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Phase-stabilized hexa(imidazole) nickel (II) nitrate Complex/Ammonium Nitrate Composite: eco-friendly chlorine-free oxidizer with high energy density and superior decomposition kinetics.

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Abstract. Ammonium nitrate (AN) has gained attention as a promising non-chlorinated oxidizer for solid propellants. However, its practical application is limited due to its high hygroscopicity, low burning rate, endothermic decomposition, and phase transitions near room temperature. This study presents the development of an energetic hexa(imidazole) nickel (II) nitrate (Ni-Im) complex as an energetic phase stabilizer with novel catalytic characteristics. The Ni-Im complex was synthesized through a solvent-free approach, yielding a highly pure crystalline structure with a decomposition enthalpy of 267 J/g. The Ni-Im complex was integrated with AN via the cost-effective dry grinding method, developing an energy-dense phase-stabilized composite. The Ni-Im/AN composite developed intermolecular interactions eliminating near-room-temperature phase transition and shifting the first phase transition to 92°C. Additionally, the Ni-Im complex reduces the decomposition endothermic peak of AN by 22.2% and introduces an exothermic peak at 281°C. The Ni-Im complex exhibited a strong catalytic effect towards AN decomposition, reducing its decomposition apparent activation energy of AN decomposition by 39.7%, 30.7%, and 31.9% based on Kissinger, it-FWO, and it-KAS models, respectively. The Ni-Im decomposition generates porous nickel oxide nanoparticles serving as effective catalysts for exothermic gaseous reactions. These findings highlight the Ni-Im/AN composite as a promising halogen-free oxidizer for solid propellants.

1. Introduction

Solid propellant systems are widely favored over liquid and hybrid ones due to their reliability and simplicity. Ammonium perchlorate (APC) is a common oxidizer in composite propellant formulations owing to its affordability, and strong oxidizing properties. However, APC-based propellants exhibit a significant disadvantage of huge toxic chlorinated smoke evolution during combustion revealing a lunch location and damaging the ozone layer. This has driven efforts to replace APC oxidizer in propellant formulations with non-chlorinated ones. Ammonium nitrate (AN) was introduced as a promising alternative due to its low cost, availability, and the production of entirely green gaseous decomposition products. Despite these benefits, utilization of AN as the main propellant oxidizer is limited due to its high hygroscopicity, low burning rate, poor ignitability, endothermic decomposition, and phase transitions near room temperature. Notably, the IV↔III phase transition of AN at 32 °C results in a 4%

volume increase causing cracks and catastrophic combustion [1]. Therefore, novel strategies must be developed to improve its viability as a sustainable green alternative to APC.

To address these challenges, researchers have explored various strategies. The energy content and burning rate limitations were handled by using energetic binders, high-energy nitramines such as HMX and RDX, metals such as Pt, Cu, and Zn, and metal oxides such as NiZnO and $CuFe_2O_4$ [2]. The hygroscopicity of AN has been reduced through techniques such as surface modification and recrystallization. The most serious challenge of room-temperature phase transitions was addressed via phase modifiers such as organic compounds, potassium-based compounds, and metal oxides [3]. However, traditional stabilizers exhibit low energy content, poor decomposition kinetics, and solid residue formation, which restrict their practical applicability. Consequently, there is an urgent demand for energy-dense phase stabilizers with enhanced catalytic efficiency and environmentally benign decomposition products.

Numerous studies have investigated methods to improve the phase stability and energetic performance of ammonium nitrate (AN). The copper oxide (CuO)/AN composites achieved phase stability up to 86.7°C but suffered from aggregation issues and a lack of gaseous products[4]. Cocrystallization of AN with crown ethers eliminated room-temperature phase transitions but reduced burning rates[2]. Potassium dinitramide (KDN) stabilized AN and improved its energy content but caused unstable combustion due to high potassium levels[3]. These limitations highlight the need for advanced materials that combine the catalytic benefits of metal oxides with the gas-generating properties of energetic organic compounds to optimize AN-based propellants.

