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# Ceramics as Catalysts and Catalyst Supports for Propulsion Applications - The Objectives and the Challenges

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**Abstract.** Propulsion (launcher, satellites and missiles) and gas generator applications (i.e. rescue systems) need the catalytic decomposition of energetic compounds. The energetic liquids, called monopropellants, are decomposed on catalytic beds, which must present very good thermal and mechanical properties to resist frequent thermal shocks and high flow rates. Compared to conventional alumina-based supports developed about 40 years ago (extrudates, pellets, spheres), honeycomb monolithic reactors represent very attractive alternatives to overcome the current and future challenges. An overview is given and different case studies are discussed: hydrazine, energetic ionic liquids, hydrogen peroxide.

## Introduction

**Energetic compounds**. A propellant is an energetic compound (or an energetic material) which undergoes rapid and predictable combustion resulting in a large volume of hot gas used to thrust a projectile (rocket, missile, launcher) or a satellite (orbit and attitude control). Liquid rocket propellants comprise monopropellants and bipropellants. Monopropellants are liquids, which burn (or more precisely decompose) in the absence of external oxygen. They show comparatively low energy content and are used in small missiles and engines, which require low thrust. Hydrazine is currently the most widely used monopropellant. Bipropellants consist of two components, a fuel (or reducer) and an oxidizer, which are stored in separate tanks and injected into a combustion chamber where they come into contact and ignite spontaneously or by using an ignition system. They display higher energetic content and higher thrust and are required for the most demanding missions).

Gas generators are parts of systems where large quantities of specific gas or gas mixture are required for a short time length. Such systems include airbags for cars, ejector seats in aircrafts, rescue systems for people working in a closed atmosphere (submarine, shuttle, space station), specific rescue systems for submarine (submarine ballasts) or to drive a turbine for different applications: projectile moving (i.e. torpedo), electric power generation.

**Ignition systems.** Three types of ignition systems can be sorted into:

- Spontaneous reaction between oxidizer and fuel as it is the case for the monomethylhydrazine-nitrogen tetroxide mixture ($CH_3N_2H_3$–$N_2O_4$); such mixtures are called *hypergolic*. The reaction is limited to bipropellant systems and can be restarted several times; this is mainly used for upper stage launchers to reach precisely the expected satellite orbit.
- Energy supply using different procedures: mechanical (impact or friction), thermal (pyrotechnic), electrical (detonator), photochemical (laser). This ignition system can be applied to non-hypergolic bipropellants (i.e. hydrogen – oxygen) as well as monopropellants. One drawback is the ability to enable restarts which depends strongly on the ignition mode.
- Catalytic ignition of bipropellant or catalytic decomposition of monopropellant, using an adequate catalyst. This is a convenient ignition system, which enables numerous restarts

**Advantages of catalytic propulsion.** The catalytic propulsion represents a very simple subsystem using one remote controlled valve and an ignition catalyst bed [1]. After injection of the monopropellant, the role of the catalyst is to trigger its decomposition in the combustion chamber and the resulting hot gases are expelled through a converging-diverging nozzle generating thrust. Figure 1 shows the scheme of a catalytic engine.

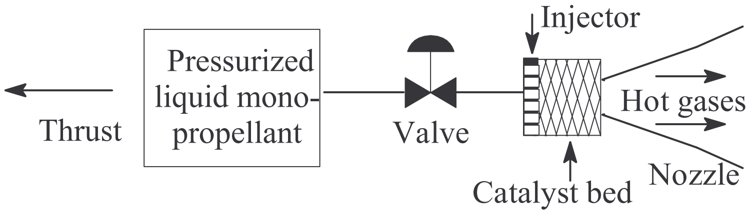

Figure 1. Scheme of a remotely controlled monopropellant catalytic engine.

The key point of such engines is the right combination monopropellant – catalyst. The monopropellant has to be stable during storage and handling, to give good material compatibility, to display low toxicity and be commercially available. The catalyst must be able to start the decomposition at low temperatures (to avoid preheating of the engine) with a short ignition delay (10 to 20 ms). It has to survive very severe conditions (high pressure and temperature rises in very short time) for long term use (up to 15 years or more) without performance degradation; the catalyst porosity must be adapted to very high reaction rates, with good heat and mass transfer during the transformation of liquid into hot gases.

