Development and Testing of Catalysts for Hydrogen Peroxide Decomposition

C. Boffa, L. Micoli**, G. Festa*, A. Russo Sorge*, M. Turco***
**Dipartimento di Ingegneria Industriale*
chiaraboffa@rocketmail.com
***Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale*
luca.micoli@unina.it
Università di Napoli "Federico II"

Abstract

The performance of innovative structured catalysts for the decomposition of hydrogen peroxide have been presented. Catalysts consist of zirconia honeycomb modules and Mn oxides as active phase, deposited on the substrates by an innovative procedure properly developed to obtain catalysts with high performance. Test results with both diluted vapour phase and non-diluted liquid phase HTP solutions, in both cold and hot start conditions, have also been presented. A comparison with previous tests has been proposed. No significant improvement of the catalyst conversion but lower response time have been verified.

1. Introduction

Highly concentrated solutions of hydrogen peroxide can be classified as HTP (High Test Peroxide, denoting H_2O_2 concentration higher than 85% wt.) and RGHP (Rocket Grade Hydrogen Peroxide, denoting H_2O_2 concentration higher than 90% wt.), both exploitable as monopropellant in space propulsion systems requiring low thrust levels (for satellite attitude control, station keeping, de-orbiting) and as oxidizer in bipropellant systems requiring thrust level up to 500N (for orbit insertion manoeuvres and attitude control of more massive systems).
The interest in hydrogen peroxide as source of power dates back in the early 1930s. The first major use of H_2O_2 was in Germany during the Second World War, when several devices, such as the V-2 missile, were developed. After the WWII also US and UK focused on the development of H_2O_2-based propulsive systems, including the gas generator for the X-15 and the attitude control system of the Mercury spacecraft as monopropellant, the Black Knight and Black Arrow vehicles as oxidizers in bi-propellant engines (burned with kerosene) [1], respectively. Highly concentrated solutions of hydrogen peroxide have also been largely used in Russia for both propulsive and gas generator systems. Currently the feeding system of two stages of the Soyuz launch vehicle consists in a gas generator H_2O_2-based.
Recently the hydrogen peroxide has seen a renewed interest in space applications as main propellant, because of its properties that make it one of the most appreciable Green Propellants, to replace hydrazine and nitrogen tetroxide [2]. Some of the most important features that make H_2O_2 interesting are its high density (1500 kg/m^3 for 100% H_2O_2 at room temperature), storability (it is in liquid phase at room temperature), safety handling, low toxicity and environmental impact. The hydrogen peroxide can decompose exothermally producing water-vapour and oxygen at very high temperatures (about 1000 °C for 100% wt H_2O_2 [3]). The hot gases can be expanded in a nozzle or react with a solid/liquid fuel in monopropellant and bi-propellant configuration, respectively. H_2O_2 decomposes both thermally and catalytically, but the focus is mainly on the last one mechanism because the first one occurs at slower rates of reaction.
Traditional methods of decomposition are based on:

- Liquid-Liquid Systems (developed in Germany during the WWII): consist in the direct injection of catalysts in liquid phase into the hydrogen peroxide flux. Despite the lower contaminant sensitivity of the catalyst, there are a number of disadvantages: a second fluid feed system is necessary, the catalyst has to be soluble and it may be expelled easily [4].

- Packed-beds (used in Germany in the late WWII) are based on solid catalyst (removing the secondary fluid feed system). These systems have short operative life and easy break-up due to non-uniform packing or low resistance to thermal and mechanical stresses occurring in repeated on-off cycles.
- Catalytic systems in precious metals (silver and nickel) arranged in the shape of metallic gauzes or screens with high packed-density to realize high surface area. Despite the high efficiency (typically above 95%) these catalysts were characterized by high shortcomings, high pressure drops, low melting points compared to the adiabatic decomposition temperatures of HTP and RG solutions, easy poisoning and high costs of materials and manufacture.

