GO_2-GH_2 Catalytic Ignition Using Ceramic Monolith Catalysts

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ABSTRACT

Catalytic ignition of GO_2-GH_2 mixtures could be used for two kinds of launcher upper stage engines. A first application could be the ignition of the thrust chamber of a LO_2-LH_2 cryogenic engine such as the VINCI engine developed by European companies. A second application, which is our main target, could be a small upper stage thruster (class 10 -100 N) using gaseous O_2 and H_2 obtained from stage main tanks in order to settle the liquid in the tanks during ballistic coast phases. In both cases, catalytic ignition allows combustion initiation at low temperatures, in the range 180-300 K, without the need of a spark delivered by high voltage electrical discharges.

A dedicated test bench has then been designed and developed by AIR LIQUIDE with CNES support and 5 test campaigns have been performed to study catalytic ignition of GO_2-GH_2 mixtures. Approximately 900 ignition tests have been performed on more than 20 catalyst samples. For all samples, the active phase is deposited onto a honeycomb-type ceramic monolith after specific wash-coating procedures (two procedures have been used: A or B) to increase the specific surface area of these supports (0.5 to 22 $m^2\ g^{-1}$ (g-monolith)$^{-1}$). The preparation of the catalyst samples is realized in LACCO, which has been in charge of optimizing the catalyst preparation method with regards to functional objectives aimed at AIR LIQUIDE dedicated test bench.

INTRODUCTION

Catalytic ignition of GO_2-GH_2 mixtures could be used for two kinds of launcher upper stage engines. A first application, which is our main target, could be a small upper stage thruster (class 10 -100 N) using gaseous O_2 and H_2 in order to settle the liquid in the tanks during ballistic coast phases. A second application could be the restart of the thrust chamber of a larger LO_2-LH_2 cryogenic engine such as the VINCI engine developed by European companies. In both cases, catalytic ignition allows combustion initiation at low temperatures, in the range 180-300 K, without the need of a spark delivered by high voltage electrical discharges.

The catalytic ignition of oxygen/hydrogen mixtures is known since the early XIXth century and the first kinetic studies by Boreskov et al. have shown a surface chain mechanism [1,2]; metals of the column 10 of the periodic table (Ni, Pd, Pt) display the best activities.

The first studies on catalytic ignition of cryogenic mixtures appeared in the sixties in the USA, in relation with the development of the Shell 405 catalyst for hydrazine decomposition. A catalytic ignition was demonstrated at 116 K and several industrial catalysts have been evaluated [3]; a minimum flow rate is necessary to avoid pressure spikes. The catalysts are in pellet shape and the catalyst bed diameter/pellet size ratio must be higher than 8 to limit the boundary effects. The best catalysts are Rh-Pt/Al_2O_3 (Engelhard) and Ir/Al_2O_3 (Shell) [4]. Raney nickel has also been evaluated with ignition at 90 K [5]. Cryogenic catalytic ignition was also demonstrated for O_2/H_2 mixtures diluted in helium [6]. The thermal resistance of Ir/Al_2O_3 under hydrogen/steam atmosphere was also tested [7]. It must be quoted that few papers appear in scientific journals and most of the results remain in industrial reports.

The active phase is deposited onto a honeycomb-type ceramic monolith after specific washcoating procedures (two procedures have been used: A or B) to increase the specific surface area of these supports (0.5 to 22 $m^2\,g^{-1}$ (g-monolith)$^{-1}$). The preparation of the catalyst samples is realized in LACCO, which has been in charge of optimizing the catalyst preparation method with regard to functional objectives aimed at AIR LIQUIDE (50 $g.L_{monolith}^{-1}$) dedicated test bench. Several preparation parameters have been tested among which: the nature of the ceramic used for the base monolith supports (mullite: $3Al_2O_3.2SiO_2$ or cordierite: $2MgO.2Al_2O_3.5SiO_2$, 100 or 400 cpsi) which have been specially manufactured by CTI company (Céramiques techniques et Industrielles, Salindres, France) [8] the wash-coating method, the nature of metal deposited onto the monolith (Pt, Pd, Ir and Rh).