**Monopropellants.** Different monopropellants have been proposed: (i) hydrazine $N_2H_4$, (ii) hydrogen peroxide $H_2O_2$; (iii) nitrous oxide $N_2O$ and (iv) energetic aqueous ionic solutions.

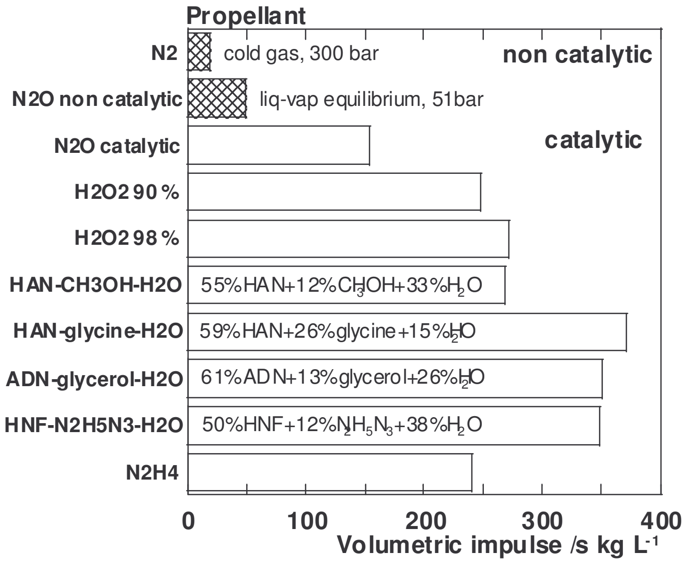

Figure 2. Thrust performance (Volumetric impulse) for different monopropellant composition. The compositions of the ionic aqueous propellants are given inside the bars in a weight basis [2].

Figure 2 compares the performances of several propellant formulations showing the strong interest for catalytic propulsion. For the aqueous ionic liquids, the meaning of the acronyms is: HAN or hydroxylammonium nitrate $[NH_3OH]^+[NO_3]^-$; ADN or ammonium dinitramide $[NH_4]^+[N(NO_2)_2]^-$; HNF or hydrazinium nitroformate $[N_2H_5]^+[C(NO_2)_3]^-$.

## Case study 1: hydrazine decomposition

The first developed ceramic catalyst was for the decomposition of hydrazine according to Eq. 1:

$$3\ N_2H_4(l) \rightarrow 4\ NH_3(g) + N_2(g) \qquad \Delta_r H°(298) = -336\ kJ\ mol^{-1} \qquad (1)$$

The entire periodic table of elements has been scanned in search of the optimum active catalyst and the most efficient catalysts contain iridium dispersed on a transition alumina carrier in granule or pellet shape ($Ir/Al_2O_3$). The iridium loading is between 30 and 40 wt.-%; despite this very high metal content, the average size of the iridium crystallites remains low (2 to 5 nm), a consequence of a strong metal support interaction (SMSI).

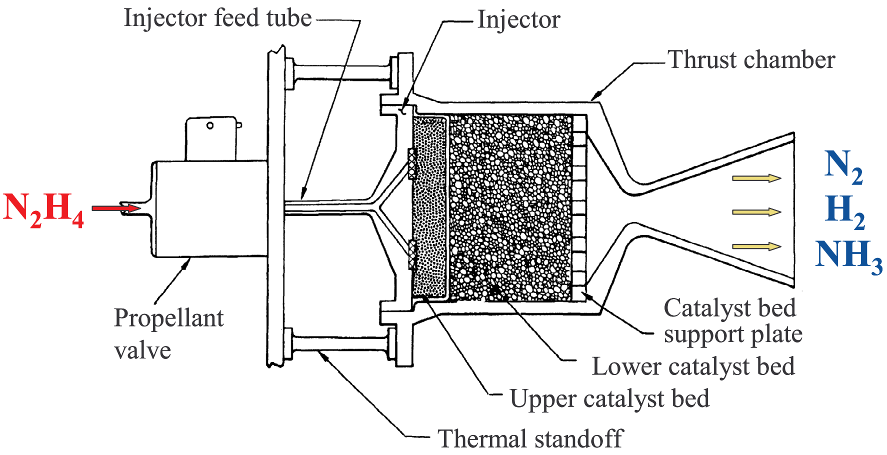

Figure 3. Scheme of a hydrazine engine (taken from ref. [3])

