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CATALYTIC DECOMPOSITION OF HAN-WATER BINARY MIXTURES

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ABSTRACT

Binary aqueous HAN (hydroxylammonium nitrate NH_3OHNO_3) of different concentrations (20, 60, 83 wt-%) have been thermally and catalytically decomposed. The catalysts were prepared by impregnation of pure or doped supports (alumina, zirconia, barium, magnesium or zirconium aluminate) with monometallic or bimetallic active phases (noble and non-noble metals). The evaluation of the catalysts was carried out using a thermal analysis apparatus and a batch constant volume reactor.

The thermal decomposition starts only when the water has been quantitatively removed and the onset temperature was 115 °C for the 83 % solution using the batch reactor. In the presence of a support alone, a catalytic effect is evidenced for the alumina and silica-doped alumina by a decrease of the decomposition temperature, due to the acidity of the surface; on the other hand, doping with barium leads to an inhibiting effect. The presence of an adequate active phase leads to a further drop of the onset temperature (< 40 °C), disclosing that the decomposition can be triggered at low temperature in the presence of water; the rate is one order of magnitude higher by comparison with the thermal decomposition. The evaluation of other active phases leads to various results; iridium supported on alumina displays a fair activity.

INTRODUCTION

In previous papers concerning the possible replacement of hydrazine by HAN (hydroxylammonium nitrate NH_3OHNO_3) based aqueous monopropellants, we have presented the design and use of a very versatile laboratory batch reactor,^{1,2} as well as the preliminary results on HAN-TEAN-water mixtures (TEAN = triethanolammonium nitrate $\text{NH}(\text{C}_2\text{H}_4\text{OH})_3\text{NO}_3$). A comparison of this ternary mixture with the more simple HAN-water binary mixture (i.e. without a fuel) has revealed similar catalytic decomposition kinetics at low temperature (50-250 °C range), despite the very different energetic content of both mixtures,³ meaning that the first decomposition steps are the same for both samples as it was already stated by Klein et Leveritt:⁴ the early reactions for the HAN-TEAN-water blends involve only HAN decomposition and the reaction initiation takes place at 120°C.

Figure 1 presents typical results obtained in batch reactor, after an injection of 50 μL of the ternary or binary mixtures onto 200 mg of the same catalyst at 130 °C. The HAN-water solution (83 wt-% HAN) displays a higher pressure slope than the ternary mixture (also called LGP 1846). Moreover, the reproducibility of the experiments is better for the binary solution and the pressure remains constant whereas it continues to increase slowly for the LGP sample. Therefore, we focused mainly on the potential reactivity of HAN-water binary mixtures in order to obtain more information regarding the first decomposition steps and the associate catalysts. The preliminary results obtained with this binary monopropellant on different catalytic formulations

and for different HAN concentrations are presented in this paper.

LITERATURE DATA

Phase diagram of HAN-water mixtures

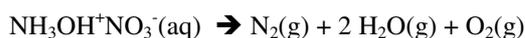
The binary phase diagram HAN-H₂O has been recently presented and discussed⁵ and is given in Figure 2, on mass fraction and mole fraction scales. Most of the solutions gave amorphous glassy mixtures when cooled up to -100 °C.^{6,7} The experimental data concern mainly the ice liquidus and the HAN liquidus has been calculated from the melting temperature of pure HAN (48 °C) and the coordinates of the eutectic point (73 wt-%, -39 °C). The HAN liquidus gives directly the variation of solubility with temperature, in agreement with literature data:

Temp. /°C	-20	0	10	20	30	40
Solub. wt-%	81.5	85.3	91.6	94	97	98.5

The high solubility of HAN in water is due to the low melting point and to the possibility to build a network of hydrogen bonds between the water molecules and the NH₃OH⁺ and NO₃⁻ ions. The concentrated solutions display the characteristic behavior of molten salts at low temperatures.

Energetic content of HAN-water mixtures

The full decomposition is given by the following equation:



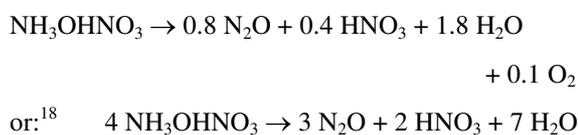
The adiabatic temperature of decomposition T_{adia} and the maximum specific impulse I_{sp} can be used to evaluate the energetic content of such mixtures; the variation of these parameters versus the composition is given in Figure 3.³ They are roughly comparable to the corresponding values of H₂O₂ and for a solution with a concentration of 80 % (i.e. the same concentration as for the HAN-TEAN-water mixture) the values are: $T_{\text{adia}} = 420$ °C and $I_{\text{sp}} = 153$ s. The densities are also comparable (1.51 to 1.65 g.mL⁻¹ at 20 °C for HAN solutions between 80 and 90 wt-%).

