) nozzle.

The pressure drop in the catalyst bed was moderate (0.02–0.1 bar in the case of the monolith and 0.3–0.7 bar in the case of the pelletized support) [123].

COMBINED CATALYST BEDS

A number of studies deal with the influence of the catalyst bed design and size on the pressure stability in the transient period of the monopropellant thruster operation [37, 56].

Surmacz [49] developed and tested a special design of the catalyst for the decomposition of 98% hydrogen peroxide, named composite catalyst bed. The catalyst name is associated with the bed structure, namely, with the alternation of beds of Mn_xO_3/Al_2O_3 ceramic pellets and packs of platinum catalyst on metal–ceramic gauze. The trials showed that the catalyst bed was resistant to thermal shock, mechanical impact, and poisoning with decomposition products. Surmacz believes that this structure should combine the advantages of different catalyst types such as good mechanical properties, high activity, good cold start characteristics, and long operation life.

Although pelletized catalysts cause considerably lower pressure drop than powder catalysts do, large pressure drop and pressure oscillation are still observed at high flow rates of hydrogen peroxide and its decomposition products (the load on the catalyst can reach $10 \text{ g cm}^{-2} \text{ s}^{-1}$) [50]. Koopmans et al. [124] studied how the granule shape and size influence the pressure drop in the catalyst bed. They showed that cylindrical pellets with the diameter to length ratio greater than 2 cause lower pressure drop than spherical pellets do.

The problem of the pressure drop becomes particularly pronounced with an increase in the thruster scale, which is accompanied by an increase in the pressure drop. Therefore, it becomes necessary to increase the pressure head with an increase in the pressure drop in the catalyst bed (decrease in pressure from the hydrogen peroxide inlet to lower layers of the catalyst). An increase in the pressure head leads to disintegration of the lower layers of the catalyst and to an increase in the engine mass due to the need for reinforcing the structure.

A doubled catalyst bed consisting of a bed with 1.18–2.00 mm granules and a bed with 3.175 mm granules was suggested for eliminating these problems (Fig. 1). The active phase of catalyst granules is manganese oxide with an addition of lead oxide. The optimum amount of the fine bed at which the pressure drop decreases is 18.3% [125].

Alternative arrangements of silver catalysts were also considered. For example, in [21] the bed consisted of two sections. The first section consisted exclusively of silver gauze disks with stainless steel gauze disks separating them, and the second section, of a pack of silver gauze disks followed by a platinum catalyst on a monolithic support. The double catalyst pack favors a decrease in the pressure drop and allows decomposition of 90% hydrogen peroxide to up to 90%.

PERFORMANCE OF DECOMPOSITION CATALYSTS IN SATELLITE THRUSTERS

The mass and size of a satellite thruster should be as small as possible to increase the useful load. The overall thruster size depends primarily on the catalyst bed vol-

ume, and the mass and volume of the catalyst bed should correspond to the hydrogen peroxide amount that should be decomposed on the catalyst [67, 126, 127]. Therefore, the overall performance of the catalyst bed (hydrogen peroxide decomposition rate, diameter and length of the catalyst bed, weight, capability for repeated starts, etc.) strongly influences the thruster mass and size. A thruster has a small size if the propellant decomposition rate in the catalyst bed is high; on the other hand, the catalyst bed should ensure repeated start of the engine.

The performance of catalyst beds can also be influenced by external factors such as preliminary heating and mode of hydrogen peroxide injection (injector design), which can also influence the thruster mass and size.

To control the orbit height, orientation, and other maneuvers of satellites differing in the size and mass, various engine systems are being developed, namely, monopropellant thrusters with the thrust from 100 mN to 50 N for micro- and small satellites [15, 42, 67, 76, 89, 128–132] and two-component (oxidant + propellant) thrusters with the thrust from 100 to 2500 N [133–135] and hybrid thrusters with the thrust from 250 to 2500 N [136–139] for large satellites. For very small satellites such as cubesats (cubic satellites), the problems of the thruster development becomes more complex. New thruster concepts with hydrogen peroxide vapor as a propellant were suggested for such thrusters recently [140].

It is known that, the more complete is the hydrogen peroxide decomposition, the higher is the engine performance. In a monopropellant rocket engine, the elevated decomposition temperature leads to the increased specific impulse. In two-component and hybrid rocket engines using hydrogen peroxide, incomplete hydrogen peroxide decomposition may be acceptable if the decomposition catalyst can generate sufficiently hot oxidizing vapor to ignite the propellant. In any case, the catalyst operation life will determine the engine operation life [81].

