INFLUENCE OF HOT-FIRING TESTS ON THE CHARACTERISTICS AND ACTIVITY OF A CATALYST FOR THE HYDROGEN PEROXYDE DECOMPOSITION

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ABSTRACT:

Hybrid propulsion technology suffers from low propulsive performances generally due to low combustion efficiency with regards to the other chemical propulsion systems. When hydrogen peroxide is used as the oxidizer combined with a catalytic bed, one solution to directly increase the propulsive performance consists in using hydrogen peroxide at higher concentration than the spatial grade (87.5%) which improves the theoretical specific impulse up to 12s for 98% hydrogen peroxide.

This paper presents the development and the characterization of a catalyst able to withstand the increased decomposition temperature associated with this highly concentrated hydrogen peroxide and will focus on the impact of firing tests on the characteristics and on the activity of the developed catalyst.

1. INTRODUCTION

Hybrid rocket could be considered half-way from solid and liquid technologies since this chemical propulsion system stores the oxidizer and the fuel in two distinguished states. The most common configuration consists in a liquid or a gaseous oxidizer which flows through a solid fuel channel and burns with the pyrolysis gases coming from the solid fuel regression. In this case, the fuel grain acts as a combustion chamber referring to solid propulsion whereas the oxidizer stored in a separated tank, and the injection system refer to liquid technology. This technology is associated to simplified, low cost, faster and thrust modulated operations with a high level of performance, reliability and availability. However, one of the factors limiting the development of this technology is the low propulsive performances resulting from low combustion efficiency with regards to the other chemical propulsion systems.

When hydrogen peroxide (H_2O_2) is used as oxidizer, one of the most promising ways to improve this efficiency consists in combining a decomposition catalyst and a swirl injector. By using such a combination, a high temperature gaseous oxidizer stream can be directly injected leading to an improved mixing between the two propellants. Some firing tests using this combination showed improved combustion efficiencies as high as 98% [1, 2, 3, 4] compared to values ranging between 80 and 90% for systems without catalytic decomposition.

Besides the use of a swirl injector, another way to increase the combustion efficiency is to use hydrogen peroxide with a higher concentration than the current standard spatial grade (87,5%). According to theoretical computation performed with thermochemical equilibrium code such as RPA (Rocket Propulsion Analysis) or CEA (Chemical Equilibrium with Applications), specific impulse can be increased by up to 12 s when using a hydrogen peroxide concentration of 98% instead of the standard current spatial grade (87.5%). However, this increase of hydrogen peroxide concentration is accompanied by an increase of the decomposition temperature of 258 K [5] and some catalyst with increased thermal stability are necessary to withstand these high decomposition temperatures.

The most conventional catalyst for hydrogen peroxide decomposition is metallic silver, which suffers from two major drawbacks, namely temperature limitations and poisoning from the stabilizers used to prevent the self-decomposition of hydrogen peroxide. Many research activities have been performed in the past few years about the catalytic decomposition of H_2O_2 [6, 7, 8, 9] and various precious metals as well as Mn oxides were extensively studied [10, 11, 12, 13, 14]. In a previous work [15], we performed a screening of various precious metal-based catalysts supported on alumina which showed that Pt is the most active metal for the decomposition of hydrogen peroxide. The activity of the developed alumina supported Pt catalyst was then further optimised by varying the

preparation method (various Pt salts and alumina carriers) and some monopropellant tests confirmed the improved catalytic activity. This paper presents the results of some of the hybrid engine tests performed on this optimised catalyst and will focus on the post-mortem characterisation after testing.

2. CATALYST PREPARATION

All the catalysts tested in the context of the present work were prepared by means of a conventional incipient wetness impregnation. The water uptake of the alumina carriers was measured, and the concentration of the platinum impregnation solution was then adjusted to reach the targeted Pt loading of 5% on the catalysts. After impregnation, the obtained catalysts were dried, calcined and reduced. Tab. 1 below presents the catalysts prepared for the monopropellant test campaign performed at ONERA. Catalyst A, B and C are supported on the flight proven γ-alumina granules used to produce the hydrazine decomposition catalyst HKC-12GA (Al_2O_3-1) and with three different particle sizes. Catalyst D is supported on an alternative alumina (Al_2O_3-2) which showed promising results in the laboratory [15] and has the same particle size as catalyst A. The Pt loading was kept constant and equal to 5%.

