Understanding Exothermic Catalytic Decomposition of Ionic Liquids Under Anaerobic Conditions: New Structure Functionality Relationships

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Abstract: An efficient heterogeneous catalytic architecture in the form of Ir/La_2O_3/CeO_2/Al_2O_3 is presented for the exothermic decomposition ammonium dinitriamide-based ionic liquid propellants. Novel structure-functionality relationships were established relating the nature of the catalytic subcomponents with activity parameters such as the on-set temperature and reaction enthalpy.

Keywords: Ionic Liquid, Propellant, ADN, Iridium Catalyst

1. Introduction

Propellants are highly energetic chemicals widely used in spacecraft propulsion. They can go through combustion or decomposition reactions producing large amount of heat and gaseous products that can be used for propulsion processes in aviation and space applications such as satellite maneuvering in the orbit [1]. Hydrazine (N_2H_4) is the most commonly used propellant for such applications. However, utilization of hydrazine in space missions has potentially negative ramifications associated with health, environment and safety risks. As a result, environmentally friendly, safer and less toxic alternative propellants have attracted a great interest in the recent years. Ionic liquids such as ADN (ammonium dinitramide) present itself as a promising alternative fuel to hydrazine [1,2]. ADN can readily undergo exothermic decomposition/combustion reactions with the help of a proper heterogeneous catalyst. Catalytic technologies developed for spacecraft propulsion systems should be resilient to high temperatures and should also be stable enough to be used in many consecutive cycles without a significant loss of activity [3,4]. The conventional catalyst used for this purpose is Ir/Al_2O_3. One of the major drawbacks of this catalytic system is the thermal aging associated with the sintering of precious metal and increase in particle size of the active Ir nanoparticles at elevated temperatures. In the current contribution, a systematic synthetic approach is presented, where metal oxide promoters such as La_2O_3 and/or CeO_2 are used in order to enhance dispersion of active sites, limit Ir surface diffusion and facilitate the exothermic catalytic decomposition of ADN in the absence of O_2. Our results reveal valuable structure-functionality relationships shedding light on the molecular level mechanisms governing exothermic decomposition of ionic liquids on heterogeneous catalyst surfaces.

2. Experimental

Iridium based catalysts with varying Ir, La_2O_3 and CeO_2 loadings and calcination temperatures were synthesized by using a conventional wet impregnation method. Detailed structural characterization of the catalysts were also performed by means of Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), Raman spectroscopy, Transmission Electron Microscopy (TEM) and BET specific surface area analysis.

3. Results and Discussion

TGA/DSC results of ADN decomposition over 22 different catalysts are shown in Figure 1. In the histogram, the onset temperatures and the energy released after the decomposition of ADN are presented. Onset temperature of ADN decomposition can be reduced to lower values in the presence of a catalyst. Among these catalysts, the lowest onset temperature, 138^0C, belongs to $10Ir/20La_2O_3/Al_2O_3 900^0$C. When the energy released during the decomposition of ionic liquid is compared for different catalysts, the highest amount of energy was found to be released from $40Ir/20La_2O_3/Al_2O_3$ 900^0C. It is apparent that the amount of heat generation increases with the active site (*i.e.* Ir) loading; however high Ir loadings has a negative impact on the onset (light-off) temperature due to the increase in iridium particle size. The presence of La_2O_3 leads to a decrease in the onset temperature. Moderate La loadings reveal optimum Ir dispersion revealing maximum activity. For low La loading, onset temperature slightly increases due to the formation of big IrO_2 particles. For high La loading, onset temperature increases as a result of $LaAlO_3$ phase formation which is detected by XRD. Catalysts calcined at 1100^0C typically reveal lower activity than that of 900^0C. This may be attributed to decrease in the specific surface area, the sintering of Ir particles and/or burial of the Ir sites below reducible oxides due to the strong metal support interaction. Moreover, Addition of CeO_2 leads to a profoundly positive effect on catalytic activity due to oxygen storage and release capabilities of the reducible CeO_2 domains, facilitating catalytic decomposition of ADN. Dispersion of Ir on Ceria domains, $Ir/Ce/La/Al_2O_3$, rather than on Lanthana domains, $Ir/La/Ce/Al_2O_3$, reveals better catalytic performance. The most active CeO_2-containing catalyst was found to be $5Ir/10CeO_2/20La_2O_3/Al_2O_3$ 900^0C.

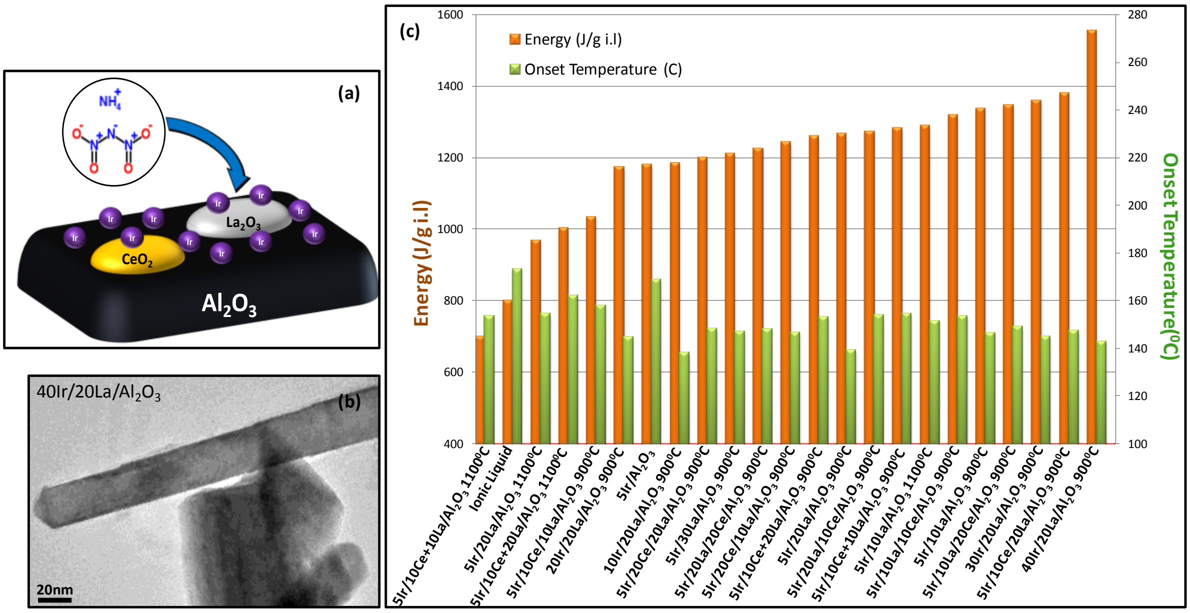

Figure 1. (a) Schematic diagram of $Ir/CeO_2/La_2O_3/Al_2O_3$ catalyst and ADN-based ionic liquid. (b) TEM image of $40Ir/20La_2O_3/Al_2O_3$ catalyst (c) DSC/TGA results showing the onset temperatures and energy release during the catalytic decomposition of ADN under anaerobic conditions over the synthesized catalysts.

4. Conclusions

Highly active Ir-La-Ce-Al containing catalytic materials for exothermic ADN decomposition were synthesized. Utilization of promoters such as La_2O_3 and/or CeO_2 significantly improves the onset temperature and the energy release during the decomposition of ADN. These important functional trends can be explained by structural properties of the catalysts at the nanometer scale, providing molecular level insight for the design of next-generation catalysts for anaerobic ionic liquid decomposition.

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