Hybrid inorganic-organic structures, particularly energetic organometallic coordination compounds, which consist of nitrogen-rich organic ligands (e.g., pyridine, imidazole) coordinated with metal ions, have emerged as an integrated system[5]. These compounds not only release environmentally friendly gases but also generate substantial heat upon decomposition, with the resulting porous metal oxide nanoparticles serving as effective catalysts. Imidazole-based metal complexes exhibit superior thermal stability and combustion heat (15 kJ/g), surpassing conventional nitramines such as RDX and HMX [6]. Our group has developed a tetra(imidazole)copper (II) nitrate (Cu-Im)/AN cocrystal via methanol solvent evaporation that demonstrates an improvement in phase stability, energy content, and decomposition kinetics[7]. Expanding on this work, a novel free chlorinated hexa(imidazole) nickel (II) nitrate complex (Ni-Im) was synthesized and integrated with AN via a solvent-free grinding technique. This method represents the first application of a chlorine-free energetic complex with AN through a mechanochemical approach, offering a cost-effective and efficient strategy for developing an energy-dense, phase-stabilized AN composite.

The free chlorine nickel-based energetic complex (Ni-Im) was synthesized through a solvent-free melt-assisted technique. The Ni-Im was subjected to comprehensive characterization, including its chemical structure, crystallographic features, morphology, and thermal behavior via attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy, X-ray diffraction analysis (XRD), scanning electron microscope (SEM), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). The Ni-Im complex demonstrates thermal stability up to 145°C and decomposes exothermically at 267°C. The Ni-Im/AN composite was fabricated using a solvent-free mechanical grinding method, resulting in an enhancement in the thermal behavior of AN. The Ni-Im/AN composite demonstrates no near-room-temperature phase transition and the first phase transition at 92 °C. The Ni-Im complex remarkably reduced the Ea of AN thermal decomposition by 39.7, 30.7 %, and 31.9% as determined by Kissinger's method, iterative Flynn– Wall–Ozawa (it-FWO), and iterative Kissinger–Akahira–Sunose (it-KAS), respectively.

2. Experimental work

2.1 Materials

The salt of Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) (purity ≥ 99 %), imidazole ($C_3H_4N_2$, Im) (purity ≥99 %), and ammonium nitrate powder (NH_4NO_3, AN) (purity ≥ 98.0 %), were purchased from Merck, Germany. All reagents were used without any further purification.

2.2 Synthesis and characterization of Ni-Im complex and Ni-Im /AN composite

The energetic organometallic hexa(imidazole) nickel (II) nitrate complex was prepared via a green simple solvent-free dry-melt technique [8]. The energetic Ni-Im complex was synthesized in a ceramic crucible where the 0.98 g of Nickel (II) nitrate hexahydrate salt was added to 1.38 g of colourless molten imidazole at 90 °C forming a green melt. The mixture was stirred at 120 °C until a violet dry powder formed. The energetic Ni-Im/AN composite (10% wt/wt) was synthesized via an economical grinding technique. The obtained pale green Ni-Im/AN composite was further dried at 80 °C for 1 hour.

The chemical structure of the as-prepared samples was analyzed via ATR-FTIR spectroscopy. Furthermore, the crystallinity, morphology, and thermal behavior were assessed via XRD analysis, SEM analysis, and DSC-TGA measurements, respectively.

2.3 Kinetic analysis of the energetic Ni-Im/AN composite decomposition

The catalytic potential of the energetic Ni-Im complex towards the AN thermal decomposition was assessed via Kinetic parameters calculation. The isoconversional free-model methods were highly recommended for reliable determination of the kinetic triplet, namely apparent activation energy E_α, the most probable reaction model g(α), and frequency factor (A). Based on the TGA and DTG measurements at four different heating rates of 4, 6, 8, and 10 °C min^{-1}, the kinetic parameters were estimated using the Kissinger model, iterative Kissinger–Akahira–Sunose (it-KAS), and iterative Flynn– Wall–Ozawa (it-FWO).

3. Results

3.1. Characterization of as-prepared energetic Ni-Im coordination complex

The energetic organometallic Ni-Im complex was synthesized via an economical green solvent-free procedure. The violet color acquired by the reaction mixture confirmed the formation of the Ni-Im complex. The ATR-FTIR spectrum analysis was carried out to investigate interactions between imidazole ligands and nickel ions within the Ni-Im complex structure. The ATR-FTIR spectrum of the Ni-Im complex exhibits absorption peaks of nitrate ions vibrations at 713 cm^{-1}, 844 cm^{-1}, 1054 cm^{-1}, and 1370 cm^{-1}, similar to those in the nickel salt spectrum (figure 1). Consequently, it was concluded that nitrate ions surrounded the coordination nickel sphere. Furthermore, the Ni-Im complex spectrum demonstrates the absorption peaks attributed to the imidazole ring, which indicates that imidazole preserves its structure during the reaction. The N-H stretching vibration in the Ni-Im complex spectrum appeared at a higher frequency range (2918-3332 cm^{-1}), compared to that in the imidazole spectrum (2800-3150 cm^{-1}). The red shift of the N-H absorption band was attributed to hydrogen bonds between imidazole molecules (N-H---:N). In the Ni-Im structure, the pyridine-like nitrogen within imidazole ligands coordinated with nickel ions, breaking down the hydrogen bonding system[9]. The absence of the H_2O bending vibration at 1600 cm^{-1} confirmed that the as-synthesized Ni-Im complex is free of water molecules.

The XRD analysis was used to investigate the purity and crystallinity of the as-synthesized energetic Ni-Im complex. The XRD diffractogram of the as-prepared Ni-Im complex exhibited clear sharp peaks fully matching those of the database card of hexa(imidazole) nickel (II) nitrate PDF card No. 21-1785 (figure 2)[10]. Consequently, the highly pure crystalline energetic Ni-Im complex was synthesized successfully via a melt-assisting solvent-free approach.

The SEM analysis was conducted to assess the morphology of the as-prepared Ni-Im complex. The as-synthesized Ni-Im complex particles exhibited irregular, rounded shapes with rough surfaces and an average size of 2 to 30 µm (figure 3).

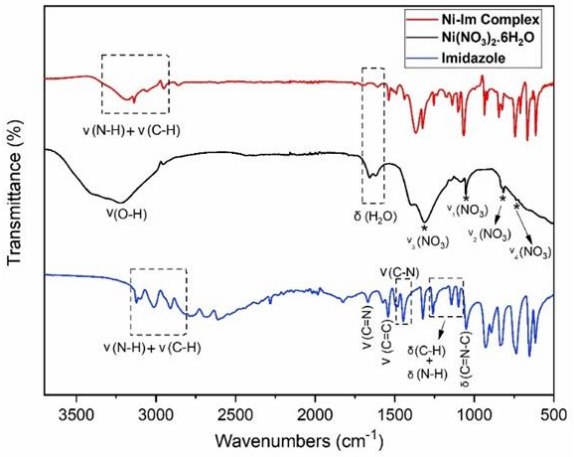

Figure 1. ATR-FTIR spectra of the as-synthesized Ni-Im coordination complex.

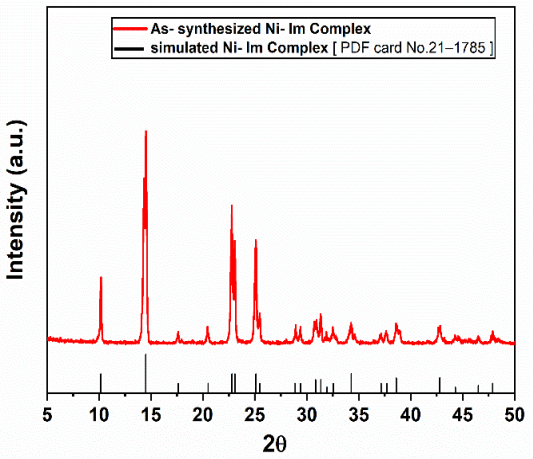

Figure 2. The XRD analysis for the as-prepared Ni-Im coordination complex.

The purity and elemental composition of the as-synthesized Ni-Im complex were assessed with energy-dispersive X-ray Spectrometry (EDX). The as-prepared Ni-Im complex exhibited a Ni content of 9.3%, nearly matching the theoretically calculated value (9.9%) for a compound consisting of nickel coordinated with six imidazole molecules and surrounded by two nitrate ions (figure 4)[8]. The as-synthesized Ni-Im complex was highly pure, containing no foreign elements.