Thermal decomposition of aqueous HAN

Most of the published data concern thermal decomposition,⁸ combustion⁹ or catalytic decomposition^{10,11,12} of ternary mixtures including different fuels. The thermal decomposition of aqueous HAN solutions of different concentrations has been

followed in different conditions. Cronin and Brill^{13,14} have studied the thermolysis of concentrated solutions (12 mol.L⁻¹ to pure HAN) at different initial pressures; the early step is the proton transfer between the cation and the anion, leading to the formation of gaseous nitric acid HNO₃ and then to the formation of N₂O and NO₂. The proton transfer was also proposed by other authors as the first step of the decomposition.^{4,15}

The formation of nitrous oxide N₂O was also evidenced by Van Dijk and Priest¹⁶ using 11 mol.L⁻¹ HAN and Raman spectroscopy at low temperature (22-120 °C) but under high pressure ((2 to 7 kbar), or by FT-IR.¹⁵ In the case of diluted solutions (0.1 to 1.7 mol.L⁻¹) and under pressure (275 bar), N₂O is the only nitrogen-containing gaseous product and the following equations have been proposed on the basis of experiments using a flow reactor:¹⁷



In the case of concentrated solutions, N₂ is formed beside N₂O whereas both NO and NO₂ appear as reaction products only late in the reaction sequence;⁴ the HAN decomposition is not pressure dependent in liquid phase. The induction time was determined for 81 % HAN (13 mol.L⁻¹) at 130 °C (1.8 s) and at 160 °C (1.2 s);¹⁵ at slow heating rate, the decomposition of HAN is known to be catalyzed by Fe and Cu. Electric discharge initiation was also used for solution from 3 to 13 mol.L⁻¹, under pressure between 227 and 397 °C.¹⁹

EXPERIMENTAL PART

HAN-water solutions

Four concentrations have been used:

20 wt-%, prepared by the SNPE (Société Nationale des Poudres et Explosifs, France);

60 wt-% prepared in laboratory, by neutralization of aqueous hydroxylamine (Aldrich, 50 wt-%) by aqueous nitric acid (Aldrich, 67 wt-%) at low temperature;

79 wt-%, prepared by concentration of the previous solution in a rotating evaporator;

83 wt-%, prepared at the University of Lyon, France.

Catalysts

More than 60 samples have been prepared using various pure or doped supports (alumina, zirconia, barium, magnesium or zirconium aluminate), various monometallic and bimetallic active phases from noble and non-noble metals, using different concentrations and various preparation procedures. They have been characterized by the following methods: X-ray diffraction, specific surface area, specific metallic area, and transmission electron microscopy with EDX elemental analysis.

Reactors

The decomposition reaction has been followed using two reactors:

(i) constant volume batch reactor already described.¹ The monopropellant (50 μL) is added to the catalyst (100-200 mg) at room temperature with a micro-syringe through a septum, and then heated with a ramp of 4 to 10 $\text{K}\cdot\text{min}^{-1}$. The pressure and temperature (catalyst and gas phase) are recorded versus time.

(ii) thermal analysis apparatus (TA instrument): 15 to 40 mg of catalyst are put in a quartz or aluminum crucible. 10 μL of monopropellant are added at room temperature and covered by glass wool. The oven is closed and flushed with an argon flow during approximately 30 min at 20 $^{\circ}\text{C}$. Then the heating begins with a slope of 10 $\text{K}\cdot\text{min}^{-1}$. The mass and temperature of the sample are recorded.

RESULTS AND DISCUSSION

Thermal decomposition

The thermal decomposition has been followed by thermal analysis of 50 μL for three concentrations (20, 60 and 83 %) and Figures 4A and 4B display the results. For 20 % HAN, the first weight loss corresponds to an isothermal plateau at 60 $^{\circ}\text{C}$ during 30 min.

Despite the high concentration range, the three solutions show the same thermal behavior (Fig. 4B): first an endothermic peak corresponds to the evaporation of water under the argon flow, resulting in a concentration of the solution; this endothermic event is followed by the exothermic decomposition of HAN leading to the complete transformation of the propellant into gaseous products. The decomposition temperatures are respectively: 135 $^{\circ}\text{C}$ (83 %), 173 $^{\circ}\text{C}$ (60 %) and 170 $^{\circ}\text{C}$ (20 %). The surface area of the endotherm follows the water content, whereas the

reverse is observed for the exotherm: the surface area depends on the amount of HAN.

The decomposition starts only when the water has been quantitatively removed (marked by the arrow on Figure 4A), leading to almost pure liquid HAN (melting temperature 48 $^{\circ}\text{C}$). Therefore the time needed for the decomposition depends strongly of the initial concentration, the initial mass of the propellant, the gas flow rate and the dimensions of the crucible. For these conditions, the recorded temperature (measured under the crucible) can be higher than the real temperature inside the propellant, due to the strong endothermic nature of the water evaporation.

From these results, we can conclude that water exhibits, as expected, a stabilizing effect on HAN which is the consequence of the dispersion of the ions. Therefore, the ions must be in contact for the decomposition to occur.

Catalytic decomposition: thermal analysis

As an example, Figure 5 shows the onset temperature for the decomposition of HAN-water propellant (83 wt-%) on 4 supports and their corresponding specific surface areas. It must be quoted that all the supports were stabilized at high temperature (1200 $^{\circ}\text{C}$, 5 h) before use, in order to take into account the real operating conditions: the presence of a fuel will increase notably the final adiabatic temperature.

Two supports Al_2O_3 and $\text{Al}_2\text{O}_3\text{Si}$ display an obvious catalytic effect (T_{onset} lower than the corresponding thermal value) and this effect is probably due to the presence of acid sites on their surfaces. On the contrary, the support $\text{Al}_2\text{O}_3\text{Ba}$ exhibits a dramatic inhibitor effect on the HAN decomposition and this peculiarity has been recently explained by the formation of barium nitrate $\text{Ba}(\text{NO}_3)_2$ inside the porosity of the support.²⁰ The last support $\text{Al}_2\text{O}_3\text{Pr}$ shows very weak catalytic properties. Another important point concerns the values of the S_{BET} surface area, which display no correlation with the catalytic activity.

The introduction of an active phase inside the porosity of the support leads to a further decrease of the onset temperature of decomposition and thus improves the catalytic activity. Figures 6 and 7 present representative results obtained on two non-noble metals supported on alumina. The thermal analysis (TGA and DTA) is given versus time. In the case of Figure 6, we can observe two endothermic peaks (A and B) followed by a strong exothermic decomposition (C) at 84 $^{\circ}\text{C}$. The weight loss is very rapid and corresponds to the whole decomposition

into gaseous products. On the contrary, Figure 7 shows a different behavior: the decomposition starts at 67 °C, i.e. at a lower temperature, but the weight loss is only partial. Two large exothermic peaks are present at 94 and 277 °C (C and E); they correspond to slow weight loss steps showing that the decomposition reaction needs a higher temperature to be completed.

Another interesting sample is the classical iridium supported on alumina used for the hydrazine decomposition (36 wt-% Ir/Al₂O₃) reported on Figure 8. The decomposition starts only at 98 °C and displays two exothermic peaks at 100 and 145 °C. It is completed at 300 °C, showing that this catalyst is not the best suited at low temperatures.

Catalytic decomposition: batch reactor

Figure 9 shows a comparison between thermal and catalytic decomposition using the batch reactor in the increase temperature procedure. For this experiment, the onset temperature for the thermal decomposition is 115 °C and the pressure slope is very low (2.1 mbar.s⁻¹). In the presence of a noble metal catalyst, the onset temperature is lowered to 42 °C (Figure 9B) proving that the decomposition can be well triggered in the presence of water. Moreover the decomposition rate (represented by the pressure slope) is more than one order of magnitude higher in the presence of the catalyst (28 mbar.s⁻¹).

The influence of the concentration of HAN solutions is given on Figure 10 using the increase temperature procedure (injection of 50 µL). The trigger of the decomposition is much lower by comparison with the thermal decomposition: 45 °C (83 %), 77 °C (60 %) and 83 °C (20 %). Therefore, the catalyst is able to start the decomposition in the presence of water, even for the more diluted solution. We can observe a similar behavior for the solutions containing 20 and 60 wt-% of HAN, in agreement with the thermal analysis results (Figure 4 and 5). The pressure increase during the decomposition depends mainly on the amount of HAN introduced in the reactor.

CONCLUSIONS

In this paper we have presented the first results concerning the catalytic decomposition of binary HAN-water solutions of various concentrations. The use of adequate catalysts can decrease the decomposition temperature from 115 °C to less than 40 °C, thus proving that the HAN decomposition can occur at very low temperatures, in the presence of water and in the absence of any fuel. Moreover the

catalytic decomposition rate is one order of magnitude higher by comparison with the thermal decomposition. Future works will focus on the following topics:

- formation of nitrogen oxides as kinetic products, and the influence of the reaction conditions and the catalyst;
- determination of the minimal concentration of HAN for a catalytic decomposition;
- research for a fuel which does not inhibit the HAN decomposition at low temperature..

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Tables and Figures

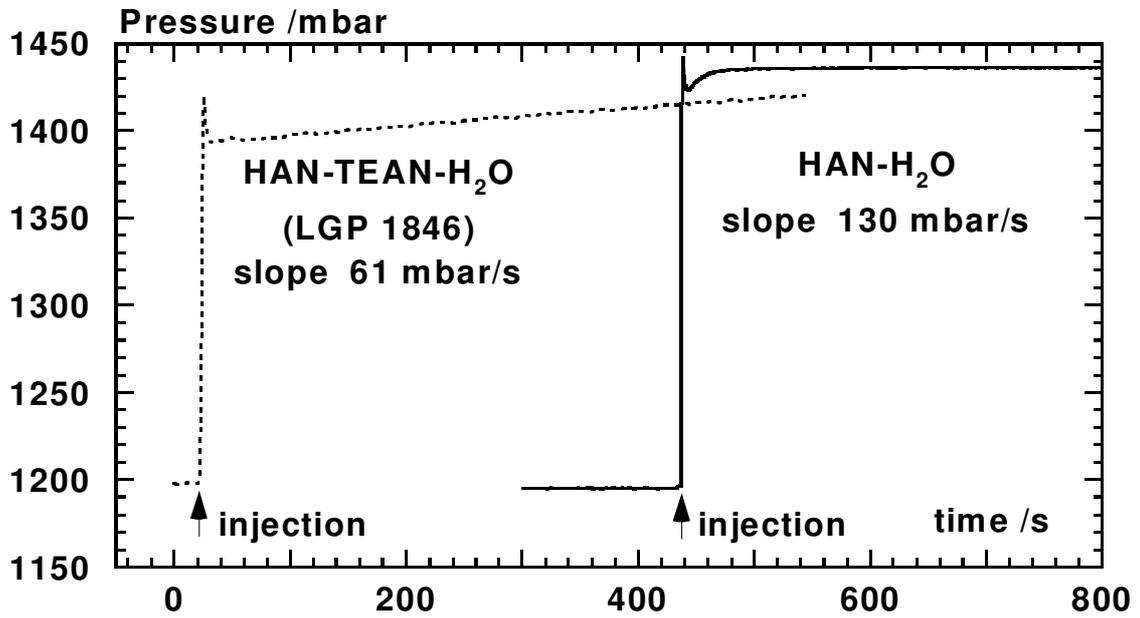


Figure 1. Pressure increase during the catalytic decomposition of ternary HAN-TEAN-H₂O (61 % HAN + 19 % TEAN) and binary HAN-H₂O (83 % HAN) monopropellants at 130 °C on the same catalyst.

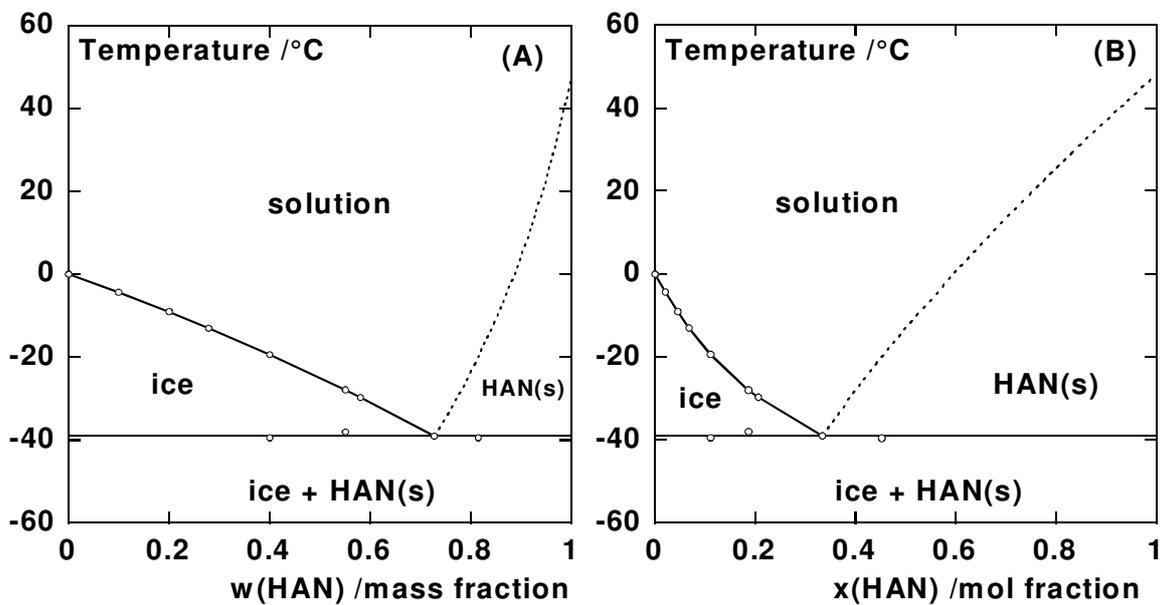


Figure 2. Phase diagram for HAN-H₂O binary system. (A) Mass fraction scale; (B) mol fraction scale.

