

DEVELOPMENT AND TESTING OF Pt/Al₂O₃ CATALYSTS FOR HYDROGEN PEROXIDE DECOMPOSITION

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ABSTRACT

Supported Pt/Al₂O₃ and Pt/SiC catalysts for hydrogen peroxide (HP) decomposition have been prepared by means of two innovative implantation techniques on spheres and granules of several alumina-based carriers (lanthanum-doped alumina, bimodal δ -alumina and ϑ -alumina, silicon carbide and α -alumina) with BET surface areas between 4 and 200 m²/g. In order to evaluate the chemical activity and thermal shock resistance of the supporting pellets, two focused sets of experiments have been carried out in a specifically-designed test bench. Scanning electron microscopy (SEM) measurements of the platinum load on the supporting surface have been used to assess the effectiveness of the deposition and monitor the degradation induced by hydrogen peroxide decomposition. Two of the Pt/ α -Al₂O₃ catalysts showed excellent activity, high thermo-mechanical strength, and negligible loss of platinum after repeated cycles of hydrogen peroxide decomposition. In addition, high surface loads of platinum (44 wt %) have been attained on the α -Al₂O₃ substrate in spite of its relatively low surface area (4 m²/g), successfully overcoming the limitations usually associated with catalyst deposition on low surface area substrates. These findings indicated that one of the proposed catalyst implantation methods may represent an effective alternative to the incipient wetness impregnation technique commonly used for the synthesis of heterogeneous catalysts.

1. INTRODUCTION

For space missions requiring low or medium thrust levels, simplicity plays a key role in the choice of the propulsion system because of its favorable impacts on reliability and the reduction of development and operational costs. Ignition and decomposition of monopropellants on a catalytic bed [1] in small rocket engines clearly offers these advantages, often contributing to make this solution competitive in a number of applications, despite its comparatively low propulsive performance. Specifically,

the use of hydrogen peroxide, a non-toxic or green propellant, combines the safety advantages in the production, storage and handling phases with the cost savings associated with the drastic simplification of the health and safety protection procedures. High concentration or "rocket grade" hydrogen peroxide has a long heritage in aerospace propulsion. A wide variety of applications on both manned and unmanned systems can be cited from the 1930's to the present time [2] and [3]. Up to the 1960s a significant amount of work has been carried out by NASA laboratories on hydrogen peroxide decomposition and its application to monopropellant rockets [4] and [5]. The development of the Shell 405 catalyst and higher purity hydrazine led to a decreased use of hydrogen peroxide due to the superior performance and long-term stability characteristics of hydrazine [6]. However, in the last decade hydrogen peroxide has been receiving a renewed interest for application to cost and safety driven systems. During operation, hydrogen peroxide decomposition catalysts are subjected to high thermal stresses, mostly due to severe and sometimes intermittent thermal shocking. It is therefore necessary for effective catalysts to combine both superior mechanical and chemical properties, which imposes a delicate trade-off between the conflicting requirements of high mechanical resistance and large surface area. Similar operational conditions are experienced by hydrazine decomposition catalysts. Several research groups devoted long and intense efforts to the development of effective hydrazine decomposition beds and the challenge to prepare an alumina support in the form of spheres or pellets for this extreme catalytic application has been met. One of the commercially available catalysts is the Shell 405 (USA), whose substrate consists of granules of Reynolds RA-1 alumina. The outstanding properties of Shell 405 are presumably due to a more open structure and to the presence of a high fraction of η -alumina crystals stuck together by amorphous alumina binder. The dense crystals prevent the penetration of hydrazine into the pellets and decrease the generation of catalyst fines by break-up caused by internal overpressures [7]. Novel alumina-based

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substrates have also been developed for HAN catalysts, which have to withstand even more severe conditions due to the higher temperatures reached during the decomposition (more than 1400 °C).

Previous studies have revealed that alumina doped with silicon, lanthanum or barium oxides displays higher thermal stability than pure transition alumina [8]. Recently, a number of experiments have been undertaken at Alta S.p.A., Pisa, Italy, in order to evaluate various metallic elements deposited on γ - Al_2O_3 supports for decomposition of hydrogen peroxide at high concentration [9]. A Pt/ γ - Al_2O_3 catalyst has then been integrated and tested in a HP monopropellant thruster in order to assess its potential for propulsive applications under more realistic working conditions. Due to the excessive thermal stresses induced by the rapid and large change of their surface temperature, the γ - Al_2O_3 pellets broke into fine particles during firing with rocket grade hydrogen peroxide [10]. To overcome this problem, the impregnation technique presented in [9] and a novel advanced method for coating ceramic spheres with metallic platinum have been implemented on a number of alumina-based substrates. The various catalyst formulations have then been tested in two series of atmospheric decomposition experiments: first using 30% and 60% hydrogen peroxide concentrations by weight in order to determine the catalyst activity and susceptibility to poisoning, and then using 87.5 % H_2O_2 at different values of the catalyst support initial temperature (20 °C, 100 °C and 200 °C), in order to identify the substrates capable to withstand the thermal stresses induced by the reaction.

2. EXPERIMENTAL APPARATUS

A dedicated test bench has been realized by Alta for the comparative characterization of the activity and reaction rates of the catalyst formulations in controlled hydrogen peroxide decomposition experiments at atmospheric pressure. Figure 1 shows a schematic drawing of the test bench. It consists of a 100 ml reaction flask contained in a glass vessel with a volume of about 2 liters. The upper part of the vessel is closed by a sealing lid with:

- the connection for the H_2O_2 supply funnel;
- two thermocouple taps, one for the measurement of the temperature of the liquid H_2O_2 and the other for measuring the temperature of the gas in the cylinder;
- the connection to the exhaust duct of the hot gas generated by the reaction.

