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The potentials of copper chromite nanoparticles on ammonium nitrate decomposition: Towards eco-friendly oxidizers for green solid propellants

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Abstract. Ammonium perchlorate (AP) is the universal oxidizer for solid propellants; AP combustion is accompanied with the release of white smoke (HCl). HCl has raised an environmental concern; it could cause acidic rain and deteriorate the fertile soil. Chlorine free and eco-friendly oxidizers are highly appreciated for green solid propellants. Ammonium nitrate (AN) could be the greener substitute for AP; yet AN expose low performance. Whereas AP demonstrated exothermic decomposition with the release of -733 J/g; AN demonstrated strong endothermic decomposition process of +1707 J/g. AN with strong endothermic decomposition process could render high burning rates. Copper chromite Nano catalyst of 45 nm was developed via hydrothermal synthesis. Copper chromite was integrated into AN matrix. Catalyzed AN demonstrated advanced exothermic decomposition enthalpy of -1492 J/g. Catalysed AN experienced diminish in activation energy by - 41.5 %, and – 40.6 % using Kissinger and Ozawa models respectively. Copper chromite NPs could secure novel catalytic effect via condensed phase reactions of chromium, and copper ions with nitrate ions (NO-3) to develop NOx gases. This catalytic effect can secure alternative pathway with low energy barrier. Consequently, catalysed AN can expose novel characteristics as a green eco-friendly oxidizer.

Keywords: Ammonium perchlorate; Ammonium nitrate; Catalyst; Copper chromite; Kinetics.

1. Introduction

Demand for eco-friendly (chlorine free) composite solid propellant (CSP) has raised many concerns due to global warming and climate change[1, 2]. Most of the current operational CSP formulations are based on of ammonium perchlorate (AP) as an oxidizer. The main disadvantages of AP-based CSP are chlorinated exhaust compounds. Hydrochloric acid (HCl), chlorine (Cl_2) are the main exhaust products[3]. These gases have raised many environmental concerns due to their corrosively, toxicity, and rain acidity[4]. HCl could result in acidic rains that would damage the fertile soil. Chlorine gases can induce

smoke signature that could impede rocket guidance. Additionally, rocket trajectory and firing site can be easily detected[5]. Eco-friendly (chlorine free) and green alternative for AP oxidizer is highly appreciated. Recent advances in eco-friendly solid propellants were directed to low-smoke signature. There is a considerable interest in ammonium nitrate (AN) to secure low smoke propellant systems[6]. AN could be the greener alternative for AP oxidizer in CSP. AN is the universal soil fertilizer; it is readily available as a stable and cheap oxidizer. However, AN exposes strong endothermic decomposition, with low oxidizing ability. AN suffers from low combustion performance[7]. Numerous investigations have been conducted to enhance the characteristics of combustion and ignition of AN. Thermal behaviour of AN and possible decomposition mechanisms have been proposed. In addition, AN exposes endothermic crystallographic phase transitions over the temperature range +17 to +125 ° [8, 9]. This strong endothermic decomposition could withstand the limited applications as efficient oxidizer. Catalysts can enhance the thermal behavior and combustion mechanism of AN. It is known that transition metals and metals oxides could be effective additives to enhance the thermal behaviour of AN. The addition of transition metal cations such as manganese (Mn), cobalt (Co), or copper (Cu) to AN matrix could secure enhanced decomposition enthalpy. For instance, the incorporation of copper particles resulted in sharp exothermic decomposition. Copper oxide (CuO) offered decrease in the activation energy of AN from 115 to 98 KJ/g, with only one endothermic transition at 55 ^{o}C over the temperature range of 20 - 100 ^{o}c. Ferric oxide has been investigated for catalytic decomposition of AN. it offered decrease in the activation energy of AN by 20 KJ/g, with exothermic decomposition. In this regard, chromium compounds can expose superior catalytic action compared with other cations. Chromium has a unique electronic configuration with six unpaired electrons that could offer high reactivity to form stable complexes with gaseous molecules[10]. Copper chromite is a very stable compound that can withstand high temperatures and pressures without significant decomposition or degradation. Copper chromite could be valuable catalyst with high reactivity and stability. This study was directed to the facile synthesis of copper chromite nanoparticles (NPs) of 45 nm via hydrothermal synthesis. Copper chromite was effectively integrated into AN matrix. The potential impact of copper chromite on AN thermal behaviour and decomposition enthalpy was investigated via TGA and DSC. Kinetic parameters of catalyzed AN was investigated using Kissinger and Ozawa method. Copper chromite secured novel decomposition enthalpy for AN. While virgin AN demonstrated strong endothermic decomposition process of +1707 J/g; catalyzed AN demonstrated exothermic decomposition enthalpy of -1492 J/g. Copper chromite NPs demonstrated significant change in AN activation energy. According to the Kissinger and Ozawa models, catalysed AN showed a decrease in activation energy of –41.5% and –40.5%, respectively.

2. Experimental Work

2.1 copper chromite Nano catalyst synthesis

$Cu(NO_3)_2.3H_2O$ (1 mmol) and $Cr(NO_3)_3.9H_2O$ (2 mmol) were dissolved in 200 ml of DI water under magnetic stirring for 1 hr; homogeneous solution was developed. After being mixed for eight hours at 300 oC, the mixture was put into the hydrothermal batch reactor.

2.2 Nano-catalyst characterization

Size and shape of synthesized copper chromite NPs was looked into using (TEM. JEM-2100F by Joel Corporation). Morphology of dry copper chromite powder was investigated using scanning electron microscopy (SEM. ZEISS SEM EVO 10 MA supported with EDAX detector). Elemental mapping using EDAX detector was adopted to assess uniform dispersion and quantification of main copper chromite elements. Crystalline structure of copper chromite NPs was looked into using a Hilton brooks X-ray diffractometer (XRD) using CuK_{α} radiation over a range of 2θ from 5° to 90°.

2.3 Integration of copper chromite into AN

After precipitating from their synthesis medium, copper chromite particles were redistributed in methanol. AN particles were then dissolved in a colloid of methanol. Copper chromite: AN had a weight ratio of 3:97. To integrate copper chromite particles into AN, toluene was used as an anti-solvent.

2.4 Thermal behaviour of oxidizers

Thermal behaviour and decomposition enthalpy of AN was assessed to AP using DSC. DSC Q20 (TA Instruments) was adopted for thermal analysis study. The tested sample was heated from 25 °C to 500 °C at 10 0C/min, under nitrogen (20 ml/min). The weight loss with temperature of AN was investigated using TGA. Tested sample was heated at 10 °C /min from 25 °C to 500 °C using TGA 55 thermal analyser (TA Instruments).

2.5 Thermal behaviour of catalyzed ammonium nitrate

AN decomposition enthalpy was examined using DSC to examine the effect of copper chromite particles. Utilising an aluminium T zero pan, the tested sample was heated to 500 °C. AN weight reduction was evaluated using TGA in regard to copper chromite particles. A heating rate of 10 °C/min-1 and a nitrogen flow rate of 50 ml/min were applied to the tested material.

2.6 Kinetic study of AN nanocomposite

Arrhenius parameters for the thermal decomposition reaction of pure AN, and catalyzed AN were calculated using Kissinger's model (Equation 1).

$$\ln \frac{\beta}{T_p^2} = \ln \frac{A.R}{E} - \left(\frac{E}{R}\right) \frac{1}{T_p} \qquad (1)$$

Decomposition kinetic study of AP, AN, and catalyzed AN was conducted via Kissinger and OZAW'S models respectively. The heat flow of tested sