

Exothermic Catalytic Decomposition of Energetic Ionic Liquids on Ir Based Catalysts: Chemical and Electronic Structure of Ir Active Site

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(ADN)

 $N(NO_2)_2$

ORG

Decomposition Products

Ir⁰ (NP)

 $X-Al_2O_3$ (X = La or Si)

Motivation

Hydrazine (N₂H₄) is the most commonly used propellant for in-orbit spacecraft propulsion. However, utilization of hydrazine in space missions has challenges associated with health, environment and safety **Ammonium Dinitramide** risks. Energetic ionic liquids (EILs) such as ammonium dinitramide (ADN) present themselves as environmentally friendly alternative fuels to hydrazine. Catalytic technologies developed for ADN based 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. The conventional catalyst used for hydrazine decomposition is ~30 wt.% Ir/Al₂O₃. The major drawbacks of this catalytic system are Ir sintering and particle size growth associated with thermal aging, as well as loss of surface area at elevated temperatures. In the current work, influence of two different catalytic promoters (i.e., La or Si incorporated into the alumina support material) on the catalytic performance of Ir active sites in anaerobic ADN decomposition were investigated [1]. Performance measurements were done via custom-design micro propulsion batch reactor. Structural characterization of the catalysts were carried out via XANES, EXAFS, *in-situ* FTIR, CO Chemisorption, XRF, TPD, XRD, TEM and BET analysis techniques. Our findings revealed that 5Ir/Al₂O₃ and 5Ir/La-Al₂O₃ catalysts favorably lowered the onset temperature of the ADN decomposition reaction, whereas 5Ir/Si-Al₂O₃ boosted the pressure generation during the reaction. The fundamental structure-functionality relationships unraveled in the current work may allow design of novel catalytic systems for aerospace monopropellant propulsion systems with higher performance by simultaneous exploitation of Ir active sites with different electronic properties.

Experimental

5 wt.% Ir/Al₂O₃ and 5 wt.% Ir/X-Al₂O₃ catalysts were synthesized using incipient to wetness impregnation method. Ir sites were incorporated on the support materials in two successive impregnation cycles. After initial impregnation and drying steps (60 °C in air for 8 h), two different preparation protocols were carried out;

First protocol: i) catalysts were calcined in air at 400 °C for 3 h, ii) impregnated with a second loading of 2.5 wt.% Ir, dried at 60 °C in air for 8 h, and calcined in air at 400 °C for 3 h, and iii) finally reduced at 500 °C for 2 h under 100 ml/min 5% H₂/Ar flow. Catalysts synthesized using this first protocol are designated in the text as "CCR".

Second protocol: i) impregnated catalysts were reduced at 500 °C for 2 h under 100 ml/min 5% H₂/Ar flow, ii) impregnated with a second loading of 2.5 wt.% Ir, dried at 60 °C in air for 8 h, and reduced at 500 °C for 2 h under 100 ml/min 5% H₂/Ar flow. Catalysts synthesized using this second protocol are designated in the text as "RR" (e.g., 5Ir/Si-Al₂O₃RR).

[1] M. Kurt, Z. Kap, S. Senol, K. E. Ercan, A. T. Sika-Nartey, Y. Kocak, A. Koc, H. Esiyok, B. S. Caglayan, A. E. Aksoylu, E. Ozensoy, Applied Catalysis A: General, 632,118500, 2022.