A proper design of catalytic systems is therefore the fundamental aspect for the development of a successful propulsive systems based on H_2O_2. In the last years several efforts have been done in order to develop innovative catalysts for H_2O_2 decomposition characterized by high activity and stability in a wide range of operative conditions, high thermal and mechanical resistance, short response time, low pressure drops, weight and costs, and long operative life [5].
The decomposition process of hydrogen peroxide solutions in presence of a number of materials has been extensively investigated [6], but those suitable for propulsive applications must to fulfil the above strict requirements. Several catalysts based on metal oxides have recently been proposed and among these manganese oxides on zirconia substrates seems to be very promising [7, 11]. In order to overcome the limits of traditional configurations, in the present work structured (honeycomb modules) catalysts for the hydrogen peroxide decomposition have been designed and prepared. Catalysts consist of a ceramic substrate (in Yttria-stabilized zirconia) and a catalytically active phase (Mn_xO_y) deposited on it, according to an in-house developed preparation procedure. The dispersion of the active phase onto the substrate has a key role in the performance of the catalyst. Typical procedures are complex and involve the washcoating of the substrates with suitable oxides (generally alumina) on which the active phase is supported. In this work catalysts have been prepared with the precipitation procedure properly modified to obtain the dispersion of Mn oxides avoiding the preliminary washcoating of the substrate. The procedure involves the calcination step (at 700°C) to have the desidered Mn oxides on to the surfaces. Catalysts have been characterized (by N_2 adsorption, SEM and H_2 TPR techniques) and tested. Typical investigation of the catalytic activity consider liquid solutions of hydrogen peroxide but catalysts mostly operate in vapour phase conditions. In this work the catalytic activity has been investigated with both vapour and liquid solutions of hydrogen peroxide in test benchs properly designed. Kinetic data resulting from the vapour phase test campaign therefore can be used as starting point for the design of a propulsive system using HTP as propellant. The performance have also been related to the results of previous tests on similar honeycomb modules prepared with the same technique and calcined at lower temperature (500°C) [12, 13].

2. Catalysts Preparation and Characterization

2.1 Materials

In this work zirconia honeycombs (HBC) stabilized with 8 mol % of yttria, Y_2O_3 have been considered as substrate for the active phase MnOx. Honeycomb cylindrical substrates ($l = 3.0$ or 6.0 cm, $d = 1.3$ cm, square channel density $= 62$ cm^{-2}) were supplied by Céramiques Techniques Industrielles Company (Salindres, France).
Mn oxides have been dispersed on the substrates by precipitation method using $Mn(II)(C_2H_3O_2)_2{*}4H_2O$ (by Sigma-Aldrich) solutions.
A concentrated H_2O_2/H_2O solution supplied by Evonik Degussa (87.5 wt% H_2O_2, $NaNO_3 < 20$ mg L^{-1}, $Sn < 9$ mg L^{-1}, $P < 0.2$ mg L^{-1}) has been used for the catalytic test both in vapour and liquid phase.

2.2 Catalysts Preparation

Precipitation technique consists in introducing the entire monolith into a 100 mL of 0.65 mol L^{-1} aqueous $Mn(II)(C_2H_3O_2)_2$ solution under stirring conditions at 50 °C. Then 2 mL of concentrated NH_4OH was added to promote the precipitation, $Mn(OH)_2$, on the monolith surface. After one hour, the material has been drained and oven dried at 120°C for 2 hours; this procedure has been repeated three times (P3) to increase the active phase content on the substrate. Finally, samples have been calcined at 700°C (T7) with 6 L h^{-1} air flow, to obtain the Mn oxides from the hydroxide [14].

2.3 Catalysts Characterization

Scanning Electron Microscopy (SEM) and the Energy Dispersive X-ray Spectroscopy (EDS) measurements have been carried out in a Philips XL30 apparatus.

N_2 adsorption isotherms at -196 °C, using a Micromeritics ASAP 2020 apparatus, have been used to measure the surface area, the pore volume and average pore diameter of the samples on the entire honeycomb catalysts with an accuracy of $\pm 0.02\ m^2\ g^{-1}$ in surface area values.

Temperature-Programmed Reduction (TPR) tests have been carried out using a laboratory apparatus with a 2% H_2/Ar mixture flow ($Q = 150\ cm^3 min^{-1}$) and heating rate of $10\ °C\ min^{-1}$ up to 800 °C [8]. The apparatus has been properly modified in order to carry out the measurement also on the entire monolith.

3. Catalytic Activity Measurements

3.1 Catalytic Activity Measurements with diluted vapour phase solutions

H_2O_2 decomposition tests have been carried out with diluted solutions of hydrogen peroxide in vapour phase. The experimental apparatus showed in Figure 1 operates at the atmospheric pressure and it has extensively been described in [12].