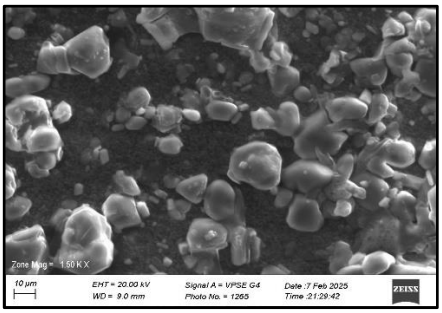

Figure 3. The SEM micrograph of as-prepared energetic Ni-Im complex.

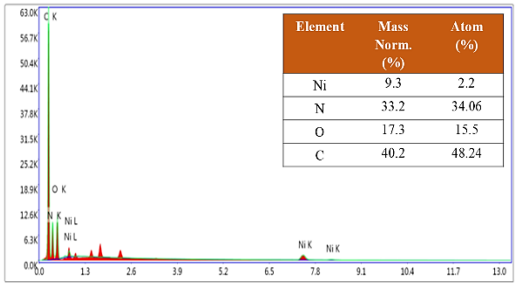

Figure 4. The EDX analysis for as-synthesized Ni-Im complex.

DSC-TGA measurements were conducted to investigate the purity and thermal behavior of the as-prepared Ni-Im complex (figure 5). The TGA profile of the as-prepared Ni-Im complex exhibited no weight loss associated with the decomposition of the pure Nickel (II) nitrate hexahydrate salt or water evaporation. Furthermore, the DSC analysis of the as-prepared Ni-Im complex shows no endothermic peak at 90 °C related to pure imidazole melting. The Ni-Im coordination complex starts decomposition at 156 °C with a slight endothermic peak at 244 °C related to partial imidazole ligands loss. The Ni-Im coordination complex is a redox system that contains oxidizing nitrate ions along with energy-intensive imidazole ligands within its structure, favoring exothermic decomposition. The DSC analysis of the Ni-Im complex exhibited saw-like exothermic decomposition with heat release of 267 J/g, corresponding to imidazole molecules removal and simultaneous oxidation with nitrate ions. The TGA analysis shows that the main decomposition of the Ni-Im complex occurred with a temperature range of 160-400 °C with a weight loss of 60%. Furthermore, The Ni-Im coordination complex contains a high nitrogen

content of 33% (w/w) that reduces the environmental issues and smoke related to solid decomposition products.

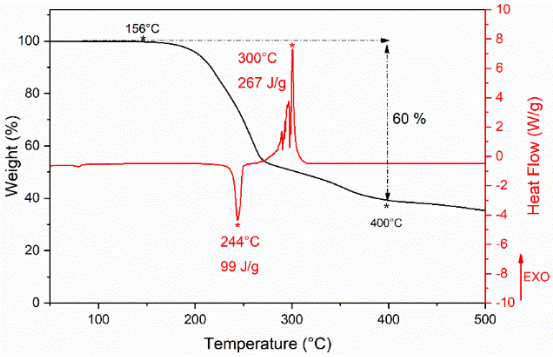

Figure 5. The DSC and TGA analysis of Energetic Ni-Im complex.

3.2. Characterization of energetic Ni-Im/AN composite

The intermolecular interactions developed within the as-prepared energetic composite between AN and Ni-Im complex were assessed via ATR-FTIR analysis. The pure AN spectrum (figure 6) exhibited vibrational modes of nitrate ions at 1289,1038, 827, and 713 cm^{-1}. The virgin AN demonstrated symmetric and asymmetric stretching vibrations of N-H at 3050 cm^{-1} and 3234 cm^{-1}, respectively. Furthermore, the bending vibration of N-H within NH^{+4} appeared at 1409 cm^{-1} in the pure AN spectrum [11]. The ATR-FTIR spectrum of the energetic Ni-Im/AN composite showed significant differences in positions and intensities of characteristic peaks compared to its constituents.