Under operation, the hydrazine decomposition catalysts are subjected to severe thermal and physical stresses due to the high temperature and constant agitation encountered. It is therefore necessary that the catalyst exhibits physical strength as well as continuous catalytic activity, particularly when the catalyst is employed to initiate a series of intermittent decompositions as in space-vehicle applications. Therefore, the catalyst is only as good as its carrier and diverging requirements have to be fulfilled to obtain a compromise between hardness and high surface area. Smaller particles (0.6 to 0.8 mm) are typically used for upstream bed and the coarser particles (1.2 to 1.6 mmm) for downstream bed as it is presented in Figure 3. The challenge was to develop a carrier (or substrate) with very good thermal and mechanical properties.

**Shell 405 catalyst (US)**. The preparation of the first developed and mainly used catalyst, Shell 405, is covered by patents published 14 years after filing because of restriction under a patent secrecy order. Description of the Shell catalyst, its preparation and its application, are provided by the inventor Voge et al. [4, 5]. Reynolds RA-1 alumina granules suffer up to 20 impregnation and drying cycles using a 6 wt.-% Ir solution. The outstanding properties of Shell 405 catalysts are presumably due to a more open structure [6] or to the presence of a high fraction of $\eta$-alumina crystals (size around 100 nm), stuck together by amorphous alumina binder. The dense crystals prevent penetration of hydrazine into the interior of the pellets and decreases the generation of catalyst fines via break-up process from internal overpressure [7]. Ir crystals display an average size of around 2 nm and show an epitaxial growth on the support with (110) orientation, which increases with firing time [8]. In 2002, Shell Chemicals USA (Houston, TX) terminated the production of Shell 405 and transferred the catalyst to Aerojet Redmond, WA location, including a strategic stock of the alumina support. Since then, Aerojet provides the catalyst under the name S-405 claiming that its product exhibits the same properties as Shell 405 [9, 10].

**KaliChemie KC12GA catalyst (Germany).** Kali-Chemie Company, Germany, developed in the seventies, independently of Shell, another commercially available catalyst KC12GA [11, 12]. The preparation procedure is different with three impregnation-drying-impregnation-drying-reduction cycles. A catalyst carrier made by sol-gel procedure to obtain nearly spherical granules for more uniform bed packing and reduced pressure drop lead to disappointing performance by comparison with conventional alumina rounded by a mechanical attrition process. An exhaustive comparison of both catalysts was published recently by Goto et al. [13]. Shell 405 and KC12GA show high BET surface areas (> 100 $m^2$ $g^{-1}$) and high iridium dispersion (particle size 1.5-2.5 nm). One application of KS12GA catalyst is for Ariane-V roll control thrusters during the launch [14].

**Cnesro catalyst (France).** Efforts to develop a catalyst similar to Shell 405 started in the late sixities [15, 16] and different preparation procedures have been evaluated. The retained method was a three-cycle procedure including impregnation of granular alumina with $H_2IrCl_6$ precursor, drying and interim reduction at 673 K; the iridium content is 36 wt.-%. In 1972, the use of a new alumina carrier calcined at 1123 K lead to a strong improvement of the catalyst, with two carrier sizes (0.63-0.8 mm and 1.25-1.60 mm). One gram of this catalyst was able to decompose 250 kg of hydrazine [17]. The Cnesro catalyst has been used for the 3.5 and 15 N thrusters on the Spot satellite family. During the eighties, the abrasion technique used to obtain the spherical shape of the alumina pellets was replaced by the new "oil-drop" procedure, but after this change, several thrusters were low or erratic, probably due to aging problems during extended storage [3]. Very thorough studies have been performed to improve the Cnesro catalyst after the change of alumina process [18, 19]. It was proven that the presence of chloride limits the on-the-shelf storage life of the catalyst; after chloride removal in the presence of steam and hydrogen, the long term stability is strongly improved.

