

PERFORMANCE OF A 2N MICROTHRUSTER USING HYDROGEN PEROXIDE AND A MIXED OXIDE BULK CATALYST

Fernanda Francisca Maia, maia@lcp.inpe.br
Leonardo Gouvea, samura.leo@gmail.com
Luis Gustavo Ferroni Pereira, luisgfp@yahoo.com.br
Fernando de Souza Costa, fernando@lcp.inpe.br
Ricardo Vieira, ricardo.vieira@lcp.inpe.br

Combustion and Propulsion Associate Laboratory (LCP)
Brazilian Space Research Institute (INPE)
P.O. Box 01, Cachoeira Paulista, SP, CEP 12630-000, Brazil

Abstract: *New bulk catalysts based on mixed oxides of cobalt and manganese were prepared by co-precipitation for decomposition of high grade hydrogen peroxide. A 2N thruster was used to evaluate and compare the catalysts in continuous and pulsed firings. The Al containing mixed oxide catalyst presented the best performance, decomposing spontaneously the propellant and sustaining several thermal cycles without presenting fractures and deactivation caused by impurities and stabilizers in the propellant. Since experimental results were close to theoretical ones, this material has a good potential for peroxide decomposition in propulsion systems.*

Keywords: *satellite propulsion, hydrogen peroxide, catalyst, mixed oxide*

1 Introduction

Monopropellant propulsion systems are commonly used for orbit correction and attitude control of satellites, rolling and other auxiliary functions. They are simpler and lower cost, but they present lower specific impulses than bipropellant propulsion systems.

Hydrogen peroxide (H_2O_2) was a liquid monopropellant studied extensively in the 1960s [1], however, with the development of Shell 405 catalyst (36%Ir/ Al_2O_3), H_2O_2 was gradually replaced by hydrazine (N_2H_4), due to its better performance and stability [2]. Thus, most satellites currently in Earth orbit employ propulsion systems based on decomposition of N_2H_4 which is an extremely expensive and highly toxic monopropellant. Other catalysts also have been suggested for decomposition of hydrazine, such as: nitrides and carbides of molybdenum and tungsten [3], bimetallic catalysts (Ru-Ir/ Al_2O_3) [4] and macroscopic composites based on carbon nanofibers impregnated with iridium [5].

Recent environmental concerns have sparked interest in storable non-toxic liquid propellants. H_2O_2 is a major candidate for use as propellant in clean and inexpensive propulsion systems [6]. The traditional catalyst employed in this reaction is silver in the form of screens. The use of more concentrated solutions of H_2O_2 leads to the increase of adiabatic decomposition temperature

of the monopropellant (632°C @ 85%; 755°C @ 90%; 953°C @ 98%). This limits the application of pure silver or plated screens as a catalyst for decomposition of H_2O_2 in the long term, since the melting point of silver (962°C) is very near the decomposition temperature [7].

Most transition metals are catalytically active in the decomposition reaction of H_2O_2 . The mechanism of the decomposition reaction follows, practically, two steps: (i) a redox reaction with electron transfer at catalyst surface, resulting in the formation of free radicals, followed by (ii) a chain reaction, where the radicals formed react, producing H_2O and O_2 . Kinetic studies of the decomposition reaction of H_2O_2 in the liquid phase showed that: single or mixed oxides of transition metals with higher oxidation state are more active in the decomposition of H_2O_2 than their lower homologous; that the determining step of this reaction is the removal of electrons from the metal; that the specific surface area of the catalyst has little influence on the reaction rate, since the O_2 prevent the diffusion of reactants within the pores of the catalyst; and that the reaction activation energy is the most appropriate criterion for catalytic activity [8,9].

The decomposition reaction of H_2O_2 for propulsion applications is extremely rapid, occurring in the vapor phase, and the thruster induction time is very dependent on the number of active sites exposed to the reaction. As this

reaction is highly exothermic, a few seconds after ignition, the catalytic bed may reach sufficient temperature to make the reaction almost entirely of thermal nature.