The Ni-Im/AN composite spectrum shows the disappearance or intensity decrease of some peaks of the raw materials such as those that appeared at 3138 cm^{-1},2947 cm^{-1},1486 cm^{-1}, and 1370 cm^{-1} for Ni-Im complex and 1409 cm^{-1} for pure AN. The spectrum of Ni-Im/AN showed the N-H asymmetric stretching at 3228 cm^{-1} compared to 3234 cm^{-1} for AN; and N-H bending at 1406 cm^{-1} compared to 1409 cm^{-1} for AN. It has been reported that intermolecular interactions developed between raw materials are responsible for slight variations occurring in the FTIR spectrum. The intermolecular interactions directly distort the electrostatic field of AN influencing its phase stability and transitions[2].

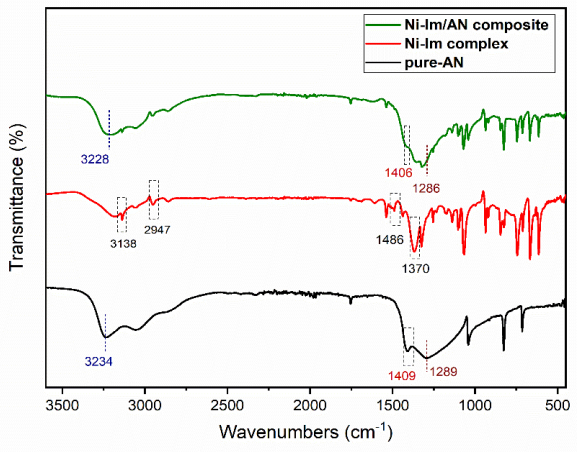

Figure 6. ATR-FTIR spectrum of Ni-Im/AN energetic Composite.

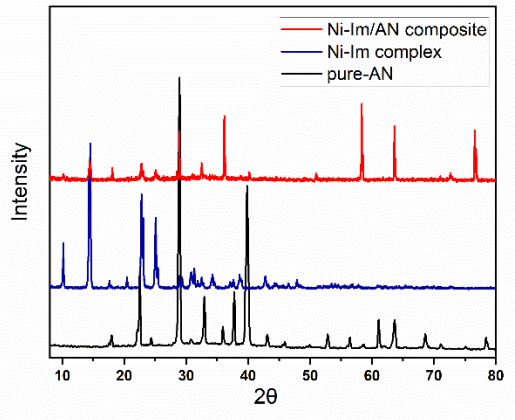

Figure 7. The XRD diffractogram of the Ni-Im/AN energetic composite.

The impact of the Ni-Im complex on the crystalline structure of pure AN was conducted via XRD study. The XRD diffractogram of pure AN aligned with all characteristic peaks of phase IV as referenced in PDF card No. 85–1093 (figure 7)[12]. The Ni-Im/AN composite retained all major characteristic peaks

of its constituents, with no emergence of new peaks or disappearance of existing ones in the diffractogram. However, XRD of the Ni-Im/AN composite demonstrates the differences in relative intensity of characteristic peaks that are caused due to intermolecular interactions developed within the composite. The DSC profile of investigated pristine AN revealed four endothermic peaks at 54 °C,128 °C, 170 °C and 294 °C corresponding to the IV↔II and II↔I phase transitions, melting, and thermal decomposition, respectively. Incorporating the energetic coordination complex Ni-Im with AN via a simple grinding technique significantly altered its thermal behavior (figure 8). The Ni-Im/AN composite demonstrates no near-room temperature phase transition and the first phase transition at 92 °C. Compared to pure AN, the DSC thermogram of the Ni-Im/AN composite exhibits intensity reduction of endothermic peaks associated with IV↔II and II↔I phase transitions and melting by 48.5%, 33.8%, and 27.4%, respectively. Additionally, the Ni-Im complex reduces the decomposition endothermic peak by 22.2 % along with introducing a new exothermic peak at 281°C. Consequently, the Ni-Im coordination energetic complex exhibited a potential for boosting overall heat and stabilizing of AN-based propellants.