Feed flow rates about 223 mL min-1 (H_2O_2 11.3 mol %, H_2O 21.4 mol % and He) corresponding to space velocities (defined as reactant gas flow rate and reactor volume) of GHSV = 2.00 and 2.67 s^{-1}, were sent to the reactor at 200 °C. The reactor was a glass tube (i.d. = 0.6 cm, l = 40 cm) with a central section (i.d. = 1.9 cm, l = 8 cm) in which the catalyst sample has been precisely accommodated. The reactor has been properly designed to allow both the vaporization and preheating of the feed mixture. Blank tests with the reactor filled with inert α-Al_2O_3 (same void space as the monolithic catalysts) showed that the homogeneous H_2O_2 decomposition is negligible under the operating conditions.

The products coming out from the reactor have been flowed through an ice trap and an anhydrous KOH trap for the separation of H_2O and not converted H_2O_2, then they were sent to a thermal conductivity detector (TCD) for the continuous analysis of O_2. The concentration of O_2 measured by the TCD allowed the calculation of the molar O_2 flow rate and consequently the H_2O_2 decomposition for each sample.

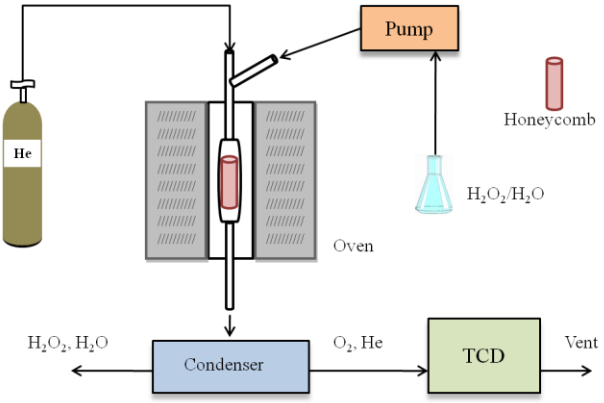


Figure 1: Apparatus for H_2O_2 decomposition tests.

3.2 Catalytic Activity Measurements with non-diluted liquid phase solutions

Figure 2 shows the test-rig for the honeycomb modules assessment, including the feeding system, the data acquisition system and the reaction chamber.

The reaction chamber consists of the inlet flange, the injector plate, the catalyst chamber (i.e. the catalytic bed and the case), the post-chamber, the exit flange and the main-casing. All the test-bench components are in AISI316-L stainless steel. The propellant is stored in a stainless steel tank, pressurized by nitrogen. The propellant mass flow rate is regulated/measured by a mass flow meter (Bronkhorst Cori Tech model Coriflow M55, accuracy +/-0.5% of reading).

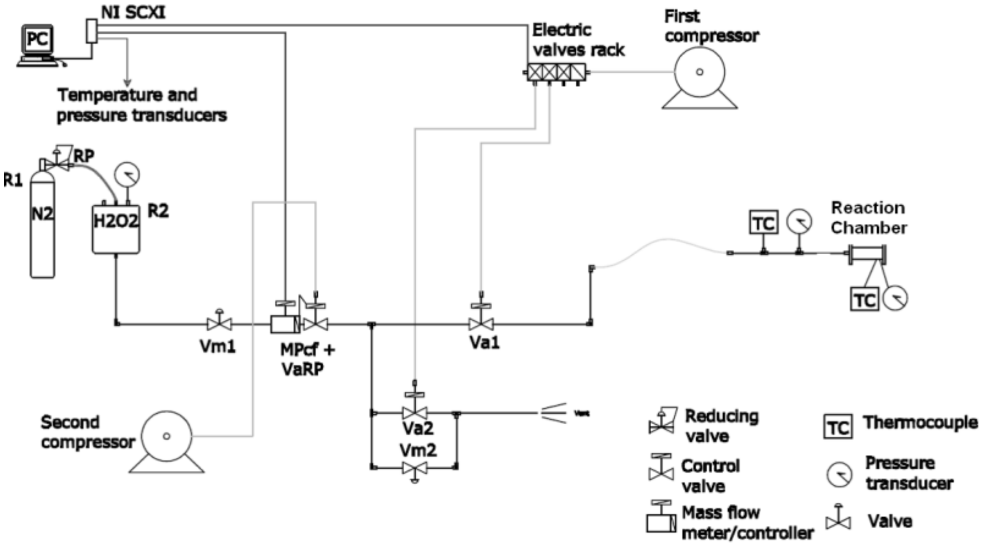


Figure 2: Test-rig layout for catalytic measurements with non-diluted liquid HTP solutions.