**GIPKh catalysts (Russia).** A deep understanding exists in Russia too, but this has become apparent only after the political changes and the published results are mainly in Russian language. The work has been done at the former State Institute of Applied Chemistry (GIPKh), now Russian Scientific Center – Applied Chemistry (RSC-AC) in Saint-Petersburg [20]. They developed a catalyst called K-201, similar to Shell 405. Fundamental aspects of the catalyst preparation and relationship with activity lead to optimized iridium loading of 31 wt.-% [21].

**Conclusion.** Different groups devoted very great efforts for years to develop a hydrazine decomposition catalyst and the challenge to prepare an alumina support in the form of spheres or pellets for this peculiar application has been overcome.

## Case study 2: Ionic liquid decomposition

Owing to their reduced toxicity, energetic ionic liquids are proposed as hydrazine substitutes. A typical mixture contains hydroxylammonium nitrate (HAN, $NH_3OH^+NO_3^-$) as oxidizer, water and an ionic or molecular fuel. Such mixtures involve more drastic conditions than for hydrazine, due to the high temperature reached during the decomposition (more than 1400 °C) and the need of frequent restarts. Therefore, the preparation of shape formed catalysts displaying high catalytic activity at low temperature (20 – 200 °C) associated with high thermal and mechanical stabilities, remains a current challenge for the future development of new engines. Previous studies have revealed that platinum supported on thermally stable Si-doped alumina displays a good activity at low temperatures [22, 23]. Powder catalysts can be evaluated at the laboratory level, but cannot be used directly in thruster engines owing to high-pressure drops. Therefore, a shape forming of the catalyst is necessary to determine the catalytic activity in real propulsion conditions.

**Preparation and characterization.** The catalysts contain 10 wt.-% Pt supported on Si-doped alumina. The support is synthesized by the sol-gel method according to the Yoldas procedure [24, 25] and is described more precisely in another paper of this Conference [26]. Samples of composition $(Al_2O_3)_{0.88}$-$(SiO_2)_{0.12}$ (Si:Al atomic ratio: 6:94) are obtained. The powder is milled and CTI Company [27] carried out the shape forming. The sample, obtained in the form of spheres, is named $^{MF}Al_2O_3Si$**.** A second shape forming has been realized using the “oil-drop” method; the. The sample displays an average size of 1.5 mm and is named $^{OD}Al_2O_3Si$**.** The metallic phase is introduced by impregnation of $H_2PtCl_6$ precursor solution, followed by reduction (r) at 400 °C for 4 h (

Figure 4). The powder catalyst was prepared from two successive impregnations, each corresponding to 5 wt.-% platinum, on xerogel powder support and a final reduction (sample $^{P}5$(i+i)rPt). The same procedure was performed on the shape formed supports but with three impregnation steps; the sample names are $^{OD}3$(i+i+i)rPt and $^{MF}3$(i+i+i)rPt.

The samples have been characterized by specific surface areas determination (BET), X-rays diffraction (XRD) and transmission electron microscopy (TEM). The catalytic activity in decomposition of aqueous 79 wt.-% HAN solution was followed by thermal analysis (TGA-DTA) to determine the decomposition onset and by means of a constant volume batch reactor [28].

**Results.** XDR analysis shows the presence of θ-alumina and δ-alumina phases for all samples. The larger BET surface areas of powder and oil-drop based samples (Table 1) can be linked to a larger content of δ-$Al_2O_3$ [23, 29] and disclose the interest of the oil-drop procedure to improve the textural properties. The introduction of platinum does not change the structural data and the thermal stability. The metal active phase content is about 10 wt.-% for all catalysts (ICP). The average Pt crystallite size is higher for the powder catalyst. Each catalyst presents a heterogeneous platinum size distribution. Numerous crystallites are around 10 nm but larger particles are detected by TEM.