MnO₂ is one of the most studied catalysts for H₂O₂ decomposition. The problem is that if MnO₂ reduces during reaction, it changes to Mn₂O₃, losing considerably its catalytic activity. In the other side, higher temperatures lead to formation of Mn₃O₄, as active as MnO₂. Manganese atoms with different oxidation states present in the same network exchange electrons, providing the mobility necessary for the activity of the surface redox [10]. Therefore, mixed oxides with perovskite or spinel type structures are commonly employed as catalysts for redox reactions, in general, and, in particular, for H₂O₂ decomposition.

Other formulations of catalysts have been proposed to replace the traditional silver catalysts [11,12], most of them based on manganese oxides supported on alumina, silica or titania. The authors reported that a support with high surface area is essential for a high activity catalyst. Rusek [11] further found that the metallic silver is more catalytically active in the decomposition of H₂O₂ than silver oxide and that Mn⁴⁺ is more active than the Mn³⁺.

Tian *et al.* [13] employed iridium supported on alumina in the decomposition of H₂O₂, i.e., the same catalyst employed in the decomposition of N₂H₄. The authors observed a deactivation of this catalyst system as a function of time, caused by oxidation of the metal and adsorption species used as stabilizers of H₂O₂ in the catalyst surface. Recently, some authors have proposed the use of platinum supported on alumina as a catalyst for the decomposition of H₂O₂ in micro-thrusters [14,15]. Despite the active phase high cost, the biggest problem on this catalytic system was the support low mechanical strength [16]. It was observed catalyst grain rupture during tests, causing loss of the active phase which is ejected by the nozzle. This creates voids in the catalyst bed, which accelerates the rate of breakage and producing instability in engine operation.

Most published studies have suggested supported catalysts for the H₂O₂ decomposition reaction. Thus, the catalyst support needs to present high thermal and mechanical resistance, elevated chemical stability and high specific surface area. The impregnation step is crucial for a good

anchoring of the active phase on the support. In the case of the use of manganese oxide as the active phase, the precursors most commonly used are permanganates and the permanganic acid. Formation of manganese oxides is usually carried out by thermal decomposition of the precursor. The low interaction precursor/support can result in a poor anchoring of active phase on the support, which may be partially ejected during the first tests in the thruster. Mixed oxides containing transition metals are often used as bulk catalysts in different chemical reactions. Generally, these oxides are prepared from thermal decomposition of different precursors, such as hydroxides, carbonates, nitrates, oxalates, etc. Cobalt and manganese may achieve various oxidation states and thus be effective catalysts used in redox reactions. Kannan and Swamy [17] tested mixed oxide of Co and Al as a catalyst for decomposition of nitrous oxide. The authors observed an increase in catalyst activity with increasing Co content in the catalyst system. Bernal *et al.* [18] synthesized mixed oxides of Fe and Co by the method of co-precipitation at pH 9.5. They noted that a molar ratio Co/Fe of 1/2 tends to generate a phase of spinel type, predominantly with Co²⁺, when calcined at high temperature. Samples with higher ratios have different amounts of Co₃O₄ and CoO formed between 800 and 900°C. Given the above and some preliminary tests already performed in our laboratory that showed promising results, we propose the use of mixed oxides of manganese and cobalt bulk catalysts, extruded, in the decomposition of high grade H₂O₂ (90%) for use as a monopropellant in satellite micro-thrusters. Different transition metals and precipitation methods were used aiming to find a material with high mechanical strength and significant surface area, even after thermal treatments at high temperatures. The materials were tested in a micro-thruster manufactured in modules, with a theoretical thrust of 2N, for efficient catalytic decomposition of H₂O₂ 90%.

2 Experimental

2.1 Hydrogen peroxide concentration

Stabilized hydrogen peroxide 50%, supplied by Solvay Chemicals, was concentrated to 90%, in mass, by a counter flow of hot dry air. Despite stabilizers can reduce catalytic activity over time,

in this work stabilized H_2O_2 was used for safer testing of the new catalyst. Alternatively, before concentration, a deionization treatment may be done to remove the stabilizers in the monopropellant.