In order to distribute homogeneously the peroxide into the honeycomb channels, the injector plate is a 1mm thick disk with 45 holes (0.1 mm in diameter) made by laser-drilling. Three pressure transducers (Setra model C280E, 0-000psig, accuracy +/-0.11% full scale) are mounted: on the tank, upstream the injector plate and on the post-chamber. Six thermocouples (type K, accuracy +/-2.2°C or +/-0.75% of reading) are mounted: one upstream the injector plate (to record the propellant temperature at the inlet) and five in the post-chamber on the catalysts axis, allowing an estimation of the conversion occurred into the catalyst, and at several distances from it in the radial direction. The higher is the temperature measured the higher is the H_2O_2 dissociation. Propellant mass flow rates in the range [3÷5] gr/s and adiabatic conditions have been considered.

4. Results and Discussion

4.1 Catalysts Preparation

During the calcinations step the Mn content can be estimated by the weight increase of the sample assuming the complete oxidation of the hydroxide into Mn_2O_3. Honeycomb catalyst calcinated at 700 °C have Mn content of about 3.39 ± 0.1 wt %, approximately the same of samples in [12] confirming the validity of the preparation procedure.

4.2 Textural and Redox Properties

SEM micrographs were obtained out on small bits taken from different points of the monoliths. These techniques provide a rapid qualitative analysis of elemental composition in a sample surface, giving an overall map, or line profile, of the Mn distribution. SEM-EDS analyses have been carried on six stations (x_i , i=1, ..., 6) along the monolith with approximately the same length.

Table 1: EDS measurements on the catalysts.

	x_1	x_2	x_3	x_4	x_5	x_6	**Average**
Mn content, wt %	3.40	3.71	3.81	3.67	2.26	3.48	3.39

As reported in Table 1, the catalysts preparation gave a uniform distribution of the active phase along the channels of the honeycomb, with an average Mn content of 3.39 wt. %.

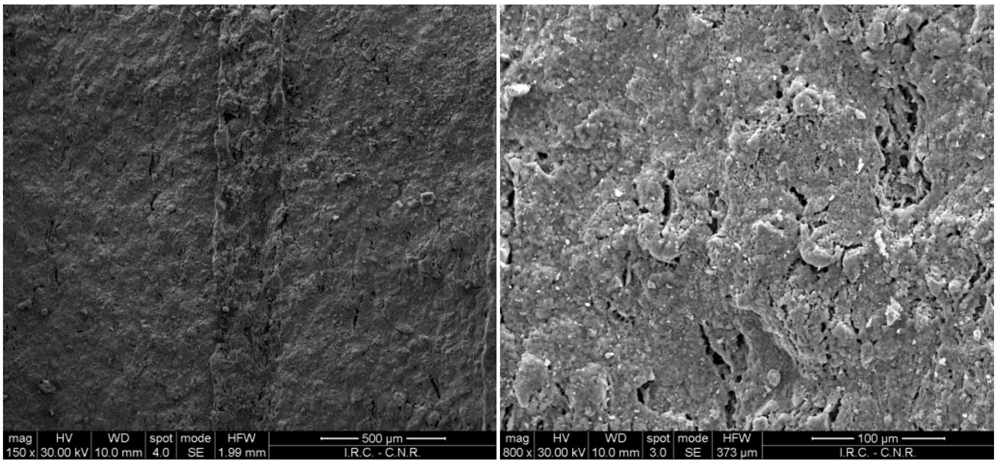


Figure 3: SEM micrograph of the honeycomb catalysts.

The redox properties of the catalysts have been investigated by TPR. In Figure 4 TPR spectra of the catalysts (T7) have been reported and a comparison with data literature (T5) [12] proposed. The amount of H_2 moles consumed is indicative of the redox properties of the catalyst surface and therefore an evaluation of the composition of the active phase is possible. The ceramic support gave no TPR signal and therefore it was not reported. The signal strongly depends on the Mn oxides. In ambient conditions the most stable Mn oxides are Mn_2O_3 and MnO_2 and therefore they have been assumed the most probable on to the catalyst surface and their spectra considered the reference. As shown in Figure 4, TPR profiles of catalyst T5 and T7 (calcined at 500 °C and 700 °C, respectively) are very different, indicating a strong influence of the calcination temperature on the Mn oxides.