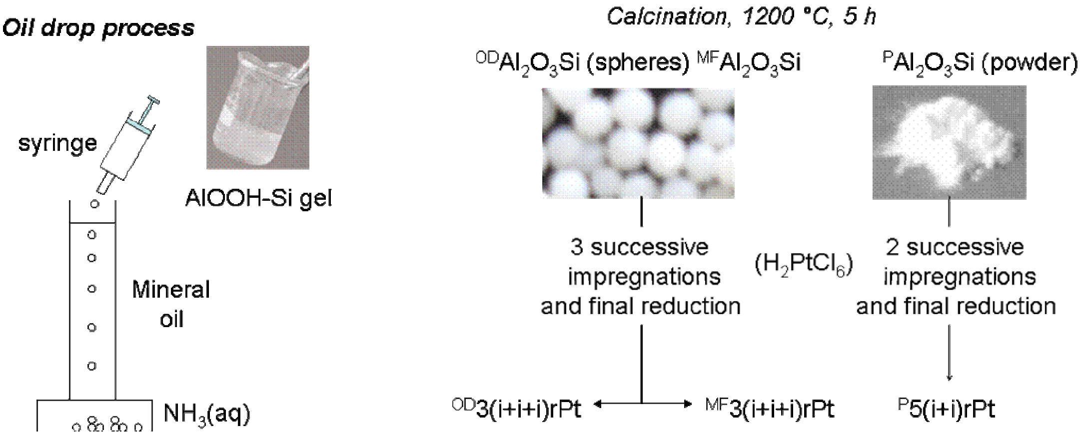

Figure 4. Scheme of support and catalyst preparation.

The catalyst evaluation using thermal analysis, gave the onset decomposition temperature and the reaction exothermicity. The equation of the HAN decomposition giving thermodynamic products is:

$$[NH_3OH]^+[NO_3]^-(aq) \rightarrow 2\ N_2(g) + O_2(g) + 2\ H_2O(g) \quad \Delta_r H°(298) = -140\ \text{kJ mol}^{-1} \qquad (2)$$

Table 1. BET surface area, Porous volume, platinum content, XRD particle size, catalytic decomposition temperature of various samples. Thermal decomposition temperature: 107 °C.

| Sample | BET /$m^2\ g^{-1}$ | Porous volume /$cm^3\ g^{-1}$ | wt.-% Pt | Size /nm | $T_{dec}$ /°C |
|---|---|---|---|---|---|
| $^{P}Al_2O_3Si$ | 67 | 1.50 | - | - | 80 |
| $^{MF}Al_2O_3Si$ | 44 | 0.48 | - | - | 77 |
| $^{OD}Al_2O_3Si$ | 62 | 0.40 | - | - | 74 |
| $^{P}5(i+i)rPt$ | 61 | | 9 | 22 | 20 |
| $^{MF}3(i+i+i)rPt$ | 40 | | 11 | 18 | 45 |
| $^{OD}3(i+i+i)rPt$ | 63 | | 9 | 14 | 68 |

All supports exhibit similar profile with broadened endothermic peaks due to water vaporization and exothermic peaks due to a weak catalytic effect. The reaction exothermicity increases in the order $^{OD}Al_2O_3Si < {}^{MF}Al_2O_3Si < {}^{P}Al_2O_3Si$. The powder sample displays the best activity owing to the highest porous volume: the propellant is more rapidly in contact with the active centers. The presence of platinum leads to a stronger exothermic peak which appears at lower temperature, thus displaying a very efficient catalytic activity. Again, the powder catalyst exhibits the highest exothermic reaction.

In the batch reactor, the supports show a decomposition temperature around 75 °C, weaker than the thermal decomposition temperature (107 °C). In the presence of the active phase, we observe that the shaped catalysts delay the decomposition temperature; the active phase is less easily accessible to HAN-water mixture due to the lower porous volume. Moreover, at the end of the reaction, the shape formed samples are broken, owing to the strong exothermicity of the reaction. Successive injections performed in isothermal conditions (85 °C), display the lowest pressure increase (i.e. the lowest efficiency) for the $^{P}$5(i+i)rPt powder catalyst; moreover, in the same conditions, the shaped catalysts are not broken thus showing their potential interest for this application.

