Thermal Versus Catalytic Decomposition of Ammonium Nitrate

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Introduction

Environmental concerns associated with running cost reduction lead to the replacement of current hydrazine (monopropellant for satellite engine) and ammonium perchlorate (launcher booster). Hydroxylammonium nitrate NH\(\text{OHNO}_3\) (HAN), ammonium nitrate NH\(_4\)\(\text{NO}_3\) (AN) and ammonium dinitramide NH\(_2\text{N(NO}_2\)\(_2\) (ADN) are proposed as oxidizer candidates for energetic aqueous ionic liquids and for new solid propellants [1,2]. They have to be associated to efficient and stable catalysts, able to trigger the decomposition at low temperature and to form selectively the thermodynamic products [3]. Moreover, ammonium nitrate is an intermediate decomposition product of ADN and HAN [4]. We present here the first comparison of the decomposition of aqueous AN solution in thermal condition (without catalyst) and in the presence of various catalysts.

Materials and Methods

Solid AN was used to prepare aqueous solutions containing 50 to 55 wt.-% AN. Variousmono M/Al\(_2\text{O}_3\)-Si (M = Pt, Cu, Zn and Fe) and bimetallic catalysts M-M'/Al\(_2\text{O}_3\)-Si (M, M' = Fe, Cu, Zn, Pt) supported on silica-doped alumina were evaluated. The decomposition reaction was followed using a batch and a dynamic reactor; the solution is injected (typically 100 µL) in a helium flow into the preheated reactor (160 to 400 °C). The liquid products are condensed in a cold trap and analyzed by acid-base titration and Raman spectroscopy. The gas phase composition is obtained from an on-line MS apparatus. The results were supplemented by thermal analysis (TGA, DTA).

Results and Discussion

Heating in the absence of catalyst shows the endothermic vaporization of water, followed by vaporization of AN into ammonia and nitric acid; only traces of decomposition products have been evidenced. In the presence of catalysts, a dramatic change is observed. On monometallic catalysts M/Al\(_2\text{O}_3\)-Si, a true exothermic decomposition is observed and the Pt-based catalyst was able to trigger the decomposition at 210 °C. Nevertheless, tests in batch reactor, reveals mediocre results associated to very slow decomposition rates. For bimetallic catalysts M-M'/Al\(_2\text{O}_3\)-Si, the decomposition depends on the active phase and on the preparation method. The addition of zinc or copper precursors on non-reduced platinum catalyst (noted PtCuAl-NR and PtZnAl-NR) increases the catalytic effect of platinum with violent one-step decomposition. On the contrary, the addition of Zn or Cu precursors on reduced platinum metal (noted PtCuAl-R or PtZnAl-R) leads to less active catalysts and the decomposition occurs in two steps (Figure 1). This activity difference could be related to the formation zinc-platinum and copper-platinum alloys when adding the second metallic precursor on non-reduced platinum, followed by a final reduction, as evidenced by XRD (Figure 2). Whatever the catalyst, the AN decomposition leads to the same gaseous and condensed products: major nitrogen and nitric acid, whereas NO and N\(_2\text{O}\) amounts depend on the catalyst nature: minor for PtAl and medium for PtCuAl-NR and PtZnAl-NR.

References