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Catalytic Decomposition of Hydroxylammonium Nitrate Monopropellant

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Abstract. Hydroxylammonium Nitrate (HAN) is being investigated as a promising substitute to hydrazine monopropellants. HAN propellants are less toxic and insensitive compared to conventional monopropellants. With the right combination of fuel and an active catalyst, HAN can be effectively used in propulsion systems. The current study focuses on developing a supported metal catalyst for HAN decomposition. An iridium supported catalyst was developed and characterized. The developed catalyst was found to be remarkably active even at very low concentration of HAN in HAN-water solutions.

Keywords: Hydroxylammonium nitate, monopropellant, catalyst

1. Introduction

Monopropellants are used extensively in reaction control systems (RCS) of satellites for orbital correction and attitude control. These are chemicals when passed through a catalytic bed decompose exothermically and produce large volume of gaseous products which can be expanded through a nozzle to get desired thrust. Propellant feed and control-system simplicity are of primary concern while choosing a propellant system. It must be easily decomposed and reactive to give good combustion properties. Among many systems that have been tried and tested over the years, hydrazine has remained as the most preferred mono propellant for over five decades due to its versatility and dependability. It offers substantially improved specific impulse over cold gas, and hydrazine systems require far less complex hardware compared to bi-propellant systems. While hydrazine has a strong heritage as a versatile monopropellant, some of the inherent problems associated with hydrazine like toxicity, high vapor pressure and associated storage and handling cost have been a major concern. These concerns along with the search for better performing alternate propellant have spurred development, though at early stages, of a few green propellants which are both environmental friendly and high performing. Some of these choices include hydroxylammonium nitrate based propellant blends, hydrogen peroxide and hydrazine blends [1-9]. Hydrogen peroxide suffers from lack of storage stability and is detonable in high concentration. On the other hand, Hydroxylammonium Nitrate (HAN) is a promising candidate and scores over other monopropellants in terms of insensitivity, toxicity and volatility. Some of the projected advantages of HAN formulations over hydrazine include its lower crystallization point, higher density and volumetric impulse. HAN (NH_3 (OH) NO_3), a nitrate salt of hydroxylamine, is a stable material and easily soluble in water. It has a density of 1.83 g/cc and oxygen balance of 33.33%. HAN is also known to be an excellent insensitive liquid oxidizer in gun propellants. HAN and its aqueous blends with fuels like glycine, methanol etc. are now perceived as hydrazine substitutes. HAN monopropellants have demonstrated and delivered specific impulse of 270 sec in laboratory engines. Besides, HAN has been employed in applications such as gas generation and pressurization. It can be inferred that even monopropellants when used with the right combination of other

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fuel ingredients can offer performance as comparable to that of bipropellant systems but without the burden of massive turbo machinery. However, the success of the propulsion system depends on the efficiency of the catalyst, especially for HAN systems which necessitate higher temperatures for the catalyst bed to ensure instant decomposition.

There are numerous studies in the past 10 years on the development of supported metal catalysts for HAN decomposition [10-11]. Many of these studies are extension of hydrazine decomposition studies as most of the catalysts that decompose hydrazine were found to be equally active in decomposing HAN. The present work was initiated with the objective of developing a supported metal catalyst for HAN decomposition. Iridium being one of the reportedly actively metal, initial studies were performed with iridium on γ-Alumina support. The supported catalyst was prepared by wet impregnation technique and characterized by various analytical techniques. The conditions for the metal loading were methodically evaluated by examining the catalyst at various stages involved in the preparation. The HAN monopropellant used for decomposition studies were prepared in-house [12].

2. Experimental

2.1. Materials

γ-Alumina pellets (Alfa Aesar; surface area: 220 m^2/g; pore volume: 0.62 cc/g), hexachloroiridic acid (Alfa Aesar; 38-42% *w/w* Ir), hydroxylammonium sulphate (S D Fine-Chem. Ltd.) and calcium nitrate (S D Fine-Chem. Ltd.) were all of analytical grade and used as received without further purification.

2.2. Preparation of HAN

HAN was prepared in-house, adopting methods reported in the literature [12]. Since the preparatory route is reported to have influence in the final decomposition of the compound when brought in contact with the catalyst, two distinctly different preparatory routes were adopted and examined separately for their activity to the prepared catalyst. In the first route HAN was prepared via a double decomposition reaction between hydroxylammonium sulphate (HAS) and calcium nitrate. In the second route reaction between hydroxyl amine and nitric acid was used to prepare HAN. Both the preparatory routes were in aqueous medium and the resulting solution was HAN-water blend which was later either concentrated or diluted according to the initial concentration obtained. The amount of HAN was estimated by following the density of the solution. Alternatively, thermogravimetric studies carried out to examine the thermal stability, also gave information on the weight percentage of HAN in HAN-water blends. Infrared and Raman spectroscopy were also adopted to extract the structural information of HAN [12].

2.3. Preparation and characterization of supported catalyst

Iridium supported on alumina was prepared by an incipient wet impregnation method. The γ-alumina pellets used as support were initially degassed in a vacuum oven at 120°C to clear the pores of adsorbed gases and vapors. The support was subsequently soaked in an aqueous solution of hexachloroiridic acid, the concentration of which was selected based on the pore volume of the support and the intended metal loading. The pellets, while being soaked, were also subjected to ultrasound in order to promote better penetration of the solution into the pores. The impregnated pellets were separated from the solution after 18 hrs of soaking and dried in air at 120°C for 20 hrs. After mild calcination in air at 400°C for 2 hrs, the pellets were reduced at 500°C in a flowing H_2-N_2 mixture for 16 hrs, to obtain the required supported catalyst. The pellets after each stage in the preparation was methodically characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) and Powder X-Ray Diffraction in order to extract information about the changes brought out at each stage and final active metal loading. The prepared catalyst was finally evaluated for its efficiency in decomposing hydroxylammonium nitrate in a thermal analyzer. The Thermo-Gravimetry (TG) experiments were carried out in a flowing N_2 atmosphere with a heating rate of 10°C/min.

3. Results and Discussion

3.1. Characterization of catalyst

The PXRD pattern obtained at various stages during the preparation of the catalyst is shown in Fig. 1. The peaks (2θ) at 40°, 47°, 69°, 83° and 88° from the X-Ray diffraction pattern confirm the presence of iridium on alumina. The EDX studies showed a metal loading of around 21% over alumina support. The EDX spectrum of the catalyst is shown in Fig. 2.

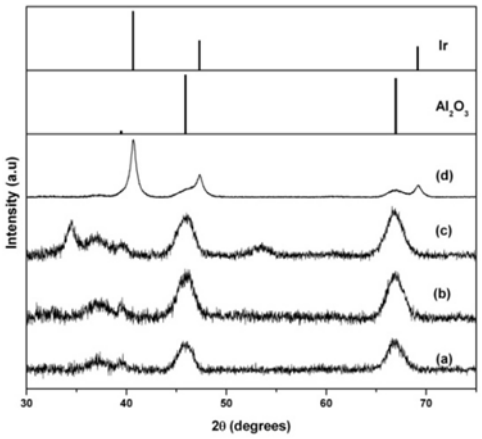

Fig.1: PXRD pattern during various stages of catalyst preparation: (a) fresh alumina, (b) impregnated alumina, (c) calcined alumina and (d) reduced alumina.

Some of the other observations made from the EDX spectrum and PXRD studies are utilized to optimize the conditions of the preparatory route. The calcinations procedure, a not so widely employed step in wet impregnation technique, ensured decomposition of most of the precursors used leaving substantial quantity of metal on the surface. The reduction condition employed in the present procedure was optimized after elemental analysis of catalyst samples using EDX at different reduction conditions. The final reaction condition for complete conversion of precursor to active metal was fixed at 500°C and 16 hrs in a flowing hydrogen-nitrogen mixture.

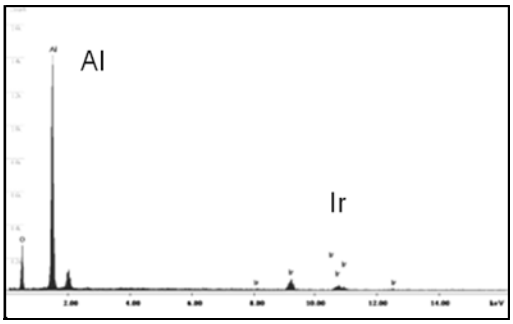

Fig. 2: EDX spectrum of iridium loaded on the γ-alumina support.

3.2. Evaluation of catalyst efficiency

The efficiency of the catalyst prepared was examined in a DTA-TG thermal analyzer. The temperature of decomposition of monopropellant and rate of weight loss during heating and decomposition were used to evaluate the thermal decomposition characteristics. A typical thermogravimetric curve for HAN-water and HAN-water-catalyst system is shown in Fig. 3. It can be seen that the thermal decomposition temperature of HAN-water is advanced significantly in the presence of catalyst. While the monopropellant decomposes at 128°C without a catalyst, presence of catalyst brought down the decomposition to less than 90°C. In some cases the decomposition was found to be taking place, instantly and also violently, at temperatures as low as 66°C. The other observations are significantly higher rate of reaction and shorter ignition delay. The implications of these observations are onboard power saving and smooth decomposition without any complications of hard start. The observations made in this study are similar to reported results in the literature [10-11]. However the catalyst prepared in the present study appears to show better catalytic

efficiency as can be seen from Fig. 4. The HAN-water blend containing HAN as low as 20% also could be decomposed with the prepared catalyst; and that too at a temperature less than 90^{o}C. In conclusion, the catalyst is active both at low temperatures and low concentrations of HAN. The other observation made in the present study was that the two monopropellant-water blends prepared differed in their catalytic decomposition behavior despite their chemical similarity. The HAN-water blend prepared by the second route demonstrated a better decomposition characteristic than the one prepared from hydroxylammonium sulfate and calcium nitrate. Rationalization for these observations demands a thorough assay examination of the monopropellant which is currently underway.