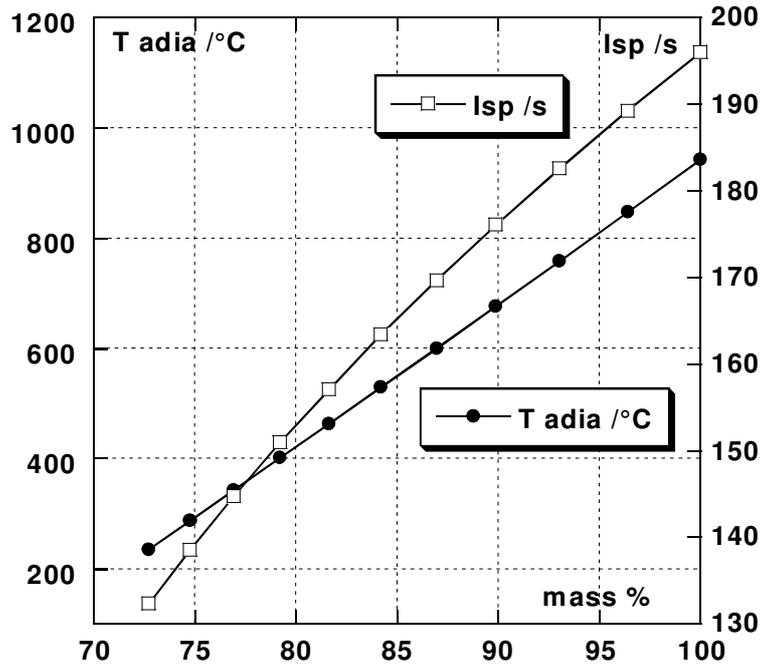


Figure 3. Adiabatic temperature and vacuum specific impulse versus concentration for HAN-water mixtures. The values of the heat capacities are taken at 1200 K.

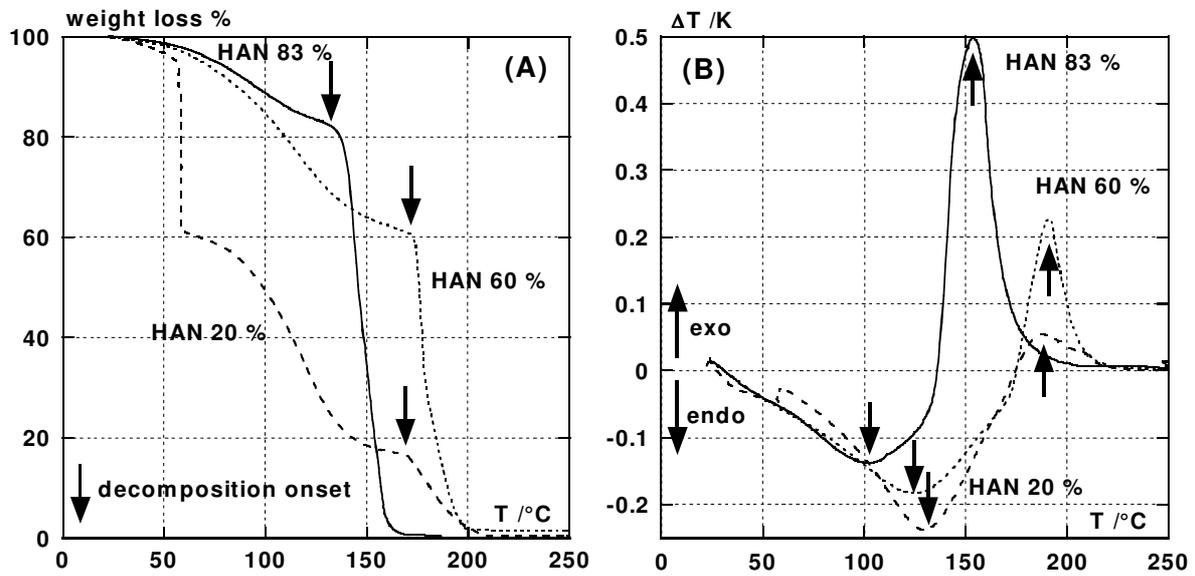


Figure 4. Thermogravimetric analysis (A) and differential thermal analysis (B) of thermal decomposition of different HAN-water mixtures.