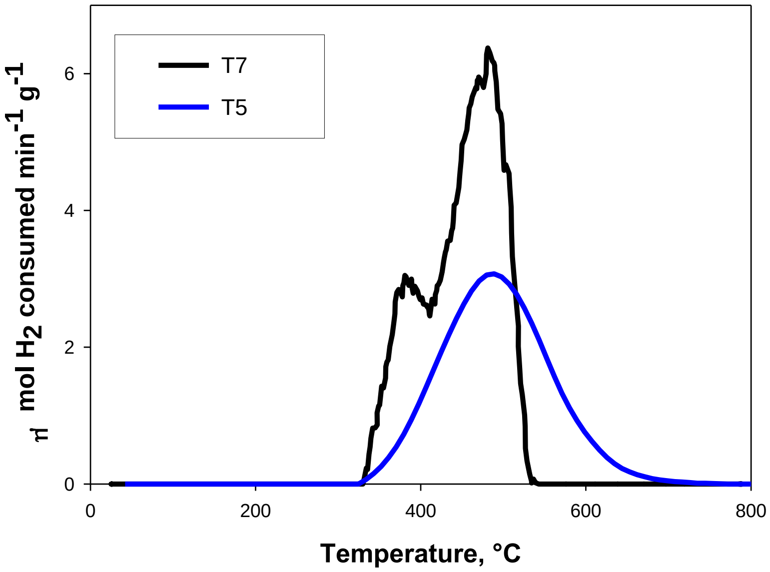


Figure 4: TPR measurements on honeycomb modules.

As reported in [12] TPR profiles showed that the calcination treatment at 500 °C should favour the formation of Mn_2O_3 but the consumption of H_2 is lower than the reference one suggesting a strong influence of the substrate material on the catalyst redox properties. The results for T7 indicate a higher MnO_2 with respect to T5 samples.

4.3 Catalytic Activity Measurements with diluted vapour phase solutions

The results of catalytic tests in diluted vapour phase conditions on 30 mm samples are reported in Figure 5 in terms of H_2O_2 conversion at 200°C, with space velocities of 2.00 and 2.67 s^{-1}. As expected, as the mass flow rate decreases the H_2O_2 conversion increases significantly, up to 95%. Tests have been carried out in isothermal conditions therefore the increased conversion cannot due to temperature effects but probably to an autocatalytic effect reaction [12]. The conversion seems to be slightly dependent on the calcination temperature: the higher is the temperature the higher is the conversion.

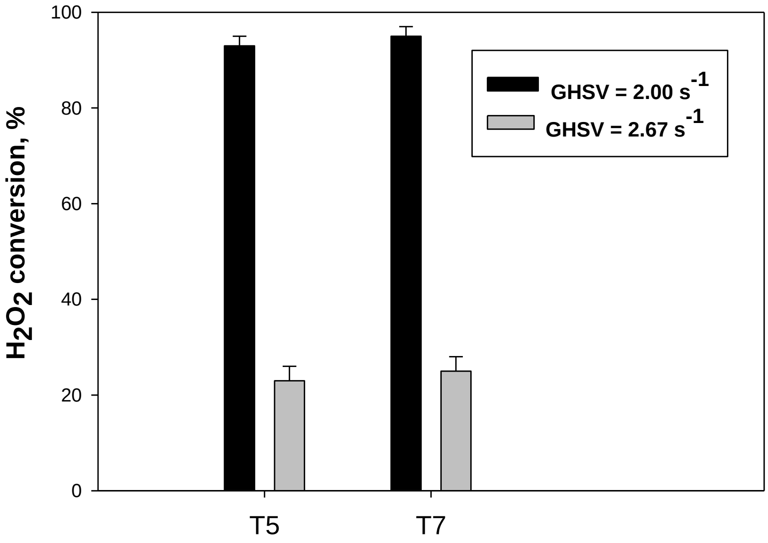


Figure 5: Conversion in honeycomb modules.