Before each test, a known mass of catalyst is put in the reaction flask. Next, a given quantity of hydrogen peroxide solution is added by opening the tap of the H_2O_2 tank. The decomposition reaction promoted by the catalyst generates a hot gas mixture at nearly atmospheric pressure, where molecular oxygen, steam and a small quantity of gaseous hydrogen peroxide are present. After leaving the vessel, these gases enter a coil heat exchanger, where their

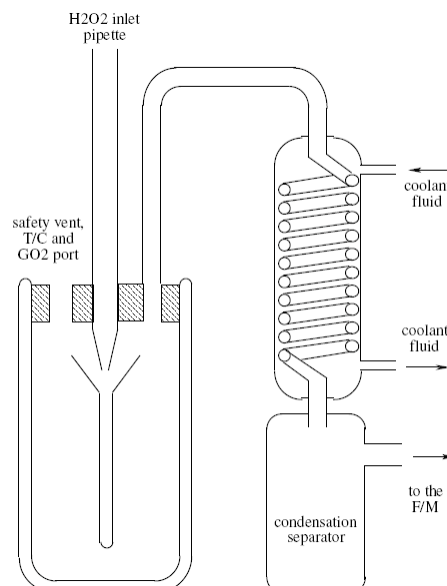


Figure 1. Schematic drawing of the batch reactor.

temperature is lowered by means of a cold liquid flow. The heat exchanger has been designed in order to condense most of water and hydrogen peroxide vapors in a liquid separator. As a consequence, the gas flow at the exit of the heat exchanger practically contains pure oxygen at known pressure and temperature conditions. In this way its flow rate, measured by means of a flow-meter, can be directly correlated to the rate of H_2O_2 decomposition [9]. Temperature measurements are carried out by means of K-type thermocouples with a diameter of 1.5 mm and a length of 250 mm. The reduced order model used for the design of the test bench and the interpretation of the experimental results has been illustrated in a previous paper [11].

3. CATALYST PREPARATION

Table 1 summarizes the physical properties of the catalyst supports used in the present study. All of them have been manufactured by SASOL and consisted in alumina spheres with monodispersed diameters ranging from 0.6 to 2.7 mm. The choice of the substrates has been driven by the aim of validating the effectiveness of the proposed platinum deposition methods on supports with different values of specific surface area and, at the same time, of assessing the thermal shock resistance of the different alumina phases. In particular, the alumina TH- L1 support has been specifically chosen in order to test the thermal stability of the substrates containing lanthanum oxides according to [8]. Silicon carbide supports in granules with an average diameter of 0.55 mm and a specific surface area lower than $1 \text{ m}^2/\text{g}$ have also been used.

Based on the observed performance of different catalysts on gamma-alumina supports [9], platinum has been selected as the most promising metallic element for H_2O_2

Table 1. Alumina support properties.

Support Name	BET Surface Area (m^2/g)	Pore Volume (ml/g)	Al_2O_3 (%)	La_2O_3 (%)	Al_2O_3 phase	Diameter (mm)
0.6/4	4	0.25	99.7	0	α	0.6
0.6/13	14	0.25	99.7	0	α	0.6
Alumina TH- L1	194	0.71	98.9	1.1	γ	2.42
Alumina $\delta+\vartheta$	104	0.45	95.6	0	δ and ϑ	0.7
0.6/170	170	0.53	96.1	0	γ	0.6

Table 2. Developed catalyst systems.

<i>Alta' ID code</i>	<i>Catalyst</i>	<i>Deposition procedure</i>	<i>Support</i>	<i>Nominal metal loading (mol)</i>	<i>SEM metal loading (At %)</i>
LR-59	Pt/ γ -Al ₂ O ₃	PT1	0.6/170	3.82×10 ⁻³	0.47
LR-II-108	Pt/SiC	PT1	SiC granules	3.82×10 ⁻³	0.42
LR-II-122	Pt/ α -Al ₂ O ₃	PT1	0.6/4	3.82×10 ⁻³	0.13
LR-II-122-B	Pt/ α -Al ₂ O ₃	PT1	0.6/4	1.5×10 ⁻³	0.12
LR-II-166	Pt/ γ -Al ₂ O ₃	PT1	Alumina TH- L1	3.82×10 ⁻³	0.6
LR-II-180	Pt// δ + ϑ -Al ₂ O ₃	PT1	Alumina δ + ϑ	3.82×10 ⁻³	0.45
LR-III-5-I	Pt/ α -Al ₂ O ₃	PT1	0.6/4	3.82×10 ⁻³	0.14
LR-III-5-C	Pt/ α -Al ₂ O ₃	PT1	0.6/4	3.82×10 ⁻³	0.13
LR-III-37	Pt/ α -Al ₂ O ₃	PT1	0.6/13	3.82×10 ⁻³	0.2
LR-III-39	Pt/ α -Al ₂ O ₃	PT2	0.6/13	2.5×10 ⁻³	7.49
LR-III-62	Pt/ α -Al ₂ O ₃	PT2	0.6/13	3×10 ⁻³	7.2
LR-III-89	Pt/ α -Al ₂ O ₃	PT2	0.6/13	2.5×10 ⁻³	7.49

decomposition. Two different methods have been used to deposit platinum on the supporting substrate. The first, indicated as PT1, consists in impregnation at 20 °C in a precursor solution with a nominal platinum load of 3.82×10⁻³ moles, washing with 50 ml of solvent, filtration, drying by mechanical depressurization at 10⁻⁴ atm and room temperature, and final calcination in muffle at 400 °C for three hours. The second, indicated as PT2, is an advanced coating technique currently under development in collaboration with the Chemistry and Industrial Chemistry Department of Pisa University, Pisa, Italy. Before catalyst deposition, all ceramic supports have been preliminarily dried in vacuum (10⁻⁴ atm) at 140 °C to eliminate the residual water bound to the matrix by hydrogen bonds. Table 2 lists all of the catalysts developed in the context of this work. Samples are identified with with Alta's identification code and the chemical formulas of the catalyst and the supporting material. The deposition technique, the nominal molar loading of platinum and the metal loading determined by SEM spectrographic analysis are also reported. The following observations are relevant to the catalysts of Table 2:

- LR-II-122-B catalyst has been obtained using the filtrate of LR-II-122 because, owing to the low surface area of the support, not all of the nominal platinum loading was absorbed by the alumina matrix; the same SEM metal loading has been attained for both catalysts;

- LR-III-5-I has been produced with no calcination in order to highlight its effects of with reference to catalysts produced according to the standard PT1 procedure;

- For the LR-59 and LR-II-180 catalysts the platinum loading detected by SEM analysis resulted to be similar, despite the different values of surface area of the supports (170 m²/g and 104 m²/g, respectively);

- The platinum content (determined by SEM analysis) of LR-59 is about three times higher than for LR-II-122 and LR-III-5-I because of the different values of specific surface area of the supports;

- A platinum loading (determined by SEM analysis) similar to the one on LR-59 has been attained on LR-II-108 despite the much lower value of the surface area of the silicon carbide support (less than 1 m²/g);

- A slightly increased platinum loading has been attained on LR-III-37 with respect to LR-II-122 because of the different support, 0.6/13 and 0.6/4 respectively;

- High load contents, 7.4 At % of Pt (equivalent to 44 wt %), have been obtained using the PT2 procedure in the LR-III-39 and LR-III-62 catalysts, in spite of the relatively low surface area of their α -Al₂O₃ substrates (4 m²/g);

- LR-III-89 has been obtained by calcinating LR-III-39 in muffle at 400 °C for 5 hours.

4. CATALYST CHARACTERIZATION

The characterization of the above catalysts has been carried out by means of the test procedures described in the following. Hydrogen peroxide decomposition activity tests have been conducted using the experimental setup previously described, with the aim of comparing the catalyst chemical activity, repeatability and susceptibility to poisoning. Drop tests starting from different initial substrate temperatures (20 °C, 100 °C and 200 °C) have been carried out in high grade peroxide in order to evaluate the thermal shock resistance of the different alumina-based supports, identify the most promising candidates for operation in a HP monopropellant prototype thruster (5 N of thrust), and assess the potential benefits of preheating of the catalytic bed for minimizing or suppressing the break-up and powdering of the support observed in previous tests [10]. Considering that the thruster has been specifically designed to operate with PROPULSE 875 HTP by Degussa, a high concentration (87.5%) hydrogen peroxide solution, drop tests have been carried out with this H₂O₂ solution. Simultaneously, the platinum load on the support has been determined by SEM analysis before and after the H₂O₂ decomposition reaction, in order to detect possible losses of platinum, investigate the accumulation of impurities, and monitor the size and distribution of platinum particles. Two hydrogen peroxide solutions were used for the activity tests: Riedel-de Haen PERDROGEN® (produced by Sigma-Aldrich), a 30% concentration solution with a particularly low content of impurities and stabilizers (PO₄³⁻<1 ppm, SO₄²⁻<1 ppm), and a 60% concentration solution by Solvay, for which no information on the presence of stabilizers is currently available.

5. EXPERIMENTAL RESULTS

DROP TESTS

The bench shown in Figure 2 has been manufactured in order to carry out drop tests on the catalysts. It consists of a 100 ml reaction flask contained in a glass cylinder filled with silicon oil. The HP supply funnel is located above the reaction flask and is connected to it by means of a rubber pipe. An electric hot plate allows to increase the oil temperature up to the desired value, which is controlled by means of a thermometer. The drop funnel has been set for delivering to the catalyst sample a repeatable stream of hydrogen peroxide droplets, at a rate of about one per second.

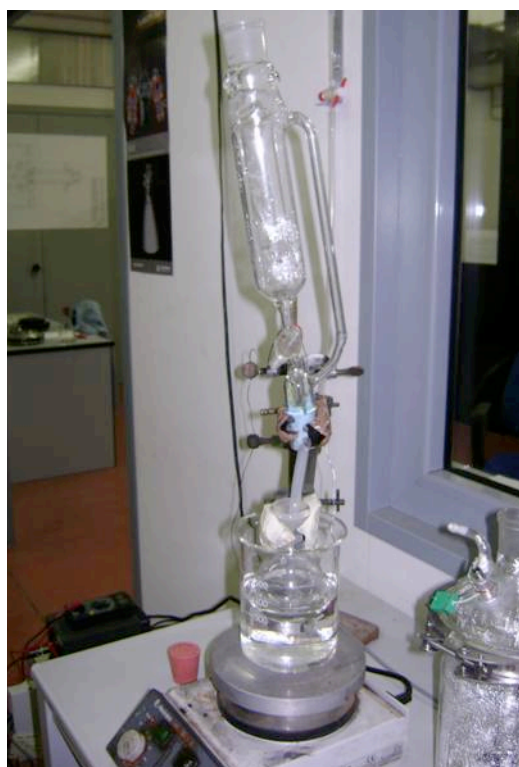


Figure 2. Picture of the experimental setup used for drop tests on the catalysts.

All of the catalysts selected for drop tests (listed in Table 3) have been prepared on different alumina-based carriers except for LR-III-89, which has been included for analyzing the effects of calcination on the platinum layer deposited using the PT2 technique and, possibly, for detecting the onset of metal losses.

The tests have been conducted as follows. A sample of 100 spheres of each catalyst has been inserted in the reaction flask and 5 ml of 87.5 % hydrogen peroxide solution have been dropped on it by means of the funnel. After completion of the reaction, the decomposition products have been removed and the catalyst samples have been recovered. The tests have been repeated at three different initial catalyst temperatures (20, 100 and 200 °C), each time on a new sample. After the conclusion of the tests, the samples have been placed in a suitable container and the

Table 3. Catalysts used for the dropping tests.

Alta code	Support
LR-59	0.6/170
LR-II-122	0.6/4
LR-II-166	Alumina TH- L1
LR-II-180	Alumina $\delta+\theta$
LR-III-39	0.6/13
LR-III-89	0.6/13

intact spheres have been counted by visual inspection and photographic pictures. Figure 3 shows the appearance of the samples after the drop tests conducted at an initial catalyst temperature of 20 °C. Table 4 lists the numbers of broken/initial spheres for each catalyst sample and initial temperature.

