Improvement of catalysts for the decomposition of monopropellants for space applications - Comparison between aerogels and xerogels

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Introduction
Monopropellants are energetic liquids whose decomposition on solid catalysts leads to the production of hot gases. This very simple reaction is used in small reaction engines (or thrusters) for the orbit and attitude control of satellites. The most popular monopropellant is presently hydrazine NH₂NH₂ associated with alumina supported iridium catalyst Ir/Al₂O₃. But the acute toxicity of hydrazine, the high vapor pressure at room temperature and the rather high melting point (1 °C) are severe drawbacks that have prompted studies towards hydrazine substitutes. New promising and non toxic propellants (also called 'green propellant') are aqueous ionic solutions containing hydroxylammonium nitrate NH₃OH⁺NO₃⁻ (or HAN) as oxidant associated with a fuel. But, unlike hydrazine, the decomposition of such mixtures releases hot gases whose temperature is much higher and can overpass 1400 °C.

The current challenge is therefore to find the best catalyst able: (i) to trigger the decomposition of the monopropellant at low temperature (much less than the thermal decomposition), (ii) to keep good thermal stability and specific area at high temperature and (iii) to avoid the loss of active phase under the propellant flow. Recently, sol-gel alumina samples doped with silicon have been proven able to sustain thermal treatments at 1200°C or more during several hours [1]. Thus, to reply this challenge, platinum supported on this thermally stable alumina has been chosen as one of the possible catalyst candidates and we present here the impacts of the drying procedure (subcritical or supercritical) and the impregnation method on the thermal stability and the catalytic activity of the prepared samples.

Results and Discussion
The doped alumina has been prepared by the sol-gel procedure using aluminum trisecbutoxide as precursor; the doping element was introduced as described in a previous paper [2]. The gel of the resulting doped boehmite has been then dried by subcritical drying (xerogel) or by supercritical drying under CO₂ (aerogel). The doped transition alumina is obtained by heating the dried gel at 1200°C under air during 5 hours. The active phase (5 wt-% Pt) is then introduced through the classical impregnation method of doped alumina from H₂PtCl₆ aqueous solutions, followed by drying and reduction by H₂ at 400 °C. A one step procedure of catalyst preparation consists to introduce the platinum solution directly onto the sol during the preparation of the boehmite. The samples have been characterized (XRD, BET area, TEM and chemisorption measurements) and evaluated for their ability to decompose a 79 wt-% HAN-water mixture, using a batch reactor [3] and a thermal analysis (TA)
equipment. The catalytic decomposition takes place under argon flow in the increase temperature mode (10 °C/min), with the same catalyst to propellant ratio (1.6) for all experiments.

Whatever the preparation mode, all the samples display platinum crystallites on θ-alumina (XRD). No α-alumina was evidenced, despite the high thermal treatment. The BET results corroborate the very good thermal stability of the aerogel samples (107 to 129 m²/g) by comparison with the xerogels (40 to 68 m²/g); moreover the X-mapping reveals a much better homogeneous distribution of aluminum and silicon atoms for the aerogel samples than for the xerogel samples. Nevertheless, we observe a platinum loss for both series and the remaining metal percentage is lower for aerogels (50 % loss) than for xerogels (30 % loss). The sol-gel catalysts display very big Pt particles (>500 Å) due to sintering effects at the high treatment temperature, whereas the impregnated materials show smaller crystallites (40 to 100 Å). Figure 1 shows that all samples as well as the supports alone decrease the decomposition temperature of the HAN solution and thus present a catalytic effect. The catalysts prepared by impregnation lead to lower decomposition temperature than the sol-gel samples. Moreover the aerogel materials are less efficient than the xerogel samples, in relation with their different insulating properties.

![Figure 1. Decomposition temperature of 79 wt-% HAN-water mixture and BET values (m²/g).](image)

The results presented here have shown that the drying technique and the platinum introduction mode display an important influence on the properties and activity of platinum supported catalysts. The Pt/Al₂O₃Si samples prepared by impregnation disclose the best activity.

**References**