4.3 Catalytic Activity Measurements with non-diluted liquid phase solutions

The present work aims to highlight the progress in the research activities for the development of catalysts able to decompose hydrogen peroxide in monopropellant and bipropellant configurations. For this purpose several tests have been carried out with non-diluted liquid HTP solutions in adiabatic conditions: the activity and the response time of catalysts have been evaluated and compared with available data literature [13]. Both cold and hot starts conditions have been considered. The following parameters have been considered to evaluate the performances of the honeycomb modules tested with non-diluted liquid phase solutions of hydrogen peroxide:

- the propellant mass flow rate entering the catalyst bed;
- the maximum temperature (T_{max}) recorded at the exit of the reaction chamber;
- the maximum conversion (X_{cat}) achieved into the catalyst, defined as:

$$X_{cat} = \frac{T_{max}-T_{in}}{T_{ad}-T_{in}} \tag{1}$$

  where T_{ad} and T_{in} are the adiabatic and inlet temperature of the HTP solution used, respectively. X_{cat} can be considered as indicative of the number of hydrogen peroxide moles decomposed into the catalyst.
- the response time (τ_{resp}), defined as the time necessary to have a sharp increase of temperature close to the boiling point of the solution [3].

Another parameter commonly used to compare catalysts performance is the CBL (Catalyst Bed Loading, defined as the ratio between the mass flow rate entering the catalyst and the wet area) with typical values in the range 60÷235 kg/(m^2·s). In this work, the CBL values are in the above range, with a maximum of 111 kg/(m^2·s).
Table 2 summarizes the results for the honeycomb modules: the maximum temperature and the corresponding mass flow rate, the conversion and the response time have been reported for the samples tested.

Table 2: Results of catalytic measurements in non-diluted liquid phase conditions.

Test No	**Catalyst Length**, mm	m_{HTP}, gr/s	T_{max}, °C	X_{cat} %	τ_{resp}, s
1	30	5	120	14	8
2.a	30	3.0	200	26	15
2.b	30	3.3	377	53	5
3.a	60	3.5	120	14	13
3.b	60	3.2	156	19	5

Notations -.a and -.b are related to cold and hot starts, respectively.

Test results showed low decomposition of hydrogen peroxide, both in cold and hot start conditions. The conversion seems to be very sensitive to the CBL: the conversion increases when the mass flow rate (therefore the CBL) decreases. No notable change has been recorded doubling the catalysts length. As reported in Table 2, the temperatures recorded in tests 1, 3.a e 3.b were close to the boiling point of the solution, indicating the on-going evaporation within the honeycomb modules. During the test 2.a, two jumps in the temperature profile have been recorded: the first one, close to 120 °C, corresponds to the evaporation of the HTP solution and the second one close to 200 °C, may be considered indicative of the light-off process going on within the catalytic bed. The best performance have been recorded during the test 2.b, on a 30 mm sample. As shown in Figure 6, for hot start conditions and mass flow rate about 3.3 gr/s the measured temperature is close to 393 K, but increasing the CBL the catalyst conversion sharply decreases, due to flooding phenomenon. In any test the X_{cat} is very low, with the maximum value (53%) corresponding to hot start conditions and low mass flow rate.

.