2.2 Catalyst preparation

Four catalysts based on mixed oxides were prepared: CoMnAl, CoMnAg, CoMnMg, in a 4:1:1 ratio, and CoMn, in a 4:2 ratio. The catalysts were synthesized by the same method employed by Kovanda [19] from the co-precipitation of solutions of nitrates of metal ions in Na_2CO_3 solution at room temperature, keeping the pH constant at 10 by adding a NaOH solution.

The product of these reactions were filtered, washed, dried and macerated. The powder was then peptized with HNO_3 solution and finally extruded, followed by drying and calcined at 900°C . The final product presented a cylindrical form with approximate dimensions of 2mm diameter and 3mm length.

2.3 Micro-thruster

Performance parameters of the mixed oxides catalyst for hydrogen peroxide decomposition were obtained by tests with a 2N thruster, which was manufactured with modules of 316 inox steel, including injector, nozzle and a chamber with catalytic bed of 30mm length and 15mm diameter. Figure 1 shows a computer view of the thruster.

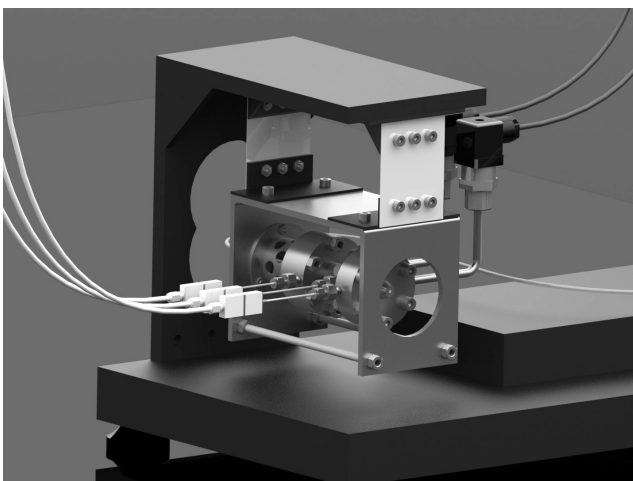


Figure 1. Computer view of thruster and thrust balance.

The CEA NASA 2004 code was used to calculate the thruster theoretical performance. Chamber

pressure was chosen as 5bar and nozzle expansion ratio was calculated as 1.45 to adapt the nozzle at 600m altitude. Assuming frozen flow, with 90% H_2O_2 , the calculated specific impulse was 1040m/s, the characteristic velocity was 940m/s and thrust coefficient was 1.106.

Pressure transducers and thermocouples were used, respectively, to measure propellant pressures and temperatures before and after injection and after the catalytic bed. Thrust was measured by a 5N load cell. A graphical user interface, written with LabView software, was used to monitor and control tests and determine induction times.

2.4 Tests

Before tests, the mass flow rate of propellant was determined as a function of differential pressure in the feeding line in order to calculate the pressure in the hydrogen peroxide tank required to provide the desired mass flow rate during a test. After this procedure, the micro-thruster was assembled and mounted on the thrust balance, the load cell was calibrated and, finally, continuous test firings of 10s were initially performed.

3 Results and discussion

The CoMnMg catalyst showed high activity in the decomposition reaction of H_2O_2 as seen in the thrust curve shown in Figure 2.