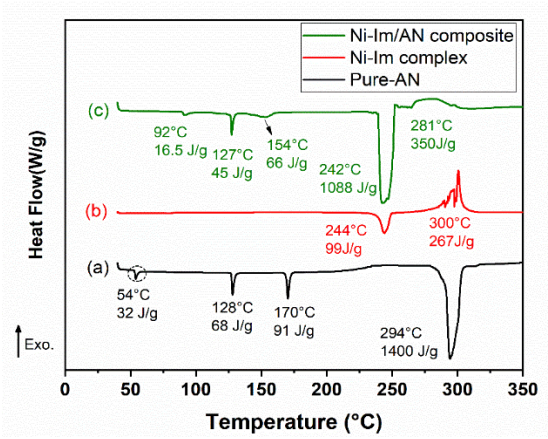

Figure 8. The DSC analysis of Ni-Im/AN composite.

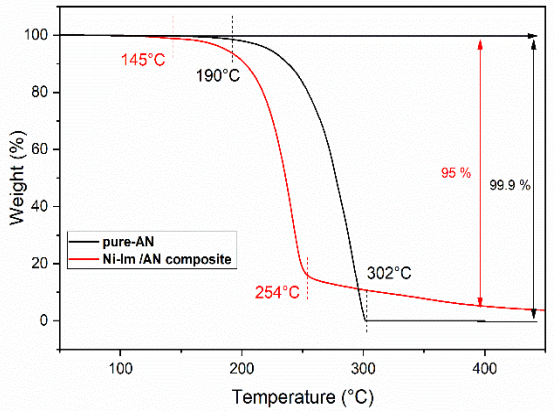

Figure 9. The TGA profile of Ni-Im/AN composite.

TGA-DSC analysis demonstrates no mass loss during solid-solid phase transitions or melting. The Ni-Im/AN composite decomposed in a single step with a 97% weight loss over a temperature range of 145-254 °C reducing the peak decomposition rate temperature by 51°C. The Ni-Im complex not only contributed to the phase stabilization of AN but also facilitated its thermal decomposition by the formation of highly porous Nickel oxide nanoparticles (NiO).

3.3. Kinetic analysis of thermal decomposition of Ni-Im/AN composite

The kinetics of thermal decomposition of Ni-Im/AN composite were conducted using three different methods: the Kissinger method and two iterative isoconversional approaches, it-KAS and it-FWO. The kinetic analysis was evaluated based on the TGA measurements at four different heating rates as shown in figure 10 and figure 11. According to Kissinger's method, the apparent activation energy (E_a) of the Ni-Im/AN composite was determined to be 87.3 kJ/mol, significantly lower than that of AN by 57.5 kJ/mol (figure 12). Additionally, the pre-exponential factor Log(A) was 8.4 min^{-1} for the Ni-Im composite and 13.15 min^{-1} for pure AN.

Iterative isoconversional kinetic methods were preferred due to their model-free nature and robustness against experimental noise[13]. These methods also revealed the dependence of E_a and the Log(A) on the extent of conversion (α). Using the it-FWO method, the mean E_a for the thermal decomposition of Ni-Im/AN composite was 98.8 kJ/mol, compared to 142.4 kJ/mol for pure AN (figure 13). Similarly, using the it-KAS method shows a mean E_a of 95.7 kJ/mol for the Ni-Im composite, while pure AN exhibited a value of 140.7 kJ/mol (figure 14). The Ni-Im complex remarkably reduced the E_a of AN

thermal decomposition by 30 %, confirming its catalytic potential. Furthermore, The dependency of E_a through the reaction demonstrates no abnormal acute change suggesting the single-step reaction. The Ni-Im/AN composite follows a random nucleation mechanism (Avrami-Erofeev, $A_{3/2}$) during decomposition while virgin AN decomposition follows a second-order chemical reaction model (F_2).

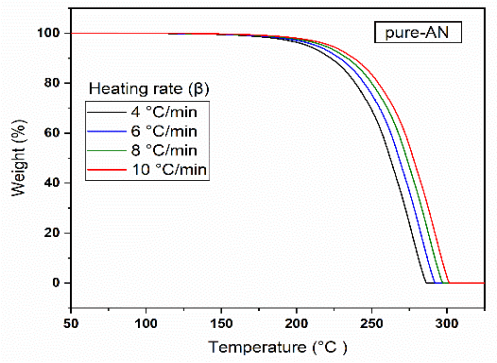

Figure 10. The TGA analysis of pure AN at four heating rates.