The following conclusions can be drawn from the drop test results:

- Both α -alumina substrates, SASOL 0.6/4 (LR-II-122) with 4m²/g and SASOL 0.6/13 (LR-III-39) with 14 m²/g of surface area, exhibited excellent mechanical resistance, since all of their sampled

Table 4. Ratio of the number of intact/initial spheres for each catalyst after tests performed at different initial temperature of the catalysts.

Alta code	$T_i=20\text{ }^\circ\text{C}$	$T_i=100\text{ }^\circ\text{C}$	$T_i=200\text{ }^\circ\text{C}$
LR-59	72/100	65/100	23/100
LR-II-122	100/100	100/100	100/100
LR-II-166	1/100	2/100	2/100
LR-II-180	91/100	85/100	89/100
LR-III-39	100/100	100/100	99/100
LR-III-89	100/100	100/100	100/100

spheres were intact after the dropping test regardless of the value of the initial catalyst temperature;

- The γ -alumina substrate (SASOL 0.6/170) used in our previous investigation [10] was not able to withstand the thermal stresses induced by the reaction (28% of the catalyst spheres broke when tested at 20 °C initial temperature) and, in addition, pre-heating deteriorated its mechanical resistance even further (77% of the catalyst spheres broke when tested at 200 °C initial temperature);
- The substrate of LR-II-180, consisting of a mixture of δ -alumina and θ -alumina, showed good resistance to thermal shocking (only 10% of the spheres broke during the drop tests);
- All of the spheres of TH-L1, the γ -alumina substrate doped with lanthanum oxides, broke by thermal shocking;
- The comparison of the LR-59 and LR-II-166 tests results revealed that γ -alumina doped with lanthanum oxides displays lower thermal shock resistance than pure γ -alumina.

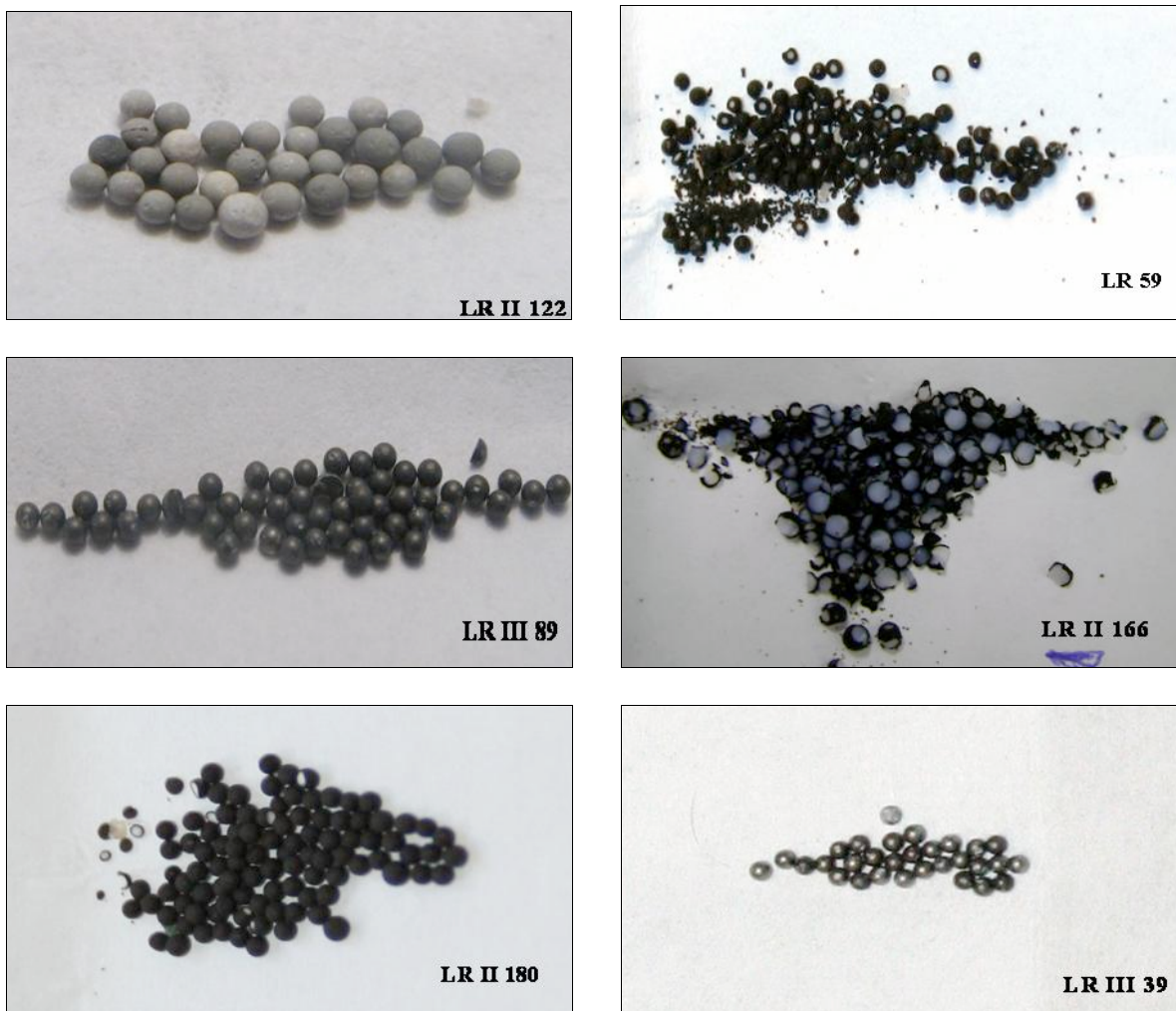


Figure 3. Appearance of the catalysts after the drop tests conducted at an initial temperature of 20°C.