A monopropellant thruster usually operates in the pulse mode with short response time; operation under the conditions of repeated starts requires that changes in the catalyst performance be insignificant. In high-thrust two-component and hybrid thrusters, a large amount of hydrogen peroxide is consumed in one run within hundreds of seconds. The two-component thruster should have a design minimizing the combustion instability and increasing the combustion efficiency [15].

Today the development of thrusters based on hydrogen peroxide is being performed in many research laboratories in the United States and China, to a greater extent in Europe (Italy, Austria, Poland, France, Germany), and very actively in the Republic of Korea and some other Asian countries (Japan, India, Malaysia). A series of two-component thrusters operating on kerosene and 94–98% hydrogen peroxide are being developed at the Moscow Aviation Institute (Russia) [135, 141].

The above-presented survey of studies performed in the past two decades on the development of catalysts for the decomposition of highly concentrated hydrogen peroxide shows that a wide range of catalysts for the development of diverse thrusters are available to engine designers. The main parameter in choosing the catalyst is the performance of the catalyst bed, because the completeness and rate of the hydrogen peroxide decomposition can play a key role in the development of any thruster.

Use of catalysts in monopropellant thrusters. Much attention in the development of monopropellant thrusters is paid to the influence of the catalyst and thruster design on the pressure stability in the course of operation. In a common rocket engine, to reach uniform combustion, the pressure fluctuations in the reaction chamber in the steady-state mode should not exceed $\pm 5\%$ of the mean pressure in the chamber. Although several analytical studies of the low-frequency instability of monopropellant thrusters taking into account their practical significance were performed, the pressure instability data available for analysis are very few [142].

Among three types of instability, high-, medium-, and low-frequency instability, major attention is paid to the low-frequency pressure instability, because it is manifested mainly in low-thrust rocket engines with low-pressure chambers (0.69–3.45 MPa) [37, 56, 142]. The catalyst performance can strongly influence the pressure stability in the decomposition chamber.

Jo et al. [37, 38, 56] studied the pulsating instability of monopropellant thrusters on hydrogen peroxide with granulated $\text{MnO}_2\text{-PbO}$ and MnO_2 catalysts on aluminum oxide support. The instability depends on the propellant feeding mode, catalyst activity, and catalyst bed size. Experimental studies [38] have shown that such characteristics of hydrogen peroxide decomposition as the pressure and temperature elevation time and residual time depend on the catalyst activity. The operation time

was determined from the pressure in the chamber. The pressure elevation time was determined as the time in which the pressure increases from 1% relative to the pressure in the chamber ($P_c + 1\%$) to 90% of P_c ($P_c + 90\%$) in the ascent phase. The residual time, or the pressure decrease time, was defined as the time in which the pressure decreased from 95 to 10% of the pressure in the chamber in the pressure descent phase. The experimental results show that the more active catalyst (the MnO_2 - PbO catalyst is more active than MnO_2) decreases both the elevation and decrease times to a greater extent.

The development of thrusters with a catalyst based on silver gauzes is still being continued [74, 75, 78, 112, 143]. High (up to 95–100%) degree of decomposition of 90–92% hydrogen peroxide [75, 77, 79, 144] and the specific impulse of 101 [144] and 104.4 s [79] have been reported.

Whereas silver catalysts were mainly used for the development of 0.5–1 N thrusters, platinum catalysts on aluminum oxide are used in 5–50 N thrusters [27, 30, 67, 89, 131]. High activity of the catalysts ensures 95–98% decomposition of 98% hydrogen peroxide [27, 67, 131]. The thruster developed in [27] had a specific impulse on the sea level of 130 s, which corresponds to 185 s in a vacuum.

Recently Baek et al. [145] reported on the development of a 10 N thruster operating on an ethanol–hydrogen peroxide mixture as a monopropellant with platinum on γ -alumina used as a catalyst. The propellant has the specific impulse in a vacuum of 214 s and the volumetric specific impulse in a vacuum of 276 g s. Fire tests of the thruster for 5 s showed that the efficiency was 95.3% and the pressure oscillations in the chamber were $\pm 13\%$. To reduce the combustion instability, highly heat-resistant lanthanum hexaaluminate was used as a support. The pressure oscillations in this case were $\pm 3.8\%$ at the 92.8% efficiency [145]. These results demonstrate the feasibility of the development of a high-performance thruster for space research with hydrazine as a propellant replaced by a nontoxic mixture of ethanol and hydrogen peroxide.