The loading level of the metal is between 15 and 40 wt.-% of the washcoat mass [9]. Dedicated apparatus have been developed for the impregnation and drying steps, in order to obtain a homogeneous distribution of wash-coat or impregnation layers. Pre-tests and post-tests chemical analyses and characterizations have also been performed to verify the characteristics of catalysts using different methods: X-Ray Diffraction, dispersion from hydrogen chemisorption on active sites (metallic accessibility), transmission electron microscopy, specific surface area determination and elemental analyses of active phase by ICP-OES technique.

EXPERIMENTAL PART

1. Determination of the geometric parameters of the monolith samples

The geometric parameters were determined from the values of the size wall of channels and the thickness of channel.

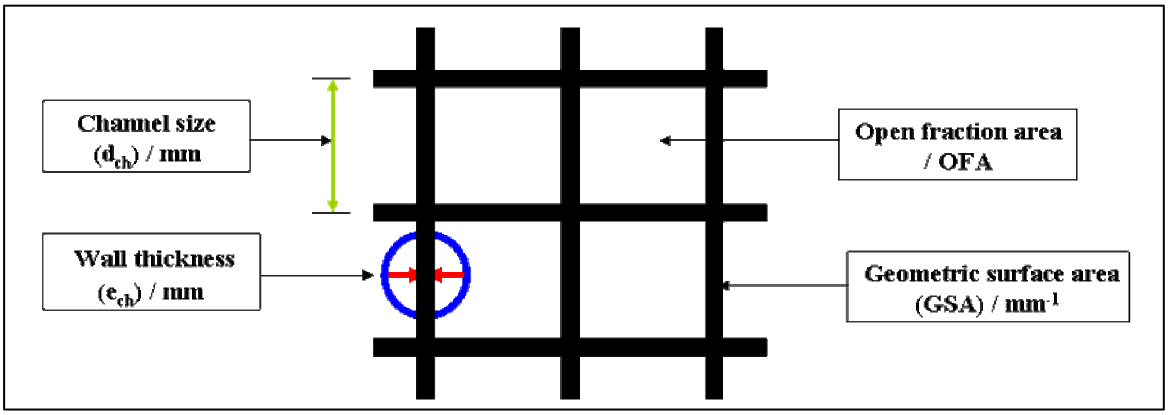

Figure 1. Geometric parameters for a monolith support with square channels.

Legend:

Cell density [mm^{-2}]	$n = \frac{1}{d_{ch}{}^{2}}$
Geometric surface area [mm^{-1}]	$GSA = 4n(d_{ch} - e_{ch})$
Open fraction area	$OFA = n(d_{ch} - e_{ch})^{2}$
Hydraulic diameter [mm]	$D_h = 4 \times (\frac{OFA}{GSA})$
Thermal integrity factor	$TIF = \frac{d_{ch}}{e_{ch}}$
Mechanical integrity factor	$MIF = \frac{e_{ch}^{2}}{d_{ch}(d_{ch} - e_{ch})}$

The thermal integrity factor (TIF) is a measure of temperature gradient the substrate can withstand prior to fracture, and the mechanical integrity factor (MIF) is a measure of the crush strength of the substrate in the diagonal direction.

The standard substrate, namely 400 / 6.5 channels per square inch (cpsi) was developed in the early 1980s to meet even more stringent emissions regulations, this substrate offered the highest values of GSA, OFA, and TIF without any compromise in D_h value; its MIF value was relatively low but adequate to meet the durability requirement as discussed later [10].

2. Wash-coating and impregnation of monolith supports

To increase the internal surface area, the monoliths were wash-coated using different sol-gel procedures. This step aims at developing a porous layer thus promoting a better dispersion of the metallic active phase as well as its better adhension. The principle of the coating step consists in immersing the monoliths in a soil suspension. The unclogging of the channels is then performed under weak flow of argon to remove excess of colloidal solution. Beside the composition of the sol suspension, key parameters are the viscosity of the sol and the duration of the wash-coating process which must be carefully controlled. Then, the wash-coated monoliths are dried in a dedicated system allowing horizontal rotation to ensure a homogeneous distribution of the coating layer. Finally, thermal treatment of the coated monoliths at higher temperature (500 °C) was carried out under air in a muffle furnace.

The technique used to introduce the active phase into the porosity of the coating layer is the impregnation of the coated substrate with the active phase precursor as the porous layer remains thin (in the order of few tens micrometers). The wet impregnation (i.e. with excess solvent) remains the simplest procedure. Thus, impregnation is performed generally from an aqueous solution of known concentration of the metal salt precursor. The procedure is to immerse overnight the coated monoliths into the precursor solution under mechanical agitation. The excess of the solution is then evaporated. When the precursor solution is completely evaporated, impregnated monoliths are carefully dried before thermal treatment.