Table 1. Catalysts prepared for the monopropellant test campaign

Catalysts	Pt (%)
A – Pt/Al_2O_3-1 – 10-14 mesh fraction	5
B – Pt/Al_2O_3-1 – 18-20 mesh fraction	5
C – Pt/Al_2O_3-1 – 20-25 mesh fraction	5
D – Pt/Al_2O_3-2 – 10-14 mesh fraction	5

3. MONOPROPELLANT TEST CAMPAIGN

Fig. 1 below presents the monopropellant test facility, which consists basically of the three following main components: the inlet manifold connected to the hydrogen peroxide feed line, an injector plate and the decomposition chamber containing the catalyst particles. The injector plate was especially designed to spread the liquid hydrogen peroxide all over the cross section of the decomposition chamber. This chamber consists of an Inconel cylinder closed at both ends by refractory steel meshes to maintain the catalyst particles inside the decomposition chamber. This chamber is connected to a measurement module measuring the decomposition temperature at the outlet of the catalytic bed (thanks to three thermocouples) and the decomposition chamber pressure. The instrumentation of this facility also includes a Coriolis oxidizer mass flow measurement and temperature and pressure measurements of the liquid oxidizer upstream the manifold.

Figure 1. Monopropellant test facility

Several monopropellant tests were performed with each catalytic bed and more details on the monopropellant test campaign are reported in [16]. Fig. 2 below presents a comparison of the decomposition temperatures measured for the four catalyst samples. First, the comparison between catalysts A, B and C shows that the smaller the particle size, the shorter the transient time and the higher the efficiency based on the normalized temperature. On the other hand, catalyst D, which was prepared with the same particle size as catalyst A but with the alternative alumina Al_2O_3-2, shows improved efficiency as well as a shorter transient phase duration. These results confirm the better catalytic activity of the catalyst D supported on Al_2O_3-2, which was already observed during the laboratory screening. Catalyst D was therefore selected for the hybrid firing tests.
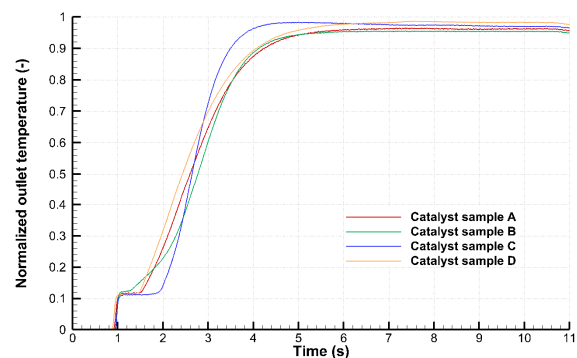

Figure 2. Comparison of the decomposition temperatures of the four catalysts

4. HYBRIDE TEST CAMPAIGN

The hybrid test campaign was performed on the HYCOM facility presented in Fig. 3 below. This engine is mostly composed of five components: a forward end plate including the injector, a pre-chamber including the igniter, a combustion chamber, a post-chamber and a nozzle. This facility was designed by making the different parts modular which enables to easily modify and adapt this engine and consequently, in order to plug the catalyst bed on the combustion chamber, the

forward end plate and the pre-chamber were replaced by an intermediate flange which is also the seat of a gaseous injector.
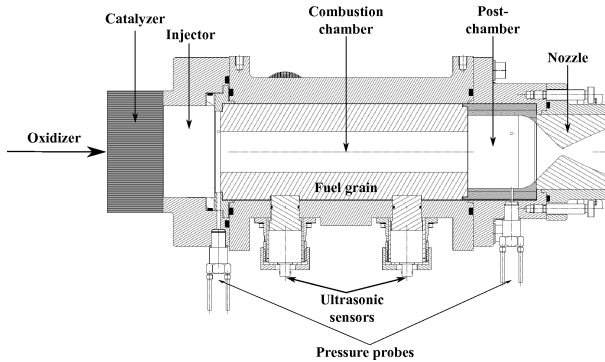