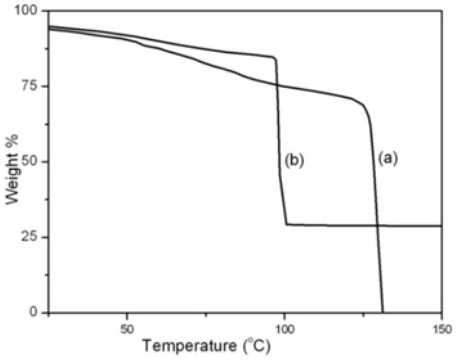

Fig. 3: Thermo-gravimetry (TG) curves for (a) HAN-water solution (74% w/w HAN) and (b) HAN-water solution with the prepared catalyst.

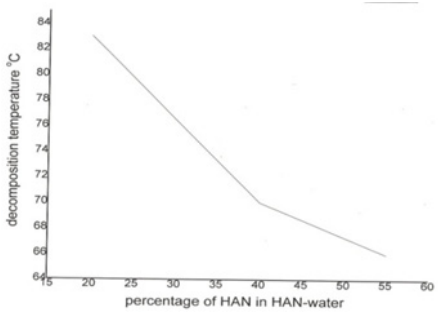

Fig.4. Variation of decomposition temperature with percentage of HAN in HAN-water

4. Conclusions

Hydroxylammonium nitrate (HAN) is being examined as a promising substitute to hydrazine monopropellants. In this context HAN-water solution and alumina supported iridium catalyst were prepared and characterized. The catalyst prepared was tested with the HAN-water solution and was found to be significantly active in decomposing the monopropellant at low temperatures. Decomposition of HAN-water systems at low temperatures by the prepared catalyst and notably high activity even with aqueous blends containing low weight percentage of HAN are the highpoints of this work.

5. Acknowledgements

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6. References

[1] E. J. Wucherer, B. Reed, *Assessment of High Performance HAN - Monopropellants*; 36th AIAA/ASME/SAE/ASEE Joint Propulsion Conference; AIAA 2000; 3872-3882.

[2] L. Courthéoux, R. Eloirdi, S. Rossignol, C. Kappenstein and D. Duprez**,** *Catalytic decomposition of HAN-Water binary mixtures*; 38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; AIAA 2002;1027-1037.

[3] H. Meng, P.Khare, Grant A. Risha, Richard A. Yetter§ and V. Yang**,** *Decomposition and Ignition of HAN-Based Monopropellants by Electrolysis*; AIAA 2009; 451-467.

[4] D.Meinhardt, G. Brewster**,** S. Christofferson, E. J. Wucherer, Development and Testing of New, HAN-based Monopropellants in Small Rocket Thrusters; AIAA 98; 4006-4016.

[5] Dieter M. Zube**,** E. J. Wucherer, B.Reed *Evaluation of HAN-Based Propellant Blends***;** 39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit; AIAA 2003; 4643-4655.

[6] D. Mittendorf, William A. Facinelli, Richard F. Sarpolus Experimental Development of a Monopropellant for Space Propulsion Systems; AIAA 1997; 1-9.

[7] Robert S. Jankovsky**,** Steven R. Oleson, *HAN-Based Monopropellant Propulsion system with Applications*-NASA Technical Memorandum 107407.

[8] A. J. Fortini and J. R. Babcock, High Temperature Catalyst Beds for Advanced Monopropellants; AIAA 2001; 3393-3398.

[9] Olwen M. Morgan, D. Meinhardt Monopropellant Selection Criteria-Hydrazine and other options; AIAA 99; 2595-2604.

[10] L. Courthe´oux, D. Amariei, S. Rossignol, C. Kappenstein**,** *Thermal and catalytic decomposition of HNF and HAN liquid ionic as propellants*; Applied Catalysis B: Environmental 2006; 62; 217–225.

[11] R. Xiaoguang, L. Minghui, W. Aiqin, L. Lin, W. Xiaodong, Z. Tao. *Catalytic Decomposition of Hydroxyl Ammonium Nitrate at Room Temperature;* Chinese Journal of Catalysis, 2007, 28(1); 1–2.

[12] Charlie Oommen, Santhosh Rajaraman, R Arun Chandru and R Rajeev, *Development and characterization of catalyst for HAN monopropellant.* Proceedings of the 27th Annual In-house symposium on Space Technology, IISc, Bangalore (2011) pp. 91-96.