The aim of the last thermal treatment is to form the active phase from the dried active phase precursor. This is carried out in a dedicated quartz reactor adapted to the size of our monolithic catalysts. Generally, this treatment corresponds to a reduction under hydrogen flow diluted in helium (to reduce the thermal effects of the reduction) to reduce the metal precursor to zero oxidation state (for platinum, rhodium, and iridium); but it could also be performed in an oxidative atmosphere to obtain the corresponding oxide (e.g. for PdO). These treatments are specific to each metal or active phase.

a. Dedicated drying apparatus

The monoliths coated by γ-alumina are being dried in a system allowing for horizontal rotation of 5 tr.min^{-1} at room temperature to ensure a homogeneous distribution of coating layer.

The technique is adopted by wet impregnation (with excess solvent) of monolith coated to deposit the active phase (iridium). Impregnation is performed from an aqueous solution of known concentration of metal salt precursor. The principle of this stage of preparation is to immerse the coated monoliths in the precursor salt solution overnight under mechanical agitation. The excess of the solution is evaporated. When the precursor salt solution is completely evaporated, the monoliths impregnated are dried and weighed before heat treatment.

b. Dedicated reactor for the reduction with online trap and analysis for HCl

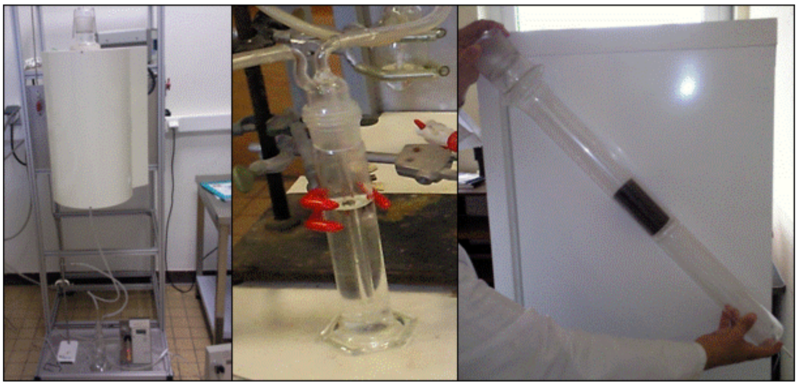

Figure 2. Heat treatments reactor.

Heat treatment of impregnated monoliths is performed to reduce the metal precursor to zero oxidation state. The reduction was carried out in a quartz reactor in the gaseous mixture of hydrogen and helium.

3. Laboratory-scale reactor

The activity and stability of the catalysts have been evaluated using the test bench developed by Air Liquide Company. The main drawback of this facility is the use of large samples whose preparation cost is directly related to their mass. Therefore, in parallel to the work described above, a laboratory-scale test reactor is under development in order to reduce the cost of the evaluation tests as well as the mass of the needed catalysts (by two orders of magnitude) thus enabling to expand the experiment parameter matrix and to determine the kinetic parameters at low temperatures. The O_2-H_2 mixtures are cooled using a cryogenic thermostat and special non-flammable oil able to cool the gas flow down to – 90 °C, and the pre-mixture gas cooling will be done in an aluminium tank from the line with a sufficient length to ensure homogeneous mixtures. To avoid too large heat transfers, the reactor itself (Figure 3) will also be cooled with liquid nitrogen or by the bath oil, and insulated with glass wool.