Figure 3. Schematic view of the HYCOM hybrid engine

Besides the instrumentation described for the monopropellant test, the HYCOM facility is also equipped with four unsteady pressure probes located in the intermediate flange and in the post-chamber. In order to measure the fuel regression rate, the engine is also instrumented with ultrasonic sensors (one located at the head-end of the fuel grain and two at the rear end). This technique has the advantage of being non-intrusive and easily implemented compared to X-rays measurement techniques. The HYCOM engine was also placed on a thrust bench to get the propulsive performances (Fig. 4). Finally, three thermocouples were also placed in the intermediate flange in order to measure the temperature of the oxidizer stream at the outlet of the decomposition chamber.
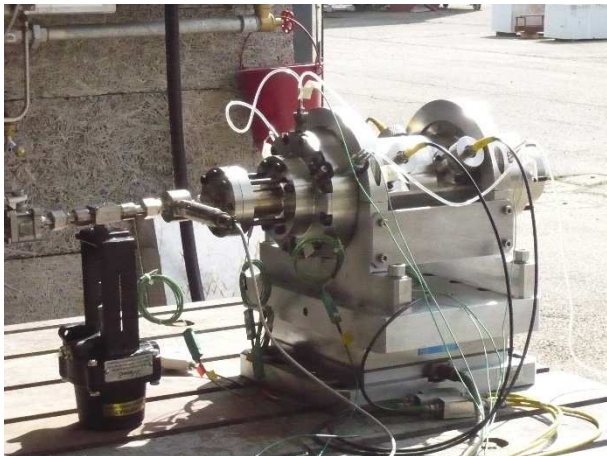

Figure 4. Picture of the HYCOM hybrid engine

Several firing tests have been performed in the HYCOM hybrid engine and more details on this hybrid test campaign are reported in [17]. The first tests with a catalytic injector were performed using a standard spatial grade hydrogen peroxide solution with a concentration of 87,5%. However, a possible way to improve the performance of the hybrid engine consists in using a hydrogen peroxide solution with higher concentration. According to theoretical computation performed with thermochemical equilibrium code such as RPA (Rocket Propulsion Analysis) or CEA (Chemical Equilibrium with Applications), specific impulse could be improved by 12 s when hydrogen peroxide at 98% is used instead of the current spatial grade of 87,5%.

To assess the influence of the H_2O_2 concentration on the performances of the hybrid engine, two firing tests were performed using the exact same configuration (swirl injector, catalytic injector, fuel grain geometry and nozzle) except for the concentration of the hydrogen peroxide which was increased to 98% in test 2 compared to 87,5% used for test 1. The temporal evolutions of the combustion chamber pressure, the oxidizer mass flow rate, the thrust and the oxidizer decomposition temperature for these tests are presented in Fig. 5 and 6 below.
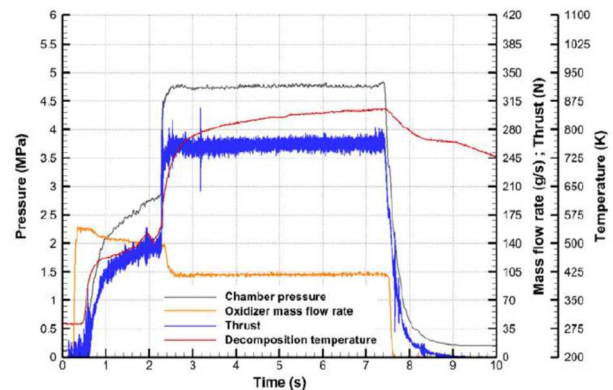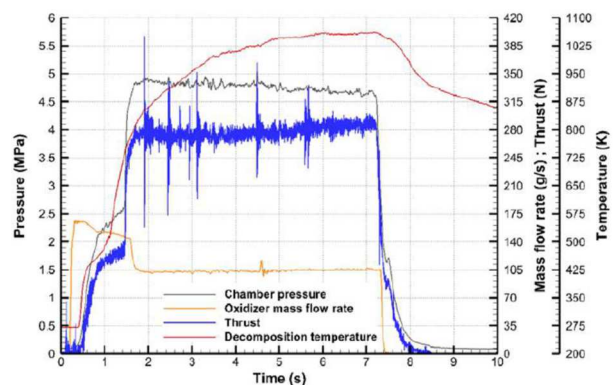

Figure 5. Test 1 with 87,5% H_2O_2

Figure 6. Test 2 with 98% H_2O_2

First, the decomposition temperature at the end of test 2 (with 98% hydrogen peroxide solution) is increased to 1060 K, which corresponds to an increase of 180 K compared to test 1 performed with 87,5% hydrogen peroxide solution. This difference is slightly lower than the 258 K difference expected according to the theoretical calculation for both grades. As can be seen in Fig. 6, the combustion chamber pressure starts to decrease after 2.5 s of hybrid mode due to the nozzle erosion caused by a much higher flame temperature. Because of this erosion, the data were averaged over the first two seconds of the hybrid mode and are reported in Tab. 3 below. These results are compared with the data obtained for test 1 and presented in Tab. 2.