ACTIVITY TESTS

For each of the catalysts listed in Table 2 fifty consecutive tests have been carried out using the following procedure:

- insertion in the reaction flask of 0.85 gr of catalyst spheres, corresponding to a standard catalyst volume of 1 ml;
- addition of 5 ml of 30% hydrogen peroxide solution;
- continuous acquisition of the following quantities during the decomposition reaction:
 1. temperature of the liquid mixture;
 2. temperature of the gas mixture;
 3. mass flow of developed gaseous oxygen;
- removal of the decomposition products after the reaction;
- return to the initial thermal conditions.

The typical time histories of the liquid and gas mixture temperatures and of the oxygen mass flow rate measured during an activity test are illustrated in Figure 4 with reference to a LR-III-39 Pt/ α -Al₂O₃ catalyst sample. The liquid mixture temperature tends to increase rapidly up to about 380 K, corresponding to the boiling point of the decomposing hydrogen peroxide solution, followed by a slower decline as the reaction tends to completion. The evolution of the gas mixture temperature is similar, apart from the delay caused by the initial presence of cold air in

the reaction vessel. In the experiments where the increase of liquid mixture temperature is very fast, as shown in Figure 4 (a), the time separation of the two temperature peaks tends to decrease. The velocity of the reaction is well illustrated by the parallel behavior of the mass flow of gaseous oxygen. When the temperature of the decomposing liquid solution approaches its peak value, the reaction becomes very fast and the residual hydrogen peroxide decomposes in few seconds, even if its temperature declines more slowly.

The time needed for the liquid to reach its peak temperature (t_{max}) and the maximum value of developed oxygen mass flow rate in each test have been used as quantitative indicators of the decomposition activity and susceptibility to poisoning of the catalysts, as well as for evaluating the repeatability of the test results. Comparative plots of t_{max} for the catalysts developed in the context of the present activity are reported in Figure 5 and Figure 6 as functions of the consecutive test number on the same catalyst sample. The maximum mass flow rates of developed oxygen for all of the catalysts obtained with the PT2 deposition technique and for LR-II-122 catalyst are presented in Figure 7 as functions of the test number. Analysis of Figure 5 leads to the following observations:

- LR-II-108, the silicon carbide-based catalyst, exhibited a strong reduction of its chemical activity after only five tests, as indicated by the rapid increase

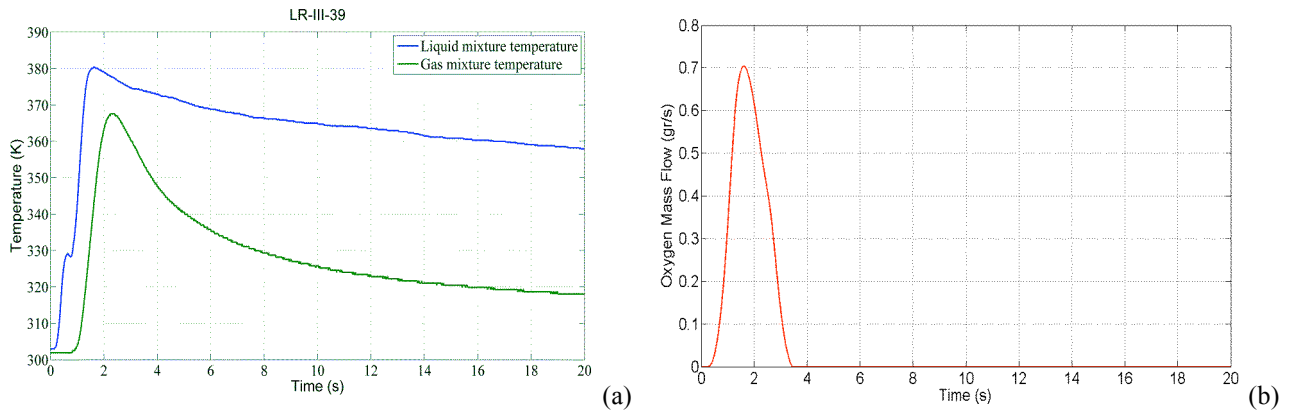


Figure 4. Liquid and gas mixture temperatures (a) and flow of gaseous oxygen (b) as functions of time during a test on the LR-III-39 Pt/ α -Al₂O₃ catalyst.

of t_{max} from 2 to about 14 seconds, followed by the stabilization at a value close to 15 seconds observed after the test number 10. Together with the deterioration of chemical activity, the loss of metallic platinum from the silicon carbide surface has been observed, as confirmed by the dark color of the reaction products. The lower value of the residual catalytic activity after the test number 10 suggests that only a small fraction of the platinum contained in the precursor solution was effectively bonded to the silicon carbide matrix, probably also as a consequence of its low porosity.

- LR-59, LR-II-180, LR-II-122 and LR-III-5-I showed an excellent repeatability and no appreciable poisoning over a sequence of fifty tests (with the exception of LR-II-180, for which only thirty tests have been conducted). The t_{max} value remained stable close to 2.5 seconds for the LR-59 catalyst and at about 4.8 seconds for the LR-II-122, LR-III-5-I and LR-II-180 catalysts.
- Reducing the specific surface area from 170 m²/g (LR-59) to 4 m²/g (LR-II-122 and LR-III-5-I) and using the same nominal molar loading of platinum in the impregnation solution only increased the value of t_{max} from 2.5 to about 4.8 seconds. This indicates that

the use of the alumina support with lower surface area and excellent thermal shock resistance (confirmed by the dropping tests carried out on LR-II-122 and LR-III-89) does not strongly deteriorate the decomposition activity. Consequently LR-II-122 and LR-III-5-I have been identified as suitable candidates for more realistic experimentation in the HP monopropellant rocket engine test facility.

- LR-III-5-I, produced without the calcination phase in muffle at 400°C for 3 hours, showed a catalytic activity comparable to that of LR-II-122, as confirmed by their similar values of t_{max} close to 4.8 seconds. Therefore the calcination phase did not seem to affect the activity of catalysts deposited with the PT1 procedure.
- LR-III-37, in spite of its higher platinum load with respect to LR-II-122, showed signs of progressive deterioration, as indicated by the increase of t_{max} from 2.5 seconds to 10 seconds after fifty tests. Further investigations must be carried out to understand the reasons of this rather anomalous feature compared to the other Pt/Al₂O₃ catalysts.