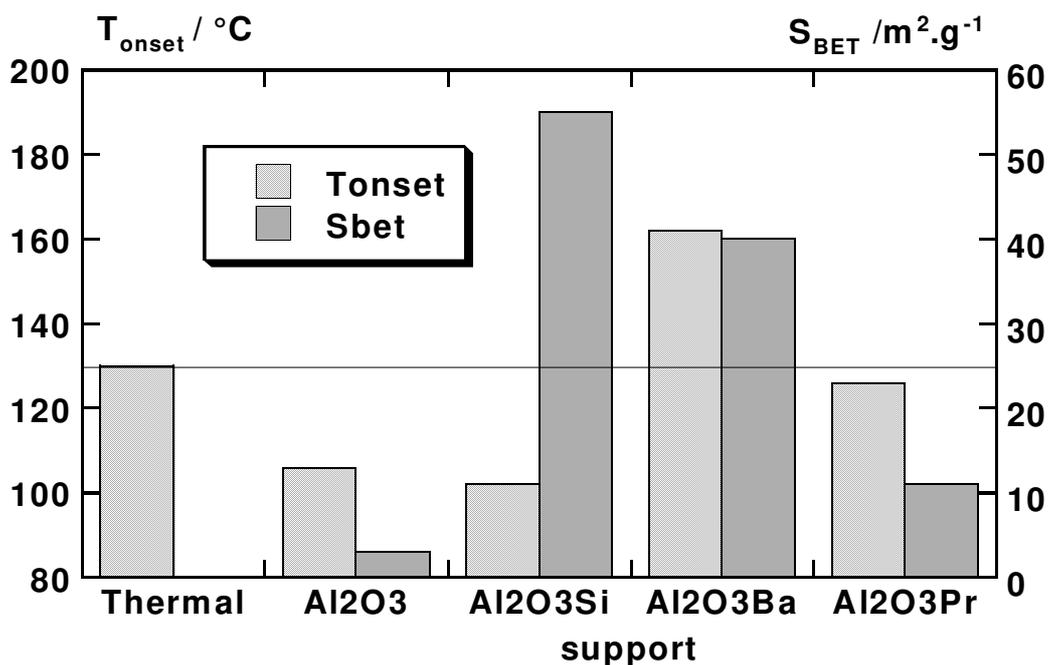


Figure 5. Onset temperature for the decomposition of 83 wt-% HAN on different supports and their BET surface area.

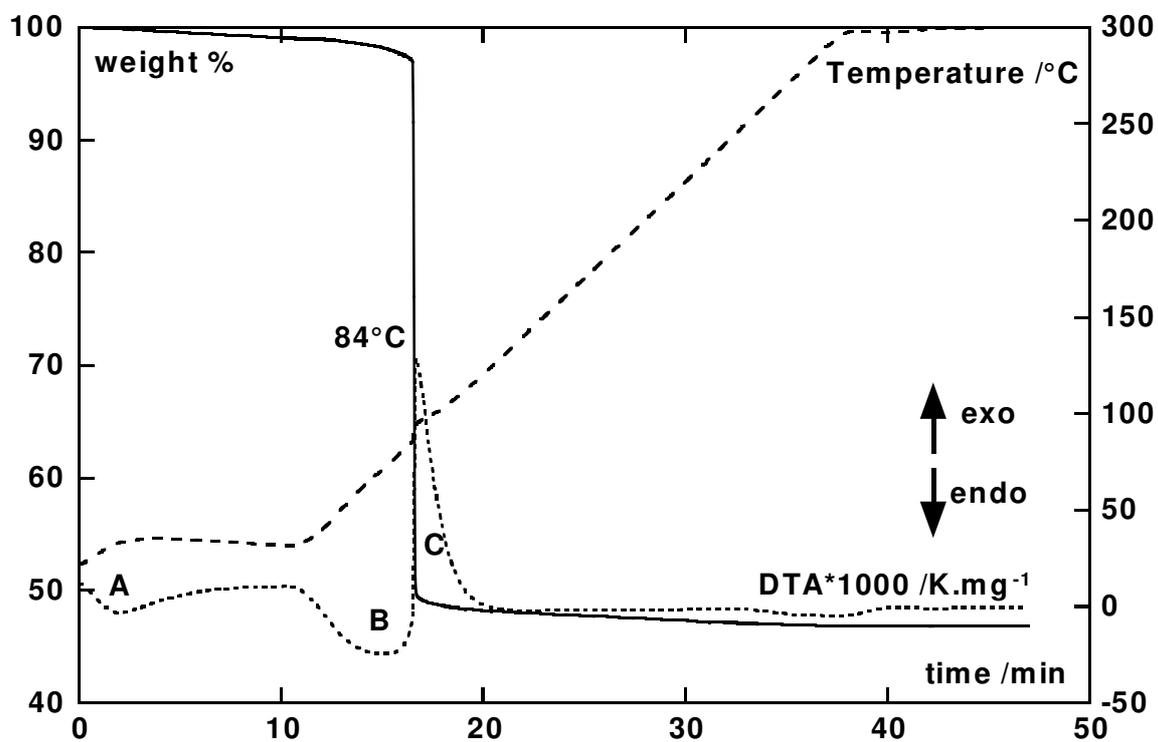


Figure 6. Decomposition of 83 % HAN on a non-noble metal supported on Al₂O₃.