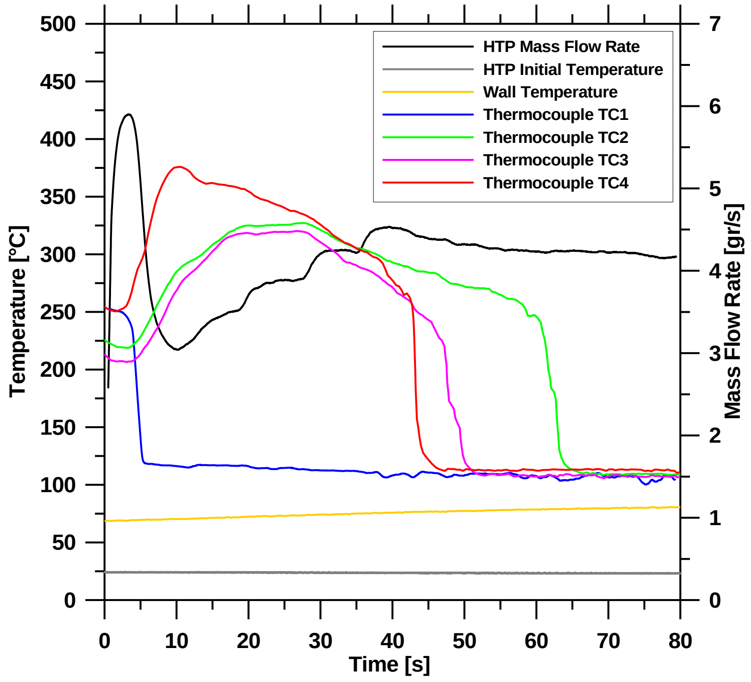
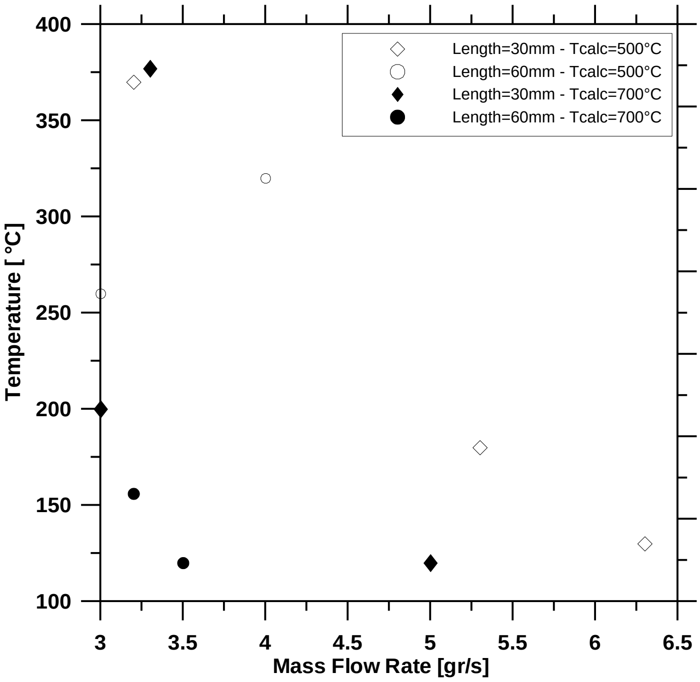
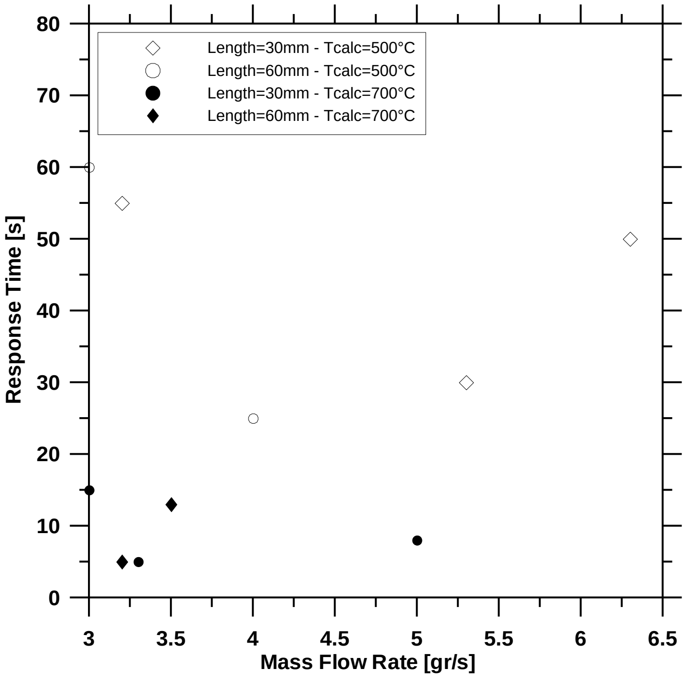


Figure 6: Mass flow rate and temperatures profiles downstream the catalytic chamber.

No significant improvement of the catalyst performances with non-diluted liquid HTP solutions has been detected with respect to tests on honeycomb modules calcined at 500 °C [13], for both 30 mm and 60 mm samples. As shown in Figure 7, although no improvement in the catalysts conversion has been recorded, the response time of the monoliths has been reduced with respect to previous tests. Both in cold and hot start conditions the values of τ_{resp} are in the range 5÷15 s, clearly lower than 25÷60 s typical of previous tests [13].



(a)



(b)

Figure 7: (a) Maximum temperature recorded and (b) catalysts response time.