All catalysts obtained with the PT2 deposition procedure and the LR-II-122 catalyst were subjected to a sequence of

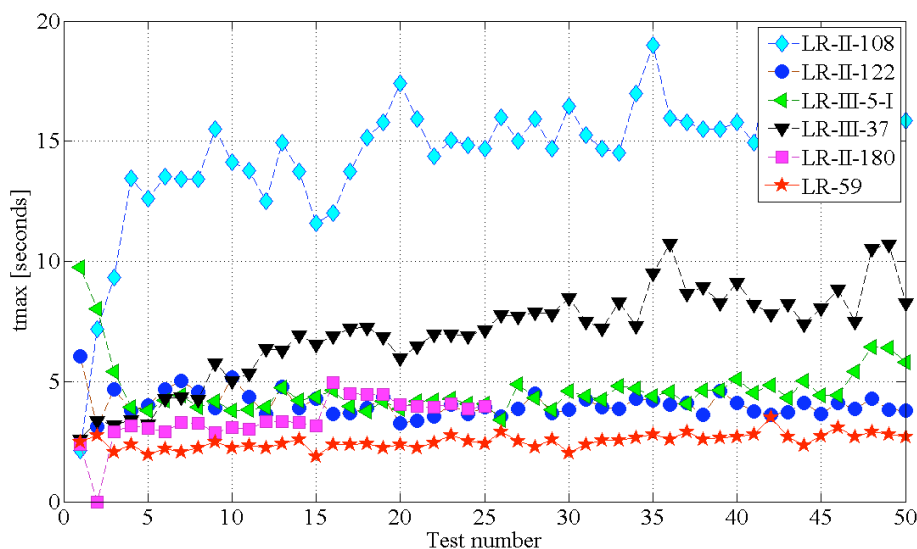


Figure 5. Time needed for the decomposing hydrogen peroxide solution to reach the peak temperature as a function of the test number for all platinum-based catalysts obtained with the PT1 deposition procedure.

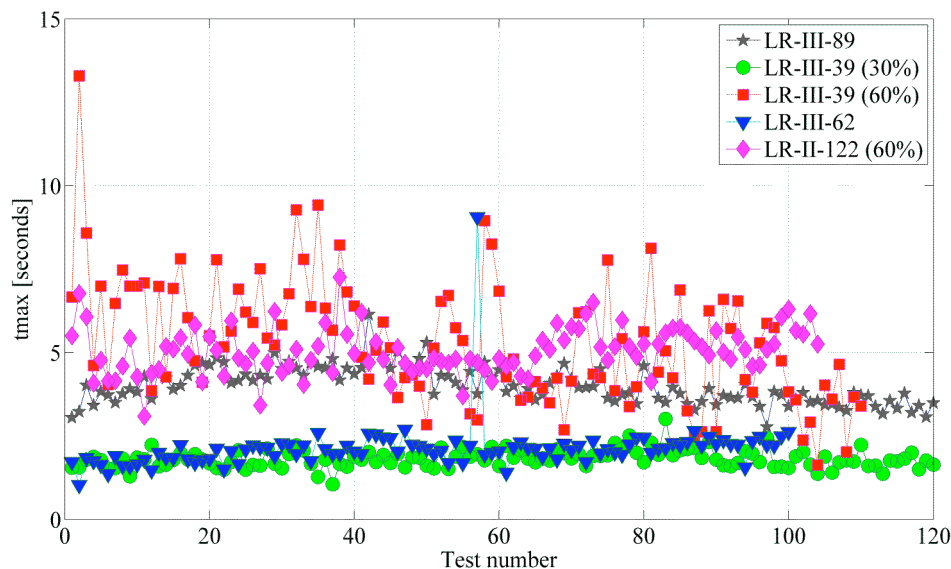


Figure 6. Time needed for the decomposing hydrogen peroxide solution to reach the peak temperature as a function of the test number for all platinum-based catalysts obtained with the PT2 deposition procedure and for the LR-II-122 catalyst.

120 activity tests, as shown in Figure 6. Two different hydrogen peroxide solutions (with concentrations of 30% and 60% by weight) were used on the LR-III-39 catalyst. In the characterization carried out at low concentration, LR-III-39 showed an excellent activity with respect to the other catalysts developed and tested in context of the present work, exhibiting a constant value of t_{max} of about 1.8 seconds. Conversely, the experimental data obtained on LR-III-39 at high concentration have revealed a strong dispersion, with t_{max} values fluctuating between 4.5 and 8 seconds over 120 tests. The two catalytic behaviours are probably due to a higher content of stabilizers in the Solvay H_2O_2 solution (60% by weight) than in the Riedel the Haen one (30% by weight). The LR-III-62 catalyst showed the same chemical activity as the LR-III-39, obtained using the same PT2 procedure and substrate. The additional calcination step in muffle at 400°C for 5 hours carried out on LR-III-39 reduced to a half the catalytic activity, as

indicated by the t_{max} value of about 4 seconds. Compared to the activity of LR-II-122, LR-III-39 exhibited a t_{max} value about three times higher, probably due to a higher superficial content of platinum (7.4 At%). Taking into account that, for LR-II-122 and LR-III-39, two α -alumina substrates have been used with a specific surface area of 4 m^2/g and 14 m^2/g respectively, the comparison of the activity of the two catalysts suggests that the PT2 procedure has been more effective than the PT1 in depositing higher contents of platinum, in spite of the significant reduction of the surface area of the support. From the analysis of oxygen flow rates in Figure 7 the following additional observations can be made:

- The observed trends of t_{max} and of the maximum oxygen flow rate for LR-III-39, LR-III-89 and LR-II-62 are in good agreement.
- LR-III-39 displayed a peak of the oxygen flow at a value of 0.7 gr/sec, which remained constant with