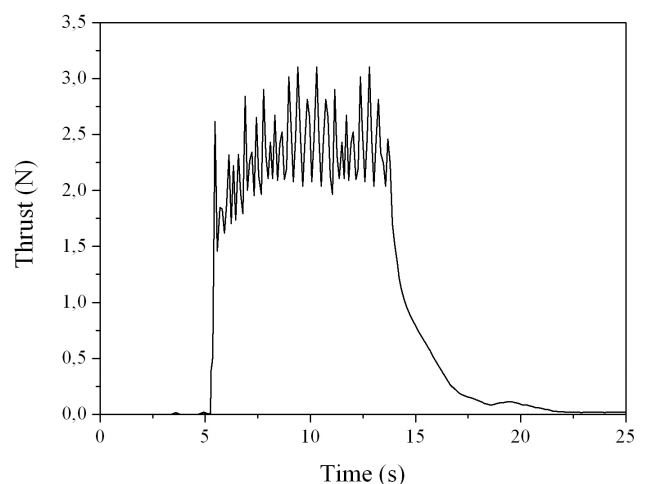


Figure 2. Thrust (N) obtained with CoMnMg catalyst.

The higher activity can be justified by the high specific surface ($23\text{m}^2/\text{g}$), formed by the strong contraction of the material during the decomposition of the magnesium hydroxide,

generating a certain porosity in the structure. However instabilities were observed as thrust peaks due to the overpressure generated inside the pores, causing fracture of the catalyst.

The addition of silver to the mixed oxides may be formed, after calcination, highly stable and less active oxides of silver in the decomposition reaction of H_2O_2 (Figure 3).

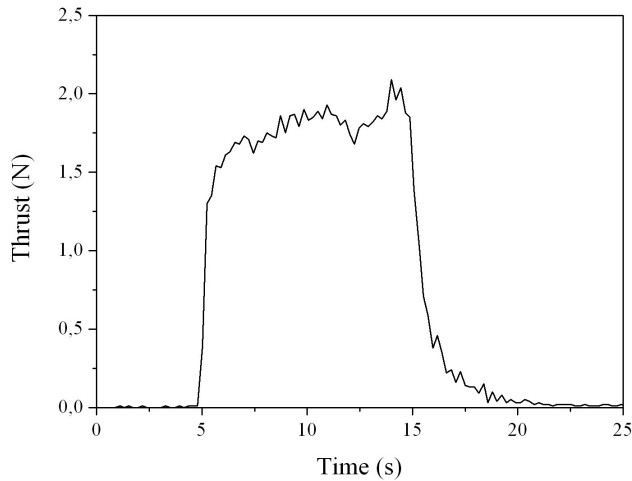


Figure 3. Thrust (N) obtained with CoMnAg catalyst.

The behaviors of CoMn (Figure 4) and CoMnAl catalysts (Figure 5) are very similar. The two catalysts were very active in this reaction. However addition of Al to the Co and Mn mixed oxide increases the catalyst mechanical strength, due to formation of α -alumina at temperatures around 400-500°C, which has high mechanical strength.

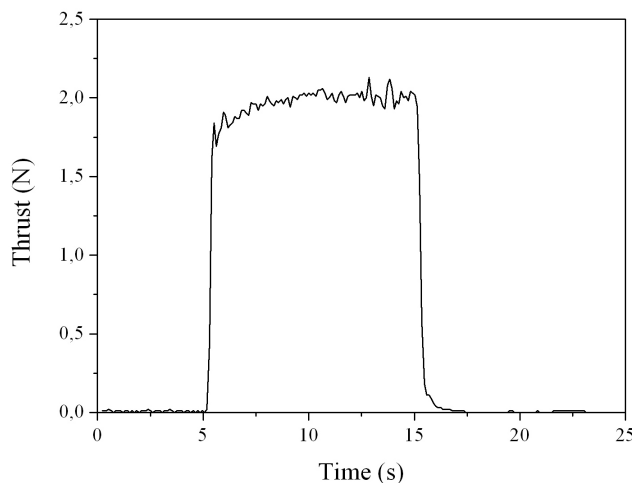


Figure 4. Thrust (N) obtained with CoMn catalyst.

Despite the high mechanical strength of the CoMnAl catalyst, its specific area was low ($\sim 6m^2/g$), due to the high temperature (900°C) in

which the material was calcinated. However, calcination temperatures lower than this tend to form products with tendency to rehydration. The average pore size calculated by the BET method was approximately 300Å corresponding to mesopores. However, catalysts for propulsion must have a bimodal pores distribution, i.e., micro and mesopores in their structure to facilitate the diffusion of the propellant and reaction products within the material.