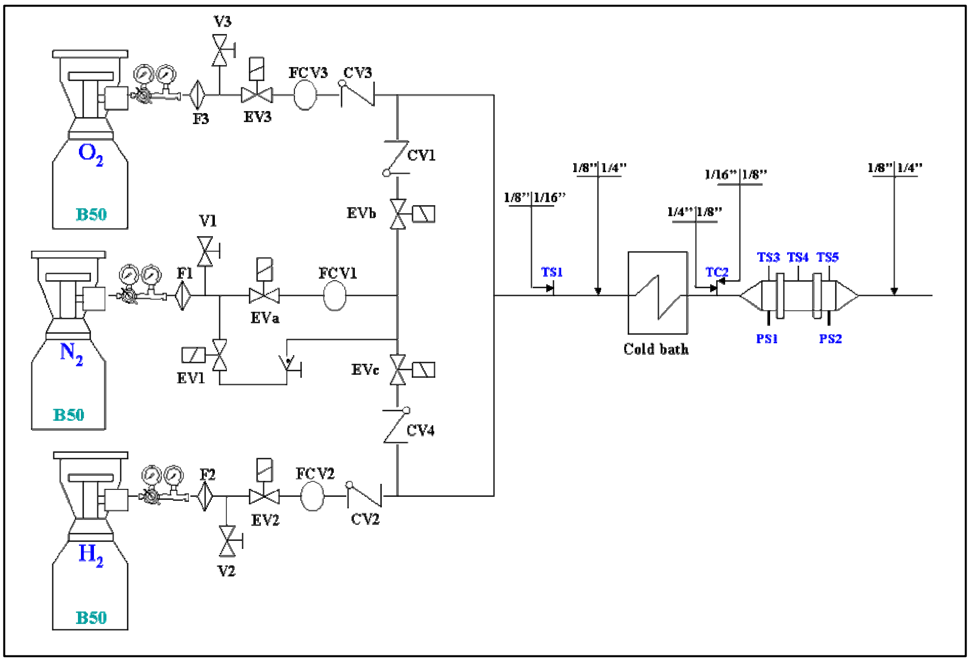

Figure 3. Representative scheme of the laboratory bench testing.

Laboratory-scale test facility and reactor are still under manufacturing phase.

RESULTS AND DISSCUSSIONS

1. Characterization of monolith catalysts

Catalysts prepared for these applications are monolithic supports (made by CTI: Céramiques Techniques et Industrielles, Salindres, France) coated with γ-alumina and impregnated with different noble metals (iridium, rhodium, platinum and palladium). Figure 4 presents the front view of two samples based on 400 cpsi monoliths.

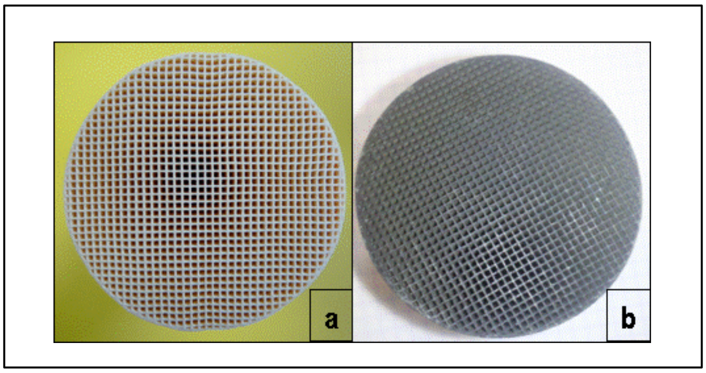

Figure 4. Front view of a 400 cpsi cordierite monolith, (a) before washcoat, (b) after impregnation with iridium.

The monolithic catalysts prepared by impregnation were characterized using different physical techniques:

- Scanning electron microscopy (coating and impregnated layers morphology)
- Energy dispersive X-ray spectrometry (atomic elements)
- X-ray diffraction (identification of phase presents and determination of the crystallite sizes)
- Transmission electron microscopy (histogram of size distribution)

For the iridium-based catalysts, the reduction corresponds to the following equation:

$H_2IrCl_6(s) + 2\ H_2(g) \rightarrow Ir(s) + 6\ HCl(g)$

The control of the reduction completion is obtained through the titration of the basic solution of the trap after the reduction; this leads to the determination of a HCl recovery factor $n_{HCl(1)}/n_{HCl(2)}$ where $n_{HCl(1)}$ represents the experimental amount of trapped hydrogen chloride and $n_{HCl(2)}$ the calculated amount (from the precursor mass). For the first set of catalysts, a recovery factor of about 0.5 was obtained, meaning that a part of chloride was not trapped or remained on the catalyst surface (Figure 5). The second assumption is in agreement with the detected presence of excess chloride by EDX measurements (vide infra). For the second set of catalysts, the hydrogen flow rate was increased, thus leading to a recovery factor of 0.92.