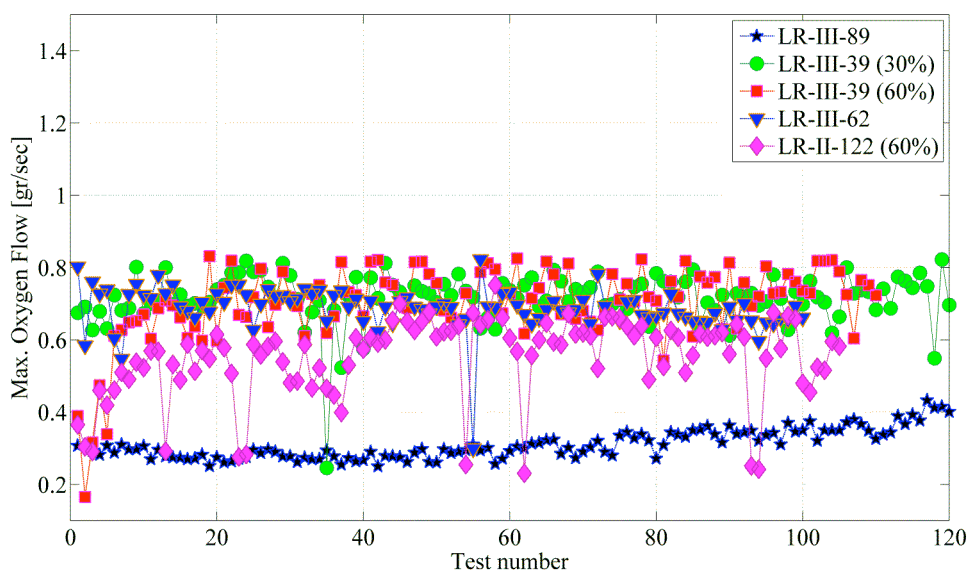


Figure 7. Maximum mass flow of developed oxygen as a function of the test number for all catalysts prepared by means of the PT2 deposition technique and for the LR-II-122 catalyst.

the increase of test number.

- Compared with LR-III-39, LR-III-89 confirmed the halving of the catalytic activity (0.35 gr/sec). A slight improvement of the chemical activity after test number 60 has been detected from both the trends of t_{max} (decreasing from 4 to about 3.5 seconds) and of the peak values of oxygen flow (increasing from 0.35 to 0.4 gr/sec).
- However, the different levels of chemical activity between LR-III-39 and LR-II-122 indicated by the t_{max} values (see Figure 6) is much less evident when comparing the peak values of the oxygen flow rate, which become almost comparable in the last 60 tests;
- For LR-III-39 no significant differences have been detected in the maximum flows of oxygen measured in the two series of tests carried out at different hydrogen peroxide concentrations. Furthermore, lower fluctuations were observed in the tests at higher H_2O_2 concentration (60 % by weight).

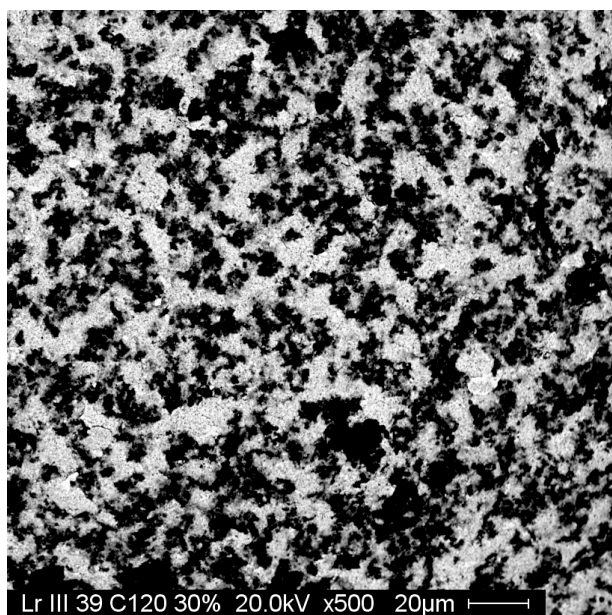
6. SEM ANALYSIS

Scanning electron microscopy analysis (SEM) has been used for measuring the surface loads of platinum (listed in Table 2), on the supporting surface before and after the H_2O_2 decomposition reaction, with the purpose of detecting possible losses of metal, investigating the presence of impurities added during the catalytic decomposition, and monitoring the distribution of the active metal. Figure 8 shows the SEM images of the LR-III-39 Pt/ α - Al_2O_3 catalyst after the decomposition of the 30% and 87.5% concentration H_2O_2 solutions used for the activity and drop tests. Large white agglomerates of metallic platinum alternated with small dark regions of more lightly loaded support are visible on the outer surface of sphere. The comparison between the surfaces of the catalyst samples after the activity tests (Figure 8 a) and the dropping tests