Catalysts based on the active phase of manganese oxides are being widely tested and are used in monopropellant thrusters [15, 42] and hybrid engines [97, 110]. Preliminary heating of the catalyst to 150°C appreciably improves the process stability, decreases

the decomposition onset time, and improves the other characteristics of the engine [103].

Along with the effect of catalysts on the thruster operation, the effect of the structural elements on the degree of the catalyst degradation and on the constancy of the hydrogen peroxide decomposition rate are also being examined. Particular attention is paid to the development of injectors for feeding hydrogen peroxide [131, 116].

Two-component thrusters. Along with monopropellant thrusters, the development of two-component thrusters with the thrust from 1 to 1200 N is a subject of active studies [51, 100, 134, 146–148]. In a two-component engine, hydrogen peroxide is fed to the combustion chamber in the liquid form, or hot products of its catalytic decomposition are injected into the combustion chamber. In this case, the decomposition products should evaporate and ignite the liquid propellant, which is also fed to the combustion chamber (Fig. 2) [149].

The latter method has a number of advantages. The injection system becomes simpler, because the stream of gaseous decomposition products, when coming in contact with the stream of the propellant injected into the combustion chamber, rapidly sprays it, favoring efficient reaction of the propellant with the oxidant. Another advantage is that the temperature of the hydrogen peroxide decomposition products is higher than the propellant self-ignition temperature; thus, the need for a separate ignition system is eliminated.

However, in this case the designs of the injector and combustion chamber should ensure appropriate flow conditions for the self-ignition and combustion sustainment. Because the oxidant/propellant weight ratio for the optimum theoretical performance of the hydrogen peroxide/kerosene propellant is about (7.5–8) : 1 (depending on the hydrogen peroxide concentration), it is difficult to fully mix a relatively small amount of the propellant with the oxidant. The injector and combustion chamber designs should favor both efficient mixing and self-ignition [8, 150].

In practical use of two-component thrusters, one of the key parameters is the ignition delay time (IDT), which depends on complex interaction of many chemical and physical factors. The most important of them are the local mixing conditions, oxidant to propellant ratio, spraying pressure, and injector size. The ignition delay includes the physical delay (spraying,

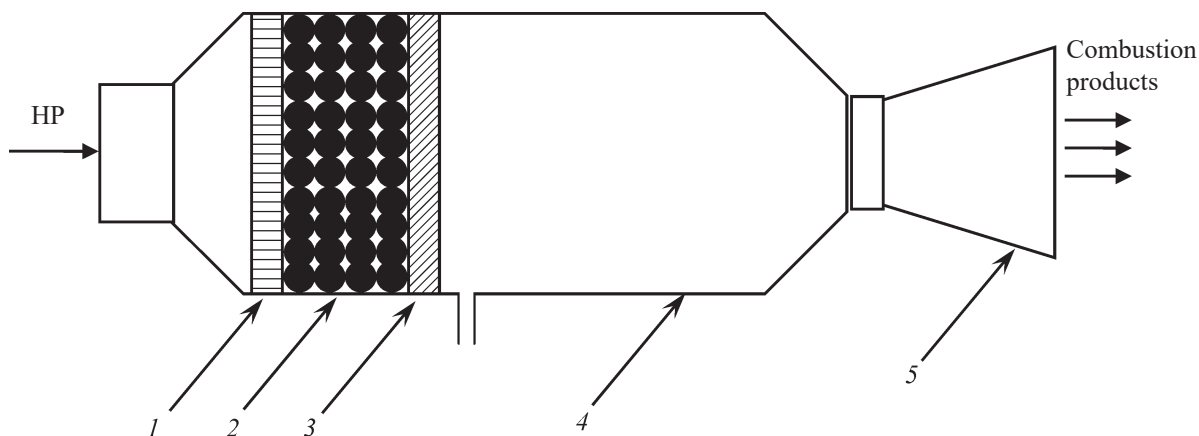


Fig. 2. Schematic of a two-component thruster: (1) injectors, (2) catalyst bed, (3) disperser, (4) combustion chamber, and (5) nozzle.

mixing, evaporation, and diffusion) and chemical delay (gas-phase reactions). The characteristic times of each process constitute the total ignition delay time [111]. The physical delay strongly depends on the injection technique, which, in turn, depends on the injector configuration and injection parameters. The chemical delay is largely determined by the activity of the hydrogen peroxide decomposition catalyst, temperature of hydrogen peroxide decomposition products, and propellant/oxidant ratio [111]. Too high IDT can lead to accumulation of the propellant in the combustion chamber, which, in turn, can lead after uncontrollable ignition to catastrophic hard start [54] or even to the engine destruction [151].