**Conclusion.** Both shaped supports display high thermal stability of alumina phases, and good BET surface areas after thermal treatment at 1200 °C. The presence of 10 wt.-% platinum does not modify the structural and textural characteristics. The platinum crystallite sizes are in the range 15-20 nm but the largest particles are aggregates of small crystallites. All catalysts display similar activity for the decomposition of aqueous HAN solution at low temperatures. However, the most efficient catalyst is the sample prepared at the laboratory level using the oil drop process. The preparation of shape formed catalysts is therefore possible at the laboratory level in the range 10 to 50 g. The next step will be the catalyst evaluation in real conditions using a vacuum facility, to check and improve the long-term stability of the catalysts for propulsion applications.

## Case study 3: hydrogen peroxide decomposition

The use of solid catalyst for decomposition of concentrated hydrogen peroxide solution (HP, 70 to 100 wt.-%)), for monopropellant and bi-propellant applications, leads to lower onset temperature and high decomposition rate [30, 31]. Currently, the decomposition of HP is initiated by catalysts based on silver metal or manganese oxides which are the best active phases [32, 33].

Conventional catalysts used for propulsion applications are in the form of wires, gauzes or grids for silver catalysts, pellets or spheres for supported manganese oxides catalysts. However, honeycomb monolith catalysts show many advantages [34, 35]: (i) lower pressure drop, (ii) better thermal shock and attrition resistance, (iii) uniform flow distribution and mass/heat transfer conditions for the whole cross section, (iv) high surface-to-volume ratio and (v) thin layer containing the active phase with shorter diffusion length and easier accessibility of catalytic active centers to reactants. Moreover, monolithic honeycomb catalysts have been widely used in cleaning of exhaust gases, especially those from cars and power stations [36].Therefore the current heritage of monolithic catalyst is large and such reactors are attractive alternatives to conventional catalysts [34, 37].

Moreover, there is a current need of miniaturized propulsion system for widening the capabilities of low cost micro-satellites. Recently, the development of a turbo-pump fed miniature bi-propellant rocket engine has been proposed as a new propulsion system for micro-satellites (10 to 100 kg) [35]; the bipropellant thruster uses 70 wt.-% $H_2O_2$ as oxidizer and ethanol as fuel. Hydrogen peroxide is decomposed by a solid catalyst in a gas generator and the gaseous hot mixture (oxygen and steam) is used for driving a miniaturised turbine. The turbine output powers micro-pumps in a self sustained cycle. After the turbine, the gaseous enters the combustion chamber. To optimize HP decomposition, different monolith-based catalysts have been prepared.

**Monolithic substrate.** Monolithic supports were obtained through cooperation with by CTI Company [27]. The chosen material is mullite $3Al_2O_3$-$2SiO_2$ and the monolith displays 7 x 7 square channels of 1 mm internal side length (see Figure 5). At low temperature, mullite is a solid solution in the range 60 to 64 mol-% $Al_2O_3$, i.e. with a slight excess of alumina. The advantages of mullite are good thermal stability and mechanical properties. The overall length of the decomposition chamber is 15 mm and it consists of two monoliths having each a length of 7.5 mm.

**Washcoat procedure.** To increase the surface area, a wash-coat layer is deposed on monolithic surface. Most often, this secondary support is a porous alumina layer which allows a good chemical continuity with the substrate and with the active phase. Three procedures have been used to prepare this alumina wash-coat:

- I: modified boehmite procedure preparation, adapted by LACCO.
- II: preparation of boehmite sol AlO(OH) starting from aluminum tri-sec-butoxide [38].
- III: monoliths wash-coated by CTI Company.

The monoliths are put into the wash-coat colloidal solution (sol) for 1 h. For procedure I, the wash-coating procedure is performed at room temperature. For procedure II, it is done at 45 °C. Then, the monoliths are retrieved and the channels are gently flushed using a nitrogen flow. Finally, the wash-coated monoliths are heated in a muffle furnace at 500 °C.