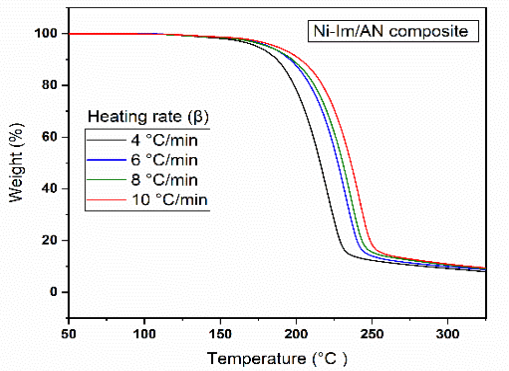

Figure 11. The TGA analysis of Ni-Im/AN at four heating rates.

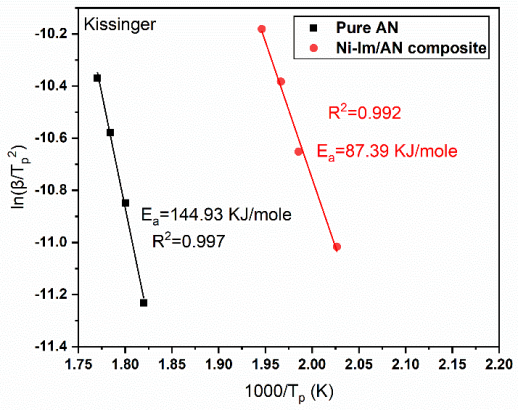

Figure 12. E_a for the thermal decomposition of AN and Ni-Im composite using the Kissinger method.

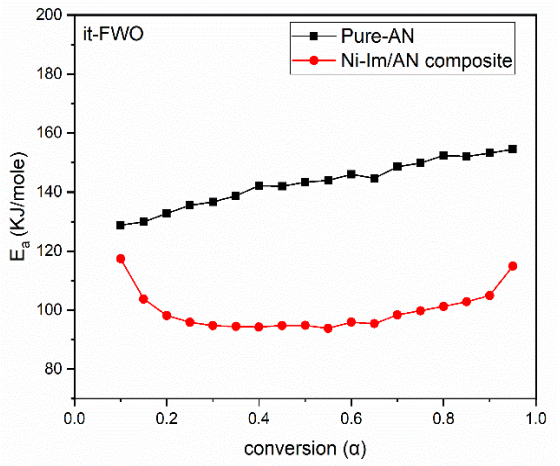

Figure 13. E_a dependency on conversion for AN and Ni-Im/AN composite based on it-FWO.

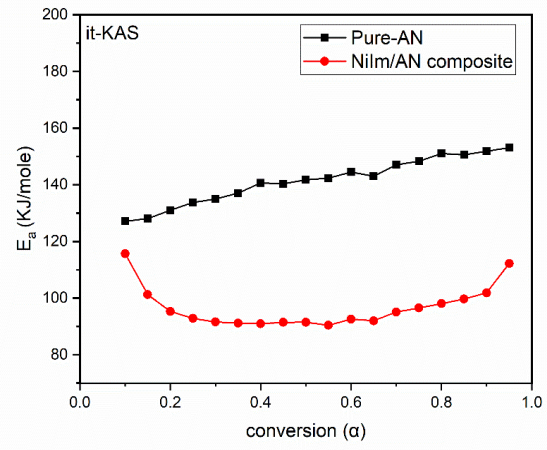

Figure 14. E_a dependency on conversion for AN and Ni-Im/AN based on it-KAS.

Based on it-FWO, the mean Log(A) for the Ni-Im/AN composite decomposition was 12.5 min^{-1}, compared to 15.6 min^{-1} for pristine AN (figure 15). Furthermore, using the it-KAS approach, the mean Log(A) for the Ni-Im/AN composite decomposition was 12.3 min^{-1}, compared to 15.4 min^{-1} for pristine AN (figure 16). Table 1 summarizes the kinetic triplet parameters for AN and the Ni-Im/AN.

