Facile Catalytic Decomposition at Low Temperature of Energetic Ionic Liquid as Hydrazine Substitute

Laurence Courthéoux,[a] Dan Amariei,[a] Sylvie Rossignol*[a] and Charles Kappenstein[a]

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Platinum supported on doped alumina catalysts were prepared and evaluated for the decomposition of NH_3OHNO_3/water energetic liquid. Powdered and shaped catalysts remain active after 23 injections at 45 °C.

Energetic liquid compounds known as monopropellants are used for propulsion and gas generator purposes. For example, the orbit and attitude control of satellites is obtained through small thruster engines using the catalytic decomposition of hydrazine, N_2H_4, on supported iridium catalysts. The high toxicity of hydrazine induces high costs and its replacement by a less toxic propellant is of current interest.[1,2] The most currently proposed and studied hydrazine substitutes are energetic aqueous ionic liquids and a representative mixture contains hydroxylammonium nitrate (or $NH_3OH^+NO_3^-$, HAN) as oxidizer, water and a fuel.[3–5] Nevertheless, the use of such mixtures involves more drastic conditions than for hydrazine, due to the high temperature reached during the decomposition (up to 1400 °C) and the need of frequent restarts that involve a preheating of the catalyst (300–400 °C). Therefore, a high catalytic activity at low temperature (20–200 °C) associated with a high thermal stability of shape formed catalysts remain critical parameters for the future development of new engines.

Previous studies performed by our group have revealed that platinum supported on thermally stable Si-doped alumina displays a good activity at low temperatures[6,7] The powder or shaped Si-doped alumina (xerogel) are obtained by sol-gel procedure and were demonstrated to be stable at high temperature (1200 °C, 5 h);[8] the metallic phase (10 wt.-% Pt) is added by the wet impregnation procedure. These catalysts have been evaluated for the decomposition of HAN/water solutions in a lab-made constant volume batch reactor,[9] and lead to decomposition at very low temperatures, less than 60 °C,[10] whereas the thermal decomposition temperature is in the range 115–120 °C.[4] Another key point concerns the long-term stability of the catalysts, particularly in the presence of a large amount of propellant. In this paper, we present the activity of powdered and shaped (spheres) catalysts for successive HAN/water injections. These successive injections were carried out to simulate the pulse mode of the satellite thrusters. The catalysts (160 mg) are preheated at 45 °C during 1 h, then 100 μL (150 mg) of a binary 79 wt.-% HAN/water mixture (i.e. 1.23 mmol) was injected manually 23 times, using a syringe, in the constant volume reactor (167 cm^3). Each injection is made after the thermal re-equilibration (approximately 4 min); the number of injections is limited by the pressure gauge and by the size of the sample holder.

The evolution of pressure and temperature (catalyst and gas phase) as a function of time during the successive injections using the sphere-shaped catalyst are represented in part a of Figure 1. Each peak corresponds to the decomposition following the injection, with an ignition delay of about 0.5 s; the catalysts are still active after all the injections. The decomposition reaction can form the thermodynamic products N_2, O_2 and H_2O [Equation (1)] or give additional kinetic products, in the form of nitrogen oxides [i.e. Equation (2)]. The calculated values of pressure increase (gas phase temperature: 25 °C) using the perfect gas formula are 365 mbar and 91 mbar, respectively, for a reaction giving thermodynamic [Equation (1)] and kinetic [Equation (2)] products.[11]

$$NH_2OHNO_3(aq) \rightarrow N_2(g) + O_2(g) + 2\ H_2O(l) \qquad (1)$$

$$NH_3OHNO_3(aq) \rightarrow NO_2(g\text{ or }aq) + 0.5\ N_2(g) + 2\ H_2O(l) \qquad (2)$$

Moreover, in both cases, the reaction produces water, which stay for the main part in the sample holder. An enlargement of a catalytic decomposition peak is given in Figure 1b; for each peak, the pressure increase (ΔP) due to the formation of gaseous products[10] and the rate of the decomposition (slope: $\Delta P/\Delta t$ in $mbar \cdot s^{-1}$) between the points 1 and 2 are determined. The catalyst temperature-

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[a] Laboratoire de Catalyse par les Métaux, University of Poitiers, LACCO UMR 6503,
40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France
Fax: +33-5-49454157
E-mail: sylvie.rossignol@univ-poitiers.fr

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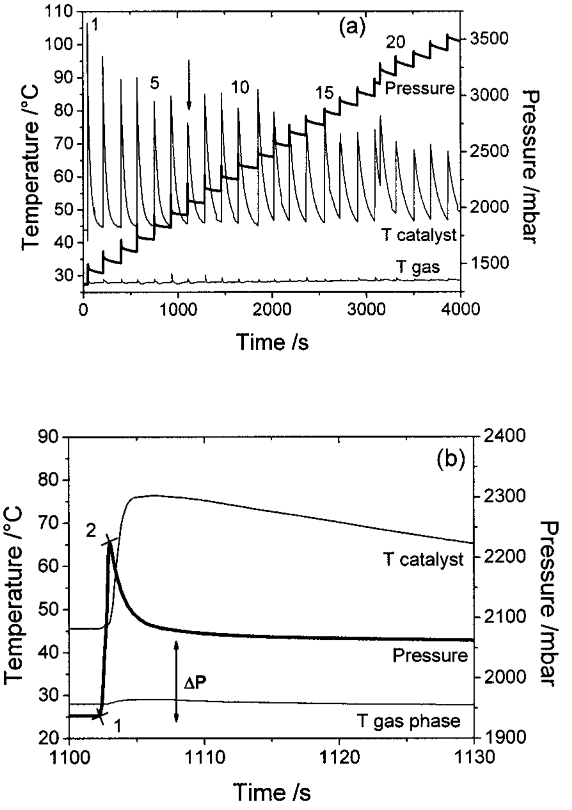