It has been found that the ignition delay time decreases with an increase in the degree of hydrogen peroxide decomposition, in the hydrogen peroxide concentration, and in pressure.

Woschnak et al. [51, 122] studied the self-ignitability of the propellants, kerosene and ethanol, in a two-component thruster using 87.5% hydrogen peroxide and monolithic catalysts: platinum metal and manganese oxides on cordierite. They noted short ignition delay, no need for a device for catalyst preheating, mild combustion mode, and high efficiency of the hydrogen peroxide decomposition. Trials of the propellant based on *n*-decane and hydrogen peroxide have shown that the ignition delay time only slightly depends on the hydrogen peroxide concentration when it is higher than 70%.

A shower-type injector for feeding hydrogen peroxide to the catalyst bed was used for studying the reaction of 90% hydrogen peroxide with kerosene in an engine with a 1200 N thrust. To increase the combustion efficiency over 90%, an axial injector for feeding

kerosene to hydrogen peroxide decomposition products was designed [100].

Hybrid thrusters. Active efforts are focused on the development of hybrid thrusters with a 250 to 2500 N thrust on highly concentrated hydrogen peroxide and polyethylene [128, 137, 138]. Kang et al. [138] describe the design and performance of a hybrid rocket engine with a 250 N thrust, using 95% hydrogen peroxide as an oxidant and polyethylene propellant for improving the specific impulse and combustion efficiency. The use of 95% hydrogen peroxide with a heat-resistant catalyst instead of 90% hydrogen peroxide allows the specific impulse and volumetric specific impulse to be increased to the values exceeding those for the hybrid rocket engine using nitrogen oxides as an oxidant. The hybrid engine with such combination of the oxidant and propellant has considerably smaller mass and volume. Fire trials of the engine with a 250 N thrust have been performed. Such engine is characterized by the minimal ignition delay time.

A catalyst bed for hydrogen peroxide decomposition was included, in addition to an electric spark igniter, into the design of a hybrid engine based on 85–90% hydrogen peroxide and acrylonitrile–butadiene–styrene copolymer. Silver gauzes and $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ pellets [152] or pellets containing potassium permanganate, manganese dioxide, and potassium nitrate were used as catalysts. Pellets based on manganese oxide showed in this case 20–22% higher performance compared to silver gauzes.

Review [153] summarized data on the influence exerted on the ignition delay time by hydrogen peroxide decomposition catalysts dissolved or suspended in propellants and used in two-component and hybrid rocket engines.

Experiments on using 98% hydrogen peroxide, yet difficultly available and expensive, are being performed to increase the specific impulse of thrusters [131, 154]. Going from 87.5% to 98% hydrogen peroxide increases the theoretical specific impulse of hybrid engines by 12 s [9]. In so doing, it becomes necessary to use catalysts on highly heat-resistant supports.

CONCLUSIONS

Analysis of the published data demonstrates increased interest in the development of so-called “green” rocket propellants based on highly concentrated hydrogen peroxide and, correspondingly, of hydrogen peroxide decomposition catalysts. The desire of rocket engine designers to use hydrogen peroxide of concentration higher than 92% (desirably 98%) leads to increased requirements to catalysts to ensure primarily high rate of catalytic decomposition, high resistance to thermal shock and mechanical impact, and long operation life of the catalyst.

The above-considered data show that the catalyst performance depends on the combination of the active phase and of the support material and shape. The previously developed catalysts based on silver gauzes start to be inferior to granulated and monolithic catalysts. Granulated catalysts with a support based on aluminum oxides exhibit enhanced heat resistance allowing use of 95–98% hydrogen peroxide. Monolithic catalysts exhibit high mechanical strength allowing their use under the conditions of rapid alternating changes in the pressure and temperature in the catalyst bed.

Among numerous compounds catalyzing the hydrogen peroxide decomposition, manganese oxides, platinum, and silver are preferred.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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