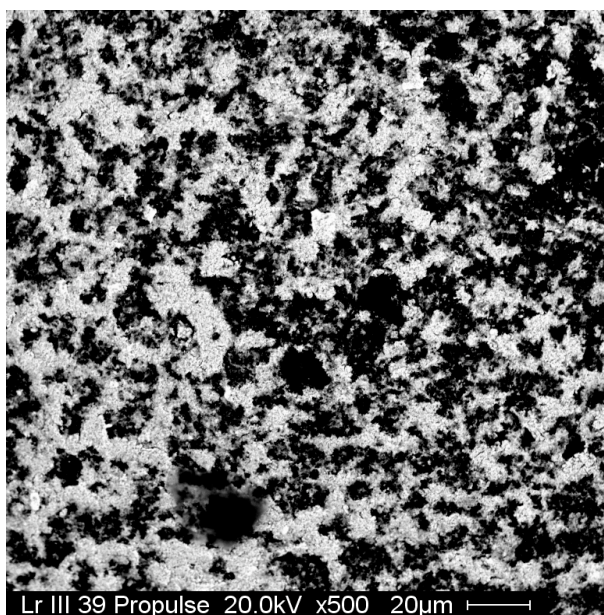
(Figure 8 b) does not reveal any macroscopic occurrence of metal loss. The platinum layer seems to be unaffected by the different H_2O_2 concentrations the two catalyst samples have been exposed to. A SEM spectrographic analysis has also been carried out to confirm this observation. A series of ten spectral measurements were made using a standard cross-over window (50×50 μm) on each catalyst sample of LR-III-39 (consisting of 10 spheres). The average metal loading was found to be stable at a value close to 44 wt % both before and after the decomposition reaction. Both SEM images and spectral analyses revealed the excellent adhesion of platinum obtained by means of the PT2 technique. Figure 9 (a) shows the image of a large crystallized agglomerate of platinum on the LR-II-108 Pt/SiC catalyst. In this case metallic platinum appears to be organized in wide clusters with a size close to 30 μm , which are not bonded to the silicon carbide matrix but simply precipitated on it. The strong reduction in the chemical activity after only five tests (see Figure 5) could probably be attributed to the rapid detachment of such clusters from the carborundum surface. A SEM image of the LR-II-122 Pt/ α - Al_2O_3 is also shown in Figure 9 (b). Due to the low surface area of the substrate, the catalyst obtained with the PT1 deposition technique does not show a homogeneous layer of the active phase: platinum appears to be finely subdivided in small particles with an average diameter of about 5 μm . In this case, however, the finer dispersion of the deposited platinum has generated a sufficient level of catalytic activity even if a platinum layer has not been obtained on the alumina surface.

7. CONCLUSIONS

In summary, the following conclusions can be drawn in view of the proposed application of the tested catalysts to a 5 N hydrogen peroxide monopropellant thruster:



(a)



(b)

Figure 8 Scanning electron micrographs of LR-III-39 Pt/ α - Al_2O_3 ; (a) after 120 tests performed for the activity characterization using the 30% hydrogen peroxide solution, (b) after the dropping test to evaluate the thermal shock resistance using a solution of H_2O_2 with a concentration of 87.5% by weight.

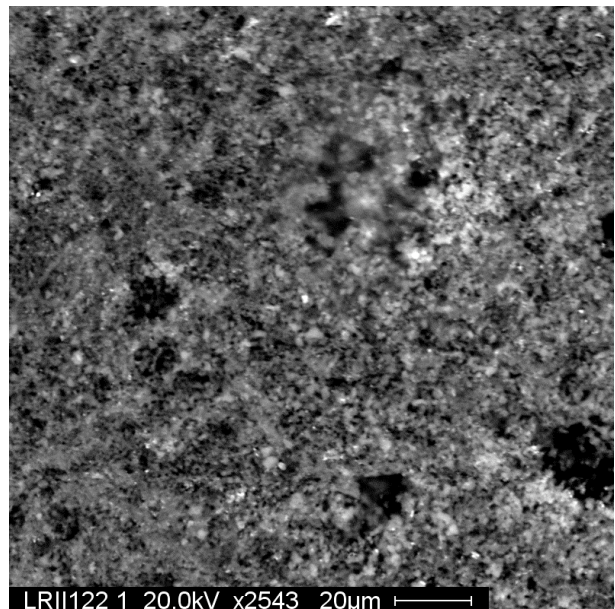
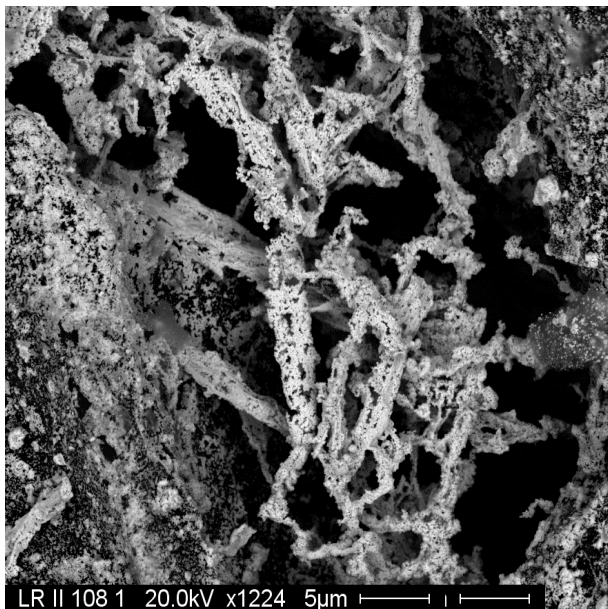


Figure 9 Scanning electron micrographs of LR-II-108 Pt/SiC catalyst; (a) and LR-II-122 Pt/ α -Al₂O₃ (b). Magnifications: 1221 \times and 2543 \times .

- Pt/ α -Al₂O₃ LR-III-39 showed high chemical activity and excellent thermo-mechanical strength, with no signs of platinum loss as a consequence of hydrogen peroxide decomposition. In addition, high surface loads of platinum (44 wt%) have been achieved on the α -Al₂O₃ substrate in spite of its low surface area (4 m²/g). This catalyst represents therefore a promising candidate for effective operation in the actual conditions typical of hydrogen peroxide monopropellant thrusters.
- Pt/SiC LR-II-108 exhibited the same activity as the alumina-based catalysts, but the PT1 impregnation technique was not able to bond all of the nominal platinum load to the silicon carbide support.
- Alumina substrate doped with lanthanum oxides showed insufficient mechanical resistance to the strong thermal shocks determined by the decomposition of high concentration H₂O₂.
- The substrate made of a mixture of the δ -alumina and θ -alumina proved to have an adequate thermal shock resistance, even if a small fraction of supporting spheres broke during the dropping tests.
- The pure γ -alumina substrate with a specific surface area of 170 m²/g was not able to withstand the thermal stresses induced by the reaction. Besides, preheating of the catalyst strongly reduced the resistance of the support. This proved that not even with pre-heating pure γ -alumina is a suitable catalyst carrier for application to monopropellant thrusters.

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