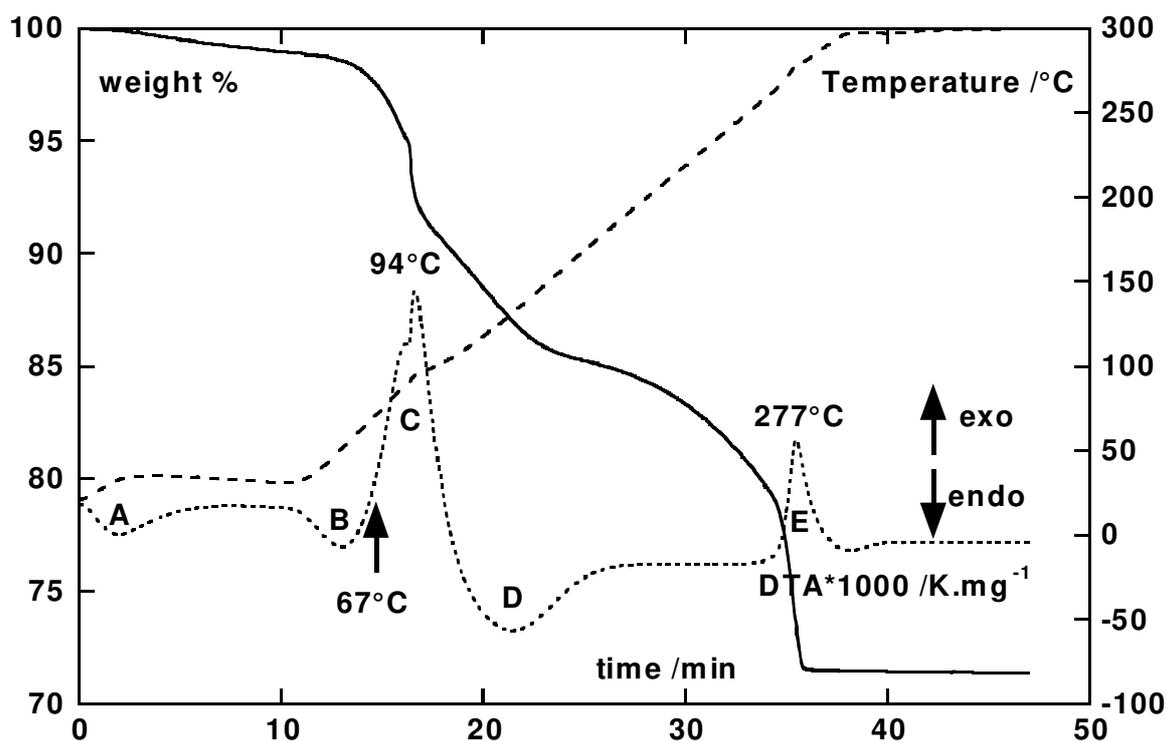


Figure 7. Decomposition of 83 % HAN on a non-noble metal supported on Al_2O_3 .

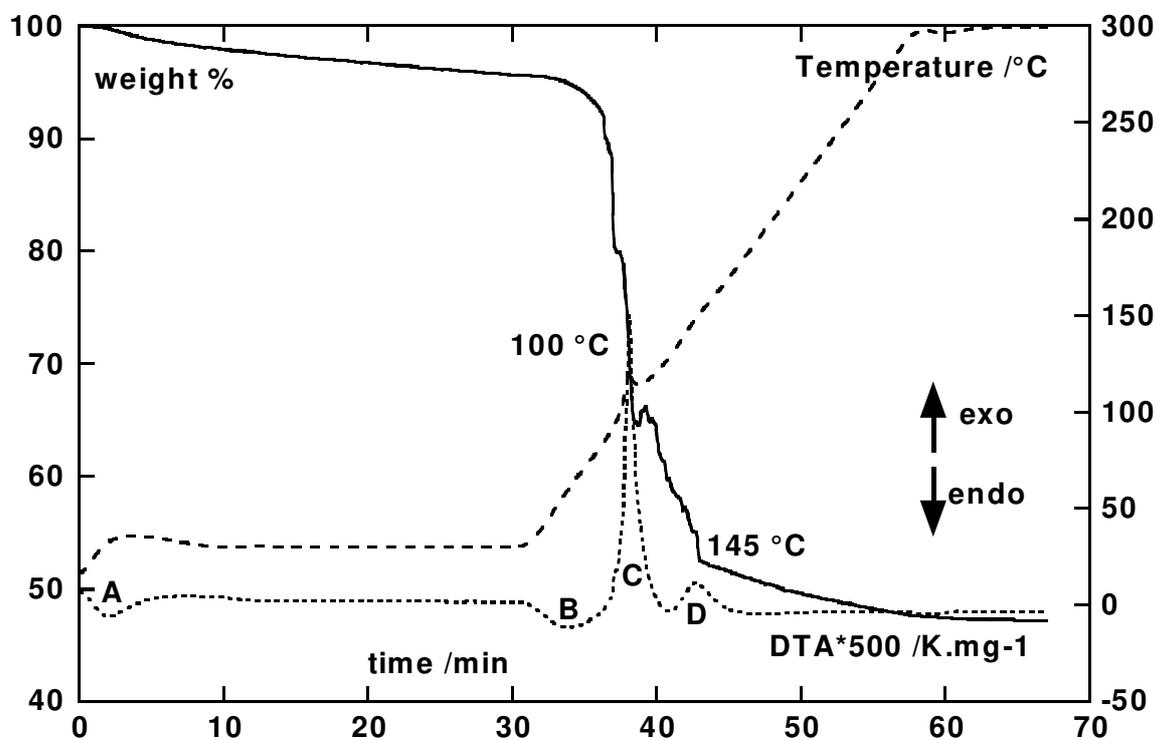


Figure 8. Decomposition of 83 % HAN on 36 wt-% Ir/ Al_2O_3 .