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Table 2. Average results of the hybrid test performed with 87,5% H_2O_2 (test 1)

	Test 1 - 87,5% H_2O_2
Monopropellant phase duration (s)	1.6
Hybrid mode duration (s)	5.1
Oxidizer mass flow rate (g/s)	101.7
Fuel mass flow rate (g/s) *	16.1
Oxidizer to fuel ratio (-)	6.3
Chamber pressure (MPa)	4.72
Thrust (N)	260.8
Characteristic velocity (m/s)	1542
Specific impulse (s)	225.7
Combustion efficiency (%)	98
Nozzle efficiency (%)	93
Engine efficiency (%)	91

*The averaged mass fuel rate was calculated based on the mass measurements before and after the firing test.

Table 3. Average results of the hybrid test performed with 98% H_2O_2 (test 2)

	Test 2 - 98% H_2O_2
Monopropellant phase duration (s)	1.1
Hybrid mode duration (s)	5.9
Oxidizer mass flow rate (g/s)	102.4
Fuel mass flow rate (g/s) *	16.6
Oxidizer to fuel ratio (-)	6.2
Chamber pressure (MPa)	4.82
Thrust (N)	273
Characteristic velocity (m/s)	1558
Specific impulse (s)	233.8
Combustion efficiency (%)	93.6
Nozzle efficiency (%)	94.4
Engine efficiency (%)	88.4

*The averaged mass fuel rate was calculated based on the mass measurements before and after the firing test.

The increase of decomposition temperature allowed a faster ignition of the engine and the monopropellant phase was reduced to about 1 s. The specific impulse is increased to about 234 s, which corresponds to an increase of only 8 s compared to test 1 performed with 87,5% hydrogen peroxide solution. This difference is again slightly lower than the 12 s increase calculated using the thermochemical equilibrium code. This smaller benefit is linked to the decrease in the combustion efficiency observed between test 1 and 2. This lower combustion efficiency could be explained by a reduced performance of the catalytic material which has already been used for a many firing test without any replacement. To investigate this slight deactivation, some characterisation was performed on the catalyst after completing the hybrid engine test campaign.

5. CHARACTERISATION OF THE CATALYST

The characterisation of the catalytic material was performed both on the fresh catalyst and after completing the hybrid test campaign. This characterisation consisted of an optical inspection, determination of the precious metal surface by CO-adsorption, determination of the pore volume and specific surface area (BET) by Hg-porosimetry and transmission electron microscopy (TEM).

The precious metal surface area tests were performed in a TPDRO 1100 device from the Thermo Finnigan Company. Before testing, the catalysts are reduced for 2h in a reductive gas mixture (95% Ar, 5% H2).

The Hg-porosimetry analyses were conducted using two devices namely a Pascal P140 and a Pascal P440 from the company Thermo Fischer Scientific. Before testing, the samples are degassed at 150°C for 12h.

TEM investigations were conducted using a FEI Talos 20-200 transmission microscope at 200 kV. The measurements were performed in TEM mode and in STEM using Bright Field (BF) imaging and HAADF detector. Energy-dispersive x-ray spectroscopy was used to detect differences in local chemical composition.

The optical inspection of the catalyst both in the fresh state (left) and after testing (right) is presented in Fig. 7 below. As can be seen, there is not sign of breakage of the particles and the catalyst particles are still intact. The particles also still have the same size and there is no sign of thermal shrinkage associated with the testing. The only small difference that can be seen is a very slight decolouration of the catalyst and the material after testing seems to have a marginally lighter grey colour. However no massive washout of the active phase was observed like it is the case for example with Mn based catalyst.

Figure 7. Optical inspection of fresh (left) and aged (right) catalyst

One of the critical parameters that can influence the catalytic activity is the specific surface aera which is directly impacted by the thermal stress associated with challenging firing tests. Tab. 4 below presents the results of the Hg-porosimetry analysis performed on the catalyst before and after testing.

Table 4. Results of the Hg-porosimetry

Parameter	fresh	aged
Pore volume (cm^3/g)	0.3	0.3
Average pore diameter (nm)	13.6	20.5
BET (m^2/g)	105	60

After testing, the catalyst has a specific surface area of 60 m^2/g, which represents a decrease of about 40% compared to the fresh catalyst. As expected,

this decrease in specific surface area is accompanied with an increase of the average pore diameter from 16.6 nm up to 20.5 nm. This big drop in the specific area can partially explain the deactivation observed during the hybrid test campaign.