5. Conclusions

The interest in hydrogen peroxide as main propellant for propulsive applications in both monopropellant and bipropellant configurations requires the development of efficient catalysts able to operate in a wide range of operative conditions. Traditional catalysts showed a number of disadvantages in terms of operative life, range of operative conditions and costs. In this work the performance of innovative structured catalysts have been presented. Catalysts consist of a zirconia honeycomb on which the active phase (Mn oxides) is deposited by an innovative in-house developed procedure properly modified to increase the catalytic activity: a higher calcination temperature (700°C) with respect to previous tests [12] have been considered. Catalysts have been characterized by N_2 adsorption, SEM/EDS and TPR. These analysis results showed a homogenous dispersion of the active phase on to the monolith surface, confirming the validity of the preparation procedure. The TPR profiles of catalysts have been investigated and compared to data literature [12]. Catalysts have been tested with both diluted vapour phase HTP solutions in isothermal plug-flow reactor and non-diluted HTP solutions in a properly designed test-bench and the results have also been related to data literature [12]. Measurements of catalytic activity in vapour phase conditions showed an increased conversion of H_2O_2 (up to 95%) with respect to previous tests. As expected, the higher is the space velocity (or the lower is the residence time) the lower is the conversion. No significant improvement of the catalyst conversion (maximum value 53% in hot start conditions) with non-diluted liquid HTP solutions has been detected with respect to tests on honeycomb modules calcined at 500 °C [13], for both 30 mm and 60 mm samples. On the contrary, a notable decrease in the response time has been verified with respect to previous tests [13], in both cold and hot start conditions.

Acknowledgments

Authors wish to thank Dr. Claudio Leone e Dr. Silvio Genna (CIRTIBS, Naples) for manufacturing the injector plate by laser-drilling. Special thanks to Dr. Salvatore Bonifacio for his precious time and suggestions.

References

[1] Wernimont, E., M. Ventura, G. Garboden, and P. Mullens.1999. Past and Present Uses of Rocket Grade Hydrogen Peroxide. *2nd International Hydrogen Peroxide Propulsion Conference*. Purdue University, IN.

[2] Scharlemann, C. 2011. Green Advanced Propulsion – A project status. *47h AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit.* San Diego, CA.

[3] Rocketdyne. 1967. Hydrogen Peroxide Handbook. Air Force Rocket Propulsion Laboratory Technical Report AFRPL-TR-67-144. North American Aviation.

[4] Wernimont, E. and P. Mullens. 2000. Capabilities of Hydrogen Peroxide Catalyst Beds. *36h AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit.* Huntsville, AL.

[5] Bonifacio, S. 2006. Analysis and Design of a Multi-phase Catalytic Reactor for the Decomposition of Hydrogen Peroxide in Space Propulsive Systems. PhD Thesis.Università di Napoli “Federico II”.

[6] Schumb, W., Sattersfield C., Wenthworth, R. 1955. Hydrogen Peroxide. Naval Research. NR-092-008.

[7] Russo Sorge A., M.Turco, G. Pilone, G. Bagnasco. 2004. Journal of Propulsion and Power, 20, 1069-1075.

[8] Kappenstein C., L. Pirault-Roy, M. Guèrin, T. Wahdan, A. A. Ali, F. Al-Sagheer, M. I. Zaki. 2002. Applied Catalysis A: General 234, Pages 145-153.

[9] Pirault-Roy, L., Kappenstein C., Guèrin M., Eloirdi R. 2002. Journal of Propulsion and Power 16, 1235-1241.

[10] Rusek, J. J. 1996. Journal of Propulsion and Power 12, 575-579.

[11] Turco, M., G. Bagnasco and A. Russo Sorge. 2005. Chem. Eng. Trans. 6, 39-44.

[12] L. Micoli, G. Bagnasco, M. Turco, M. Trifuoggi, A. Russo Sorge, E. Fanelli, P. Pernice, A. Aronne. 2013. Vapour phase H2O2 decomposition on Mn based monolithic catalysts synthesized by innovative procedures. Applied Catalysis B: Environmental, Volumes 140–141, Pages 516-522

[13] Bonifacio, S., F. Scelzo, D. Maiello, G. Festa and A. Russo Sorge. 2010. Catalytic Decomposition of Hydrogen Peroxide in Space Propulsive Systems: Modelling Approach and Experimental Assessment. *Space Propulsion 2010,* San Sebastian, Spain.

[14] Liu, X. M., S.Y. Fu, C.J. Huang, Powder Technol. 154 (2005) 120-124.

[15] A.K.H Nohman, H.M. Ismail, G.A.M. Hussein, J. Anal. Appl. Pyrol. 34 (1995) 265-278.

[16] Turco M., G. Bagnasco, C. Cammarano, L. Micoli, M. Lenarda, E. Moretti, L. Storaro, A. Talon, Appl. Catal. B: Envir. 102 (2011) 387–394.