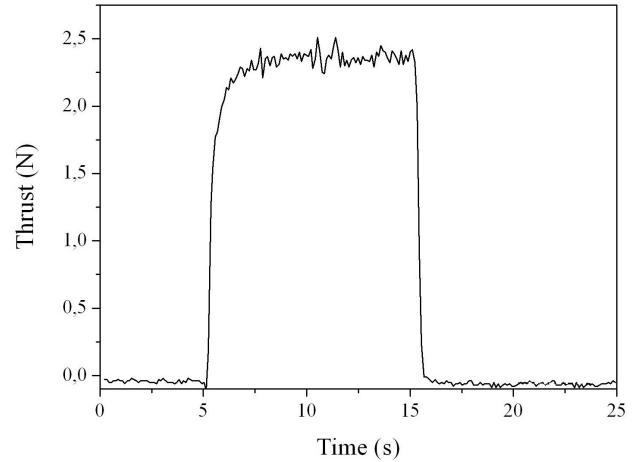


Figure 5. Thrust (N) obtained with CoMnAl catalyst.

The thruster mass flow rate, $\dot{m}$, was calculated from measured injection pressure and equation:

$\dot{m} = -0.009\Delta P^2 + 0.613\Delta P + 0.766$, obtained by studying the mass flow rate of propellant as a function of feed pressure difference, ΔP . The specific impulse, I_{sp} , was then determined by:

$$I_{sp} = \frac{F}{\dot{m}g_o} \quad (1)$$

where F is the measured thrust and $g_o = 9.8065m/s^2$ is the standard gravity acceleration. An average experimental specific impulse of 97s was calculated (Figure 6). This value is close to 106s, the value calculated with NASA CEA code (2004). Therefore the experimental result is satisfactory, since various losses occur in the process.

The experimental characteristic velocity was obtained, for nozzle throat area $3.6mm^2$, by equation:

$$c^* = \frac{A_t P_c}{\dot{m}} \quad (2)$$

Since the characteristic velocity is a function only of temperature and gas properties in the combustion chamber, one can use this parameter to examine the chamber independently of the nozzle. The theoretical value obtained was 940m/s and the experimental mean value was 822m/s (Figure 7). According to Sutton [20] the experimental characteristic velocity should be 92 to 99.5% of the theoretical value. Then, it can be concluded that a characteristic velocity efficiency of 87% is evidence of incomplete catalytic decomposition.

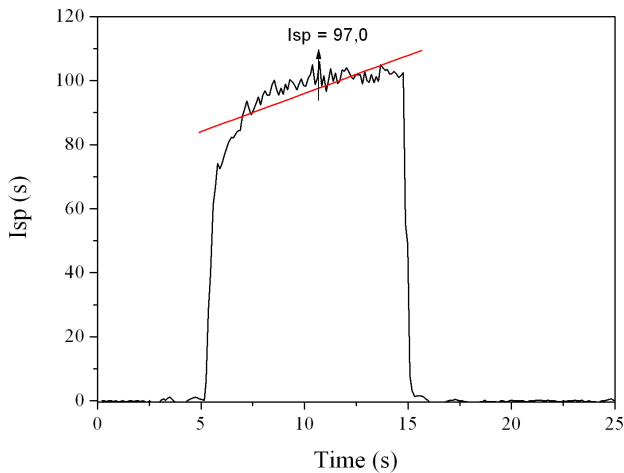


Figure 6. Specific impulse (s) obtained with CoMnAl catalyst.