Another important parameter for the catalytical activity is the size of the Pt nanoparticles supported on the alumina. The TEM pictures presented in Fig. 8 below clearly show the sintering of the precious metal and the formation of bigger particles during the firing tests.
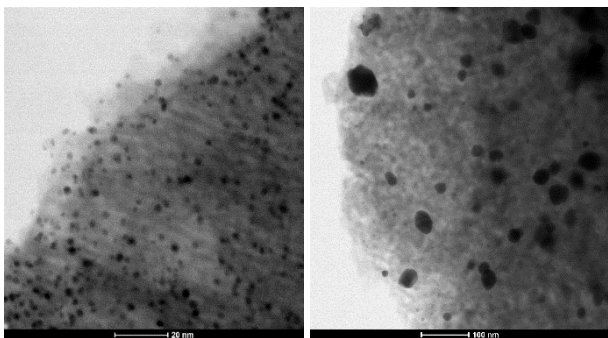

Figure 8. TEM pictures of fresh (left) and aged (right) catalyst

This was confirmed by the crystallite size distributions presented in Fig. 9 (fresh) and Fig. 10 (aged). For the fresh catalyst, a very narrow distribution is observed and most of the nanoparticles of Pt have a diameter comprised between 1 nm and 4 nm. On the other hand, for the catalyst after testing, a very broad distribution is obtained and most of the particles have a diameter comprised between 3 nm and 60 nm.
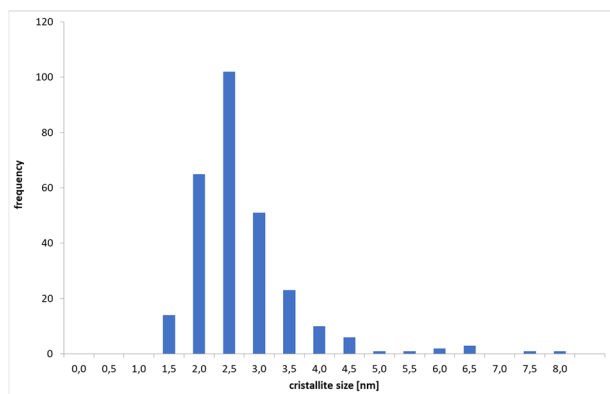

Figure 9. Crystallite size distribution for the fresh catalyst
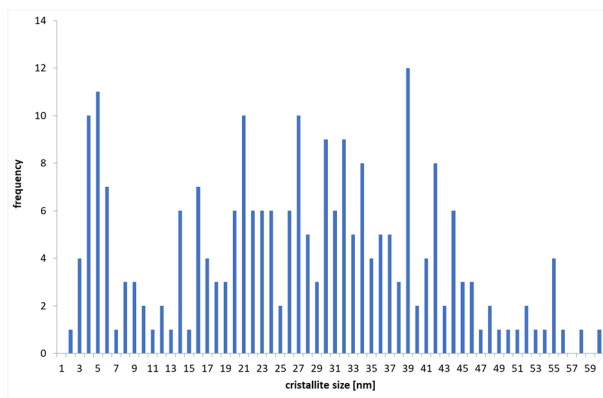

Figure 10. Crystallite size distribution for the catalyst after testing

This increase in the crystallite size was also confirmed by the results of the CO adsorption experiments presented in Tab. 5 below. The metallic surface area decreases from 11 m^2/g down to 0,6 m^2/g, which represents a big decrease of the metallic dispersion.

Table 4. Results of the CO adsorption

Parameter	fresh	aged
Metallic surface area (m^2/g)	11.0	0.6

6. CONCLUSION

The development of hybrid chemical rocket engines is currently limited because of their low propulsive performances generally due to low combustion efficiency with regards to the other chemical propulsion systems. One way to improve these performances is to combine a catalytic bed for the decomposition of hydrogen peroxide with a swirl injector. To further improve the propulsive performances, a highly concentrated hydrogen peroxide solution (98%) can be used instead of the current standard spatial grade (87,5%). However, this leads also to a huge increase in the decomposition temperature and a reliable, effective and highly thermally stable catalytic bed is necessary. The Pt supported on alumina catalyst developed during this study showed very promising decomposition activity during the monopropellant test campaign. After a challenging hybrid test campaign and more than 50 kg throughput of highly concentrated hydrogen peroxide without any catalyst replacement, the catalytic material showed some slight deactivation. A post-test characterisation of the material showed that the thermal stress associated with firing tests had an impact on two key parameters for the catalytic activity namely the specific surface area and the Pt crystallite size. One possible way to improve the thermal stability of the catalyst carrier could be the doping of the alumina with various elements like La or Si. On the other hand, alloying Pt with another precious metal like Pd should lead to the formation of more thermally stable nanoparticles and reduce the sintering effect observed during firing tests.

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