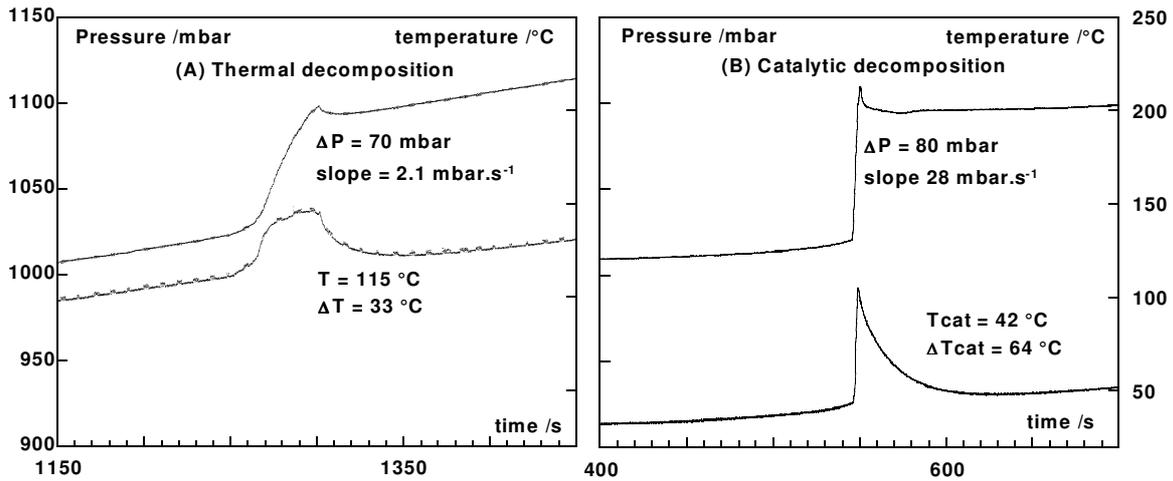


Figure 9. Thermal (A) and catalytic decomposition (B) of 83 wt-% HAN monopropellant on a supported noble metal catalyst. The scales are the same for both figures.

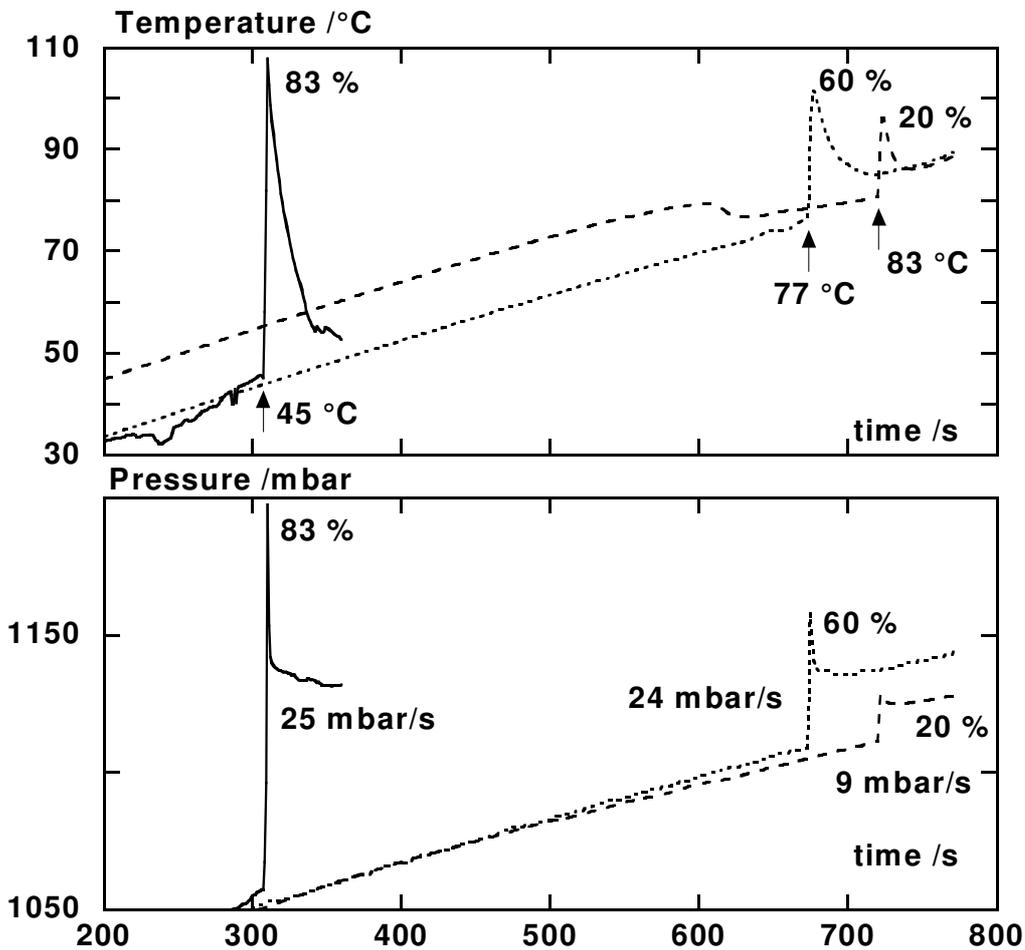


Figure 10. Influence of the concentration of HAN on the catalytic decomposition. Variation of catalyst temperature and gas pressure versus time.