Figure 1. (a) Catalytic decomposition of 79 wt.-% HAN/H_2O at 45 °C with the sphere-shaped sample (23 injections) and (b) enlargement of one decomposition peak (see arrow, part a): Determination of pressure increase and the slope between points 1 and 2.

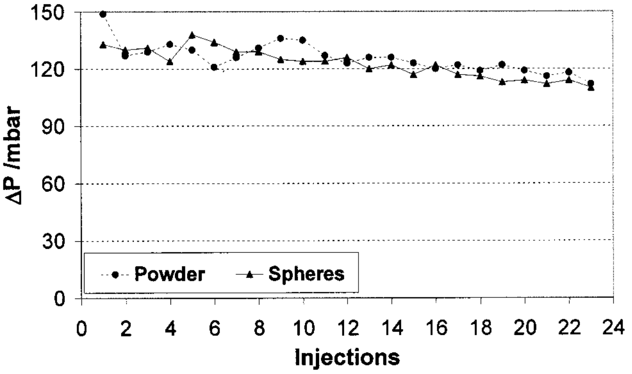

Figure 2. Evolution of pressure increase (ΔP) values during the 23 successive injections of 79 wt.-% HAN/H_2O at 45 °C on both catalysts.

decrease is due to the heat transfer to the reactor; the progressive reduction of the temperature maxima (106 to 70 °C; Figure 1a) is related to the increasing amount of water in the sample holder. The pressure increase (ΔP) variations of the two catalysts are similar, as shown in Figure 2. The values gradually decrease from 140 mbar at the beginning, to 110 mbar at the end of the 23 injections, corresponding to 0.94 and 0.74 mmol of gaseous product formed during the decomposition reaction. This decrease can be explained by a small deactivation of the catalyst related to the increasing amount of water in the sample holder. The pressure-increase values for both samples are close to the kinetic value (91 mbar), indicating the formation of nitrogen oxides. Other experiments carried out in a dynamic reactor with on-line MS analysis are in progress in order to determine the gas phase composition during the decomposition reaction. The first results show the formation of kinetics products, such as NO, NO_2 and lower amounts of N_2O.[12]

The evolution of the decomposition rate (measured by the $\Delta P/\Delta t$ slope) during the 23 successive injections on both catalysts is given in Figure 3. Whatever the catalyst, an increase of the reaction rate is evidenced until the seventh injection to reach 434 mbar·s^{-1} for the sphere-shaped sample and 323 mbar·s^{-1} for the powder, indicating a fast reaction rate. Then, the slope values oscillate between 200 and 400 mbar·s^{-1}. The nonreproducible oscillations are due to the manual injection procedure. An automatic injection system using a microburette failed for this pulse injection mode. These results show the very good efficiency of both catalysts and the noninhibiting effect of the shaping. Nevertheless, mechanical breaking of the spheres has been observed during the reaction probably due to the strong exothermic decomposition of the HAN/H_2O solution. This mechanical breaking could be avoided by a preheating at 100 °C.

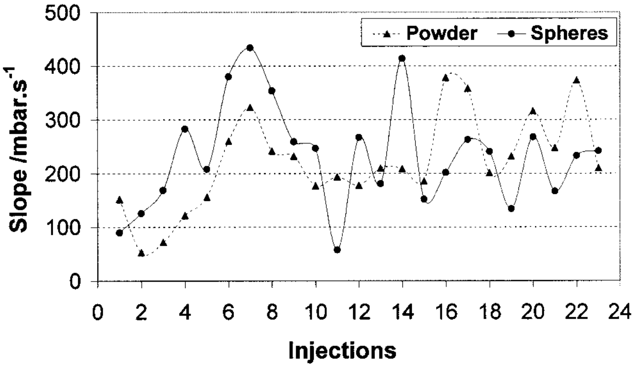

Figure 3. Evolution of $\Delta P/\Delta t$ slopes during the successive injections of HAN/H_2O at 45 °C on the powder and sphere-shaped catalysts.

All these experiments display the very good activity and stability of our catalysts. Indeed they allowed the efficient decomposition of the HAN/water solution at low temperature (45 °C) even in presence of a large amount of solution. Moreover, these materials remain active, showing a high reaction rate and an important pressure increase, after 23 monopropellant injections which remains a challenge for the development of new satellites thrusters. Nevertheless, the breaking of the sphere implies to find a more mechanically stable shaped catalyst support.

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