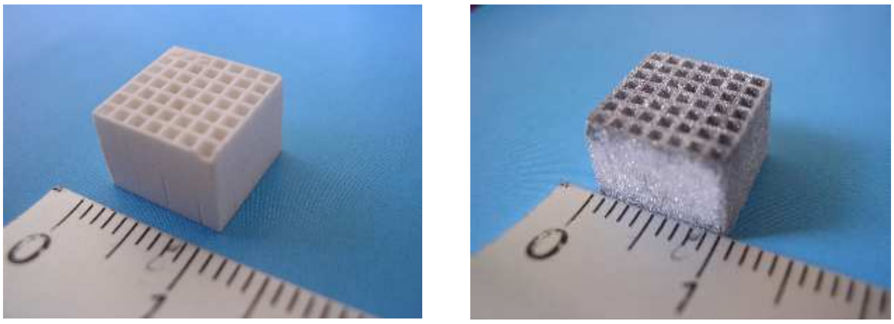

Figure 5. Pictures of monolithic substrate before (left) and after (right) wash-coat, impregnation and reduction procedures (Ag-based catalyst) [39].

**Impregnation procedure.** Two active phase were selected: metallic silver and manganese oxide. The active phase precursors (silver nitrate or sodium permanganate) were deposited from aqueous solutions by impregnation performed in small beakers. The monolith is put into the precursor solution for a night. Then the remaining solution is evaporated in a sand-bath at 45 °C. Drying and calcination are carried out under air in a muffle furnace at 500 °C. The samples impregnated with silver nitrate are finally reduced under hydrogen flow at 300 °C for 3 h. Table 2 gathers data of selected samples.

Table 2. Characteristics of some silver and manganese oxide based catalysts.

| code | Washcoat procedure | wt.-% wash-coat after calcination | wt.-% active phase after reduction | $S_{BET}$ /m$^2$ g$^{-1}$ | wt.-% loss after firing |
|---|---|---|---|---|---|
| A | III | Not known | 8.1 % Ag | 0.25 | -2.5 % |
| B | II | 1.5 % | 17.5 % Ag | 5.0 | -8.1 % |
| C | I | 7.5 % | 11.3 % Ag | 19.6 | -0.9 % |
| D | III | Not known | 28.9 % $MnO_x$ | 12.8 | Not fired |
| F | I | 8.4 % | 22.1 % $MnO_x$ | 14.4 | -12.7 % |

**Characterization and evaluation**. The following techniques have been used: (i) specific surface area (BET method) and porosity; (ii) X-rays powder diffractometry (XRD) before and after firing; (iii) crystallite size determination. A simple test rig was set up consisting of pressurization system, monolith catalyst, and control and diagnostic system [35]. The purpose of the tests is to focus on four principal characteristics of $H_2O_2$ decomposition: (i) transient time to reach steady-state decomposition, (ii) initial temperature of the decomposition chamber, (iii) steady–state decomposition temperature, and (iv) $H_2O_2$ mass flow rate. The efficiency of the decomposition was assessed from the final temperature. The concentration of hydrogen peroxide was 70 wt.-% and the decomposition equation is:

$$2\,H_2O_2(l) \rightarrow 2\,H_2O(g) + O_2(g) \qquad \Delta_r H°(298) = -108\ \mathrm{kJ\ mol^{-1}} \qquad (3)$$

**Results.** Mullite (major phase) and corundum (minor phase) are identified but no structural information can be obtained for the wash-coat layer due to its amorphous nature

Metallic silver is clearly evidenced by XRD After the evaluation tests, we can observe an important loss of active phase during the hydrogen peroxide flow and this loss can be linked to wash-coat procedure II. The silver crystallites display large average size (70 to 100 nm) which limits strongly the number of free surface silver atoms. Moreover, the specific surface area depends strongly on the wash-coat procedure, the procedure I being the most efficient. From the firing tests, we can sort the samples: sample A < sample B < sample C.