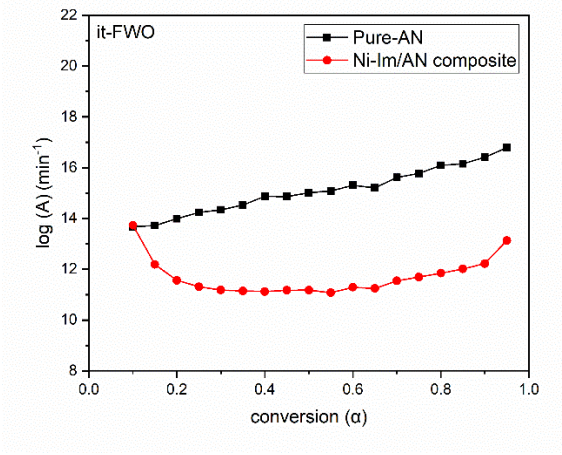

Figure 15. log(A) dependency on conversion for AN and Ni-Im/AN based on it-FWO.

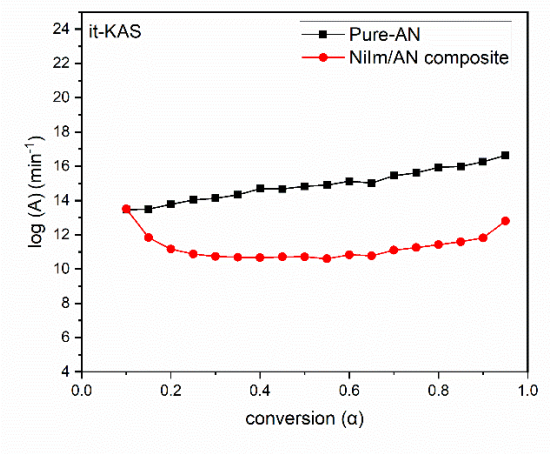

Figure 16. log(A) dependency on conversion for AN and Ni-Im/AN based on it-KAS.

Table 1. Kinetic parameters of Ni-Im/AN composite compared to pure-AN

method	sample	Kinetic parameter		
		Mean Ea (KJ/mole)	Mean Log(A) (min^{-1})	Integral reaction mechanism g(α)
It-FWO	pure-AN	142.4	15.6	$F_2= ((1-\alpha)^{-1}-1)$
	Ni-Im/AN composite	98.8	12.5	$A_{3/2}=[-\ln(1-\alpha)]^{2/3}$
It-KAS	pure-AN	140.7	15.45	$F_2= ((1-\alpha)^{-1}-1)$
	Ni-Im/AN composite	95.7	12.3	$A_{3/2}=[-\ln(1-\alpha)]^{2/3}$

4. Conclusions

The energetic organometallic Ni-Im complex was successfully synthesized using a simple solvent-free method, yielding a highly pure crystalline structure with a decomposition enthalpy of 267 J/g. The Ni-Im complex was integrated with AN via the cost-effective dry grinding method, developing an energy-dense phase-stabilized AN composite. The Ni-Im/AN composite demonstrates no near-room temperature phase transition and the first phase transition at 92°C. This novel phase stabilization was attributed to intermolecular interactions within the composite structure. The Ni-Im/AN composite exhibits intensity reduction of endothermic peaks associated with IV↔II and II↔I phase transitions and melting by 48.5%, 33.8%, and 27.4%, respectively. Additionally, the Ni-Im complex reduces the decomposition endothermic peak by 22.2% along with introducing a new exothermic peak at 281°C. The Ni-Im complex exhibited a strong catalytic effect towards AN decomposition, reducing apparent activation energy (Ea) of AN decomposition by 39.7%, 30.7%, and 31.9% based on Kissinger, it-FWO, and it-KAS models, respectively. Upon decomposition, the Ni-Im complex generated dispersed NiO nanoparticles, which provided a large surface area for exothermic gaseous redox reactions. The Ni-

Im/AN composite, synthesized via a simple solvent-free grinding approach, demonstrates novel characteristics, making it a promising candidate for advanced solid propellant formulations.

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