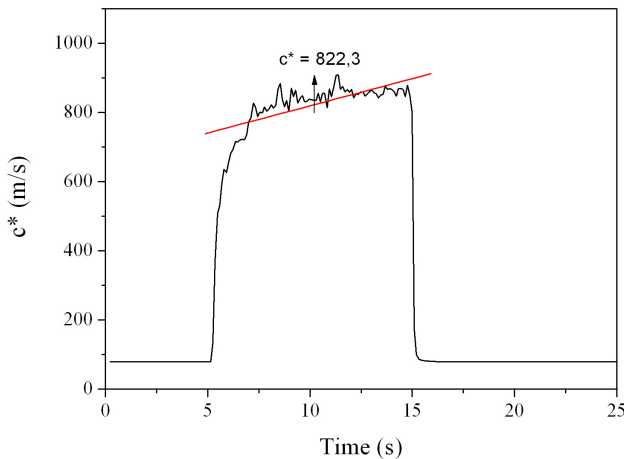


Figure 7. Characteristic velocity (m/s) obtained with CoMnAl catalyst.

Finally, a continuous firing of 30 seconds (Figure 8) and a sequence of 12 pulsed firings of 5 seconds at intervals of 5 seconds (Figure 9) were performed to check the stability of the CoMnAl catalyst. There was no evidence of catalyst deactivation with respect to time, despite the use

of stabilized hydrogen peroxide. No fragmentation of the catalyst grains was observed after tests. However, long duration and shorter pulse tests will still be performed.

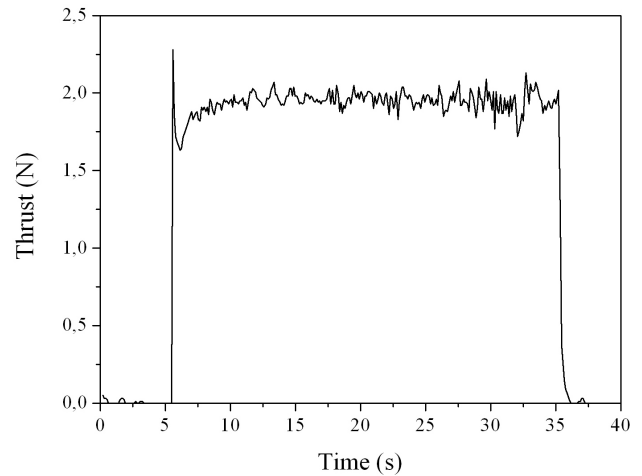


Figure 8. Thrust curve during a continuous 30-second test with CoMnAl catalyst.

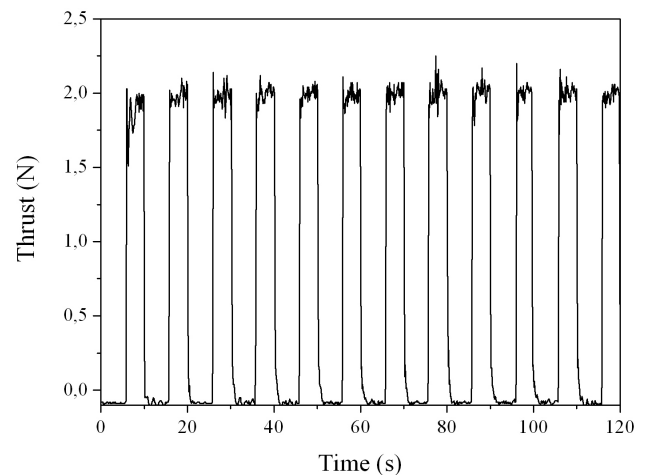


Figure 9. Thrust curve obtained during pulse test with 5s on / 5s off with CoMnAl catalyst.

4 Conclusions

Catalysts based on mixed oxides, containing Co, Mn and a promoter, were prepared and tested, showing capable of yielding various cold starts in the decomposition reaction of H_2O_2 90% in a 2N micro-thruster. The catalyst showed a high catalytic activity, despite its low specific surface. New methods of precipitation of these oxides are being studied, to generate a greater texture on the substrate.

In relation to engine performance, a specific impulse of 97s was experimentally obtained, which is satisfactory when compared to the

theoretical value of 106s, since there are several losses in the process. The characteristic velocity efficiency was 87%, indicating an incomplete decomposition of the hydrogen peroxide.

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