The non-fired sample D displays a high surface area due to the manganese oxide layer. The X-rays diffraction permits to identify the badly crystallized manganate phase $Na_{0.7}MnO_{2.05}$ as the major phase which covers the substrate. After firing, an important weight loss is observed (- 12.7 wt.-%, Table 2) and the sodium-containing phase disappears, due to the washing of the sample by liquid hydrogen peroxide. A non-identified $MnO_x$ phase still remains. Sample F showed a very good activity at room temperature. No preheating of the monoliths was required and no liquid hydrogen peroxide was visible even at the beginning of firing. It reached a total operation time of 100 min without significant problems although the temperature changed over the course of the endurance test between 120°C and 220°C. Evaluation of new monolithic catalysts is currently under progress.

**Conclusion.** Manganese oxide supported on washcoated monoliths are efficient catalysts for the decomposition of 70 wt.-% $H_2O_2$ and one of the key parameters is the specific surface area of the washcoat layer. The next challenge will be to develop monolithic catalysts for the decomposition of more concentrated HP solutions (up to 98 wt.-%) on the long term use.

## Future prospective applications

New applications of catalytic propulsion will depend strongly on the development of efficient shaped catalysts based on ceramic substrates and honeycomb monoliths will play a key role.

**Decomposition of nitrous oxide.** Nitrous oxide $N_2O$ displays liquid-vapor equilibrium under 50 bar at room temperature, thus allowing a self-pressurization of the tank. Its decomposition is very exothermic with an adiabatic temperature higher than 1600 °C (Eq. 4):

$$2\,N_2O(l) \rightarrow 2\,N_2(g) + O_2(g) \qquad \Delta_r H°(298) = -163\ \text{kJ mol}^{-1} \tag{4}$$

The finding of catalysts efficient to trigger the decomposition at low temperature (less than 200 °C) and able to survive very high temperatures are one of the most important current challenges.

**Air breathing supersonic or hypersonic jets.** The development of future scramjet (Supersonic Combustion Ramjet) needs a propulsion system that operates from Mach 4.0 to 8.0 using liquid hydrocarbon. The liquid hydrocarbon has to be transformed into lighter molecules before reaching the combustion chamber and liquid fuels that will suffer this transformation are known as *endothermic fuels* [40]. This transformation, well known in petroleum industry as the *cracking process*, corresponds to a set of endothermic reactions whose energy supply comes from the combustion chamber. The current challenge is to develop thermally stable cracking catalysts displaying very high activity and thermal conductivity (for rapid heat exchange) associated with limited coking and deactivation ability [41].

**Pulse Detonating Engine (PDE).** The new concept of pulse detonating engine increases the engine performance versus conventional rocket by using a different combustion cycle: the Humphrey cycle, which includes a detonating step that corresponds to a constant volume combustion step. This increases the yield up to 30 %. Liquid fuels are more convenient for rocket or missile applications but the detonability of the fuel-air mixture is low. Therefore, a transformation of the injected fuel into a mixture of more detonable lighter unsaturated hydrocarbons is needed. This could be obtained by using a catalytic cracking reaction and the challenge is obviously related to the previous one: to find and develop catalysts able to transform liquid fuels into more detonable hydrocarbon mixtures with a limited deactivation. [42].

**Ignition of gaseous hydrogen-oxygen mixtures.** Engines for launcher upper stage use the hypergolic monomethylhydrazine-nitrogen tetroxide mixture, which allows restarts during the launch. The replacement by $H_2$-$O_2$ mixtures needs an ignition system with the same restart possibility and the development of a monolithic catalyst to ignite such mixtures is a current challenge [43, 44].

**Micropropulsion.** The development of small satellites needs microengine propulsion subsystems. Catalysts in the form of small pellets cannot meet the requirements of low pressure drop and monolith substrate with a limited number of small-sized channels seems to be the best solution to this challenge. Moreover the drawbacks due to microfluidic flow could be overcome by specific internal treatment to render a part of the surface hydrophobic.

## Summary

This overview present different case studies concerning catalytic decomposition of energetic compounds for propulsion and gas generator applications. The energetic liquids are decomposed on catalytic beds, which must present very good thermal and mechanical properties to resist frequent thermal shocks and high flow rates. Compared to conventional alumina-based supports developed 40 years ago, honeycomb monolithic reactors present very attractive alternatives to overcome the current and future challenges.

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