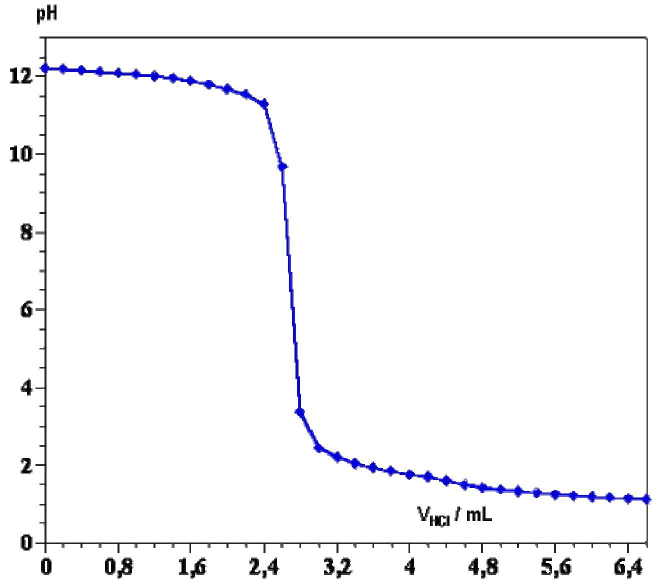

Figure 5. Titration curve of sodium hydroxide remaining after reduction of catalyst.

a. Scanning electron microscopy

The γ-alumina wash-coat layer and the filling of the wash-coat porosity by the iridium active phase were observed by SEM in order to see the quality of the coating layer and the active phase impregnation. Figure 6 shows that the improvement of the wash-coating procedure leads, as expected, to a homogeneous wash-coat layer whereas the iridium impregnation shows slight transformations of this layer:

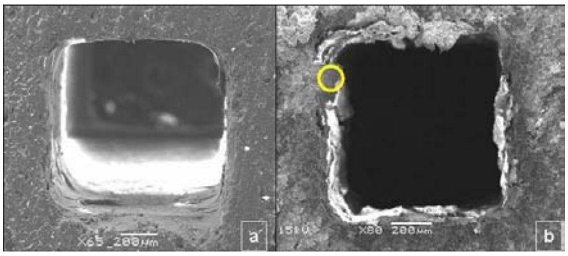

Figure 6. Photo of a channel 400 cpsi cordierite coated by the γ-alumina (a) and impregnated by iridium (b).

b. Energy dispersive X-ray spectrometry

This technique is based on the analysis of the energy of radiation after during the excitation of an atom from a given energy level to a lower one. The photon is then recorded and analyzed according to its energy. This energy is characteristic of an electronic transition characteristic of a chemical species.

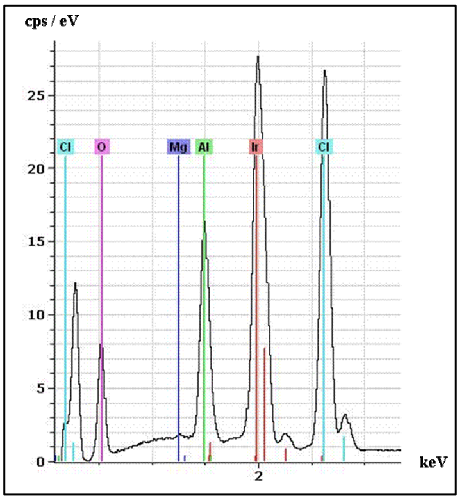

Figure 7. EDX spectrogram of part of active phase.

The EDX spectrum of phase iridium metal (yellow circle, Figure 6) shows the characteristic peaks of the elements that constitute the cordierite (Mg, Al and O), a peak of active phase (Ir) and the remaining chlorine from the precursor H_2IrCl_6.

c. X-ray Diffraction

Different monolithic catalysts were crushed and characterized by X-ray diffraction. This method shows the characteristic peaks of different metals deposited:

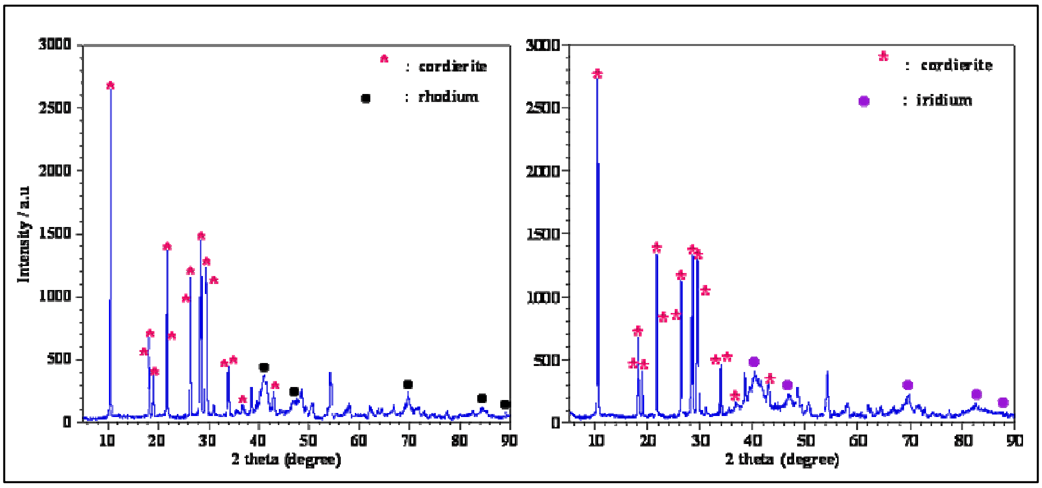

Figure 8. Diffractograms of rhodium and iridium active phases deposit.

Diffractograms of two catalysts based on rhodium and iridium highlight the presence of the support phase cordierite (PDF file 13-0294 > ref. Figure 8), the phase of rhodium metal (PDF file 05-0685 > ref Figure 8) and the phase of iridium metal (PDF file 06-0598 > ref. Figure 8).

d. Transmission electron microscopy

Photo taken by transmission electron microscopy of a monolithic catalyst based on platinum and iridium is displayed in Figure 9.

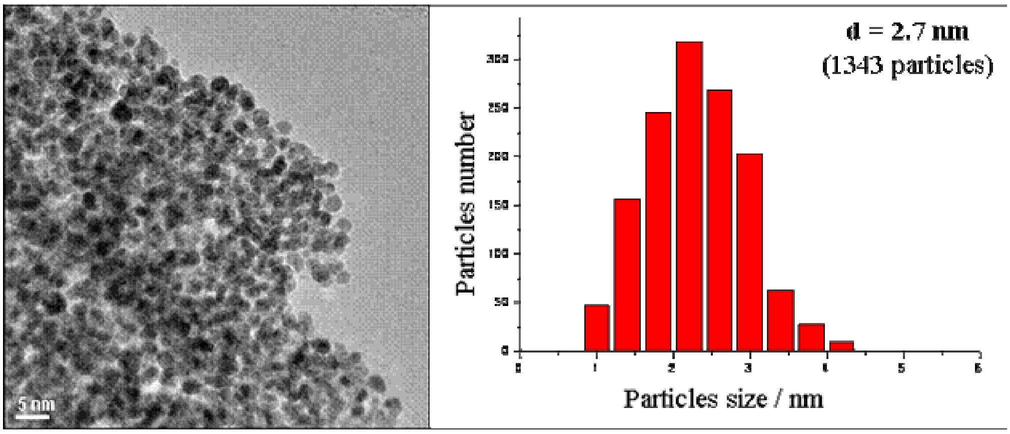

Figure 9. TEM Photo of iridium deposed on coated cordierite and histogram of sizes distribution.

- The particle size is uniform and varies between 2 and 4 nm
- The metallic phase is in the form of particles widely distributed on the alumina spread support

CONCLUSIONS

The active phase is deposited onto a honeycomb-type ceramic monolith (CTI) after specific wash-coating procedures to increasing the specific surface area of these supports.

The viscosity of the sol, contact time, the nature of the precursor, ... are very important parameters to improve the preparation of catalysts.

On going studies at LACCO aim at improving catalysts efficiency by using sol-gel procedures for the wash-coating and impregnation steps. Efficiency of improvements will first be tested on a lab-scale reactor to enable a larger test matrix for catalyst preparation parameters. The most efficient catalysts could then be tested on a full scale R&D reactor at Air Liquide.

In parallel, on going activities are done at Air Liquide, under CNES support, to design a full-scale flight thruster and to test it inside a vacuum chamber equipped with thrust measurement capability, in the frame of HX program. In this frame, catalysts characterization has been pursued, including mechanical characterizations useful for the choice, justification and validation of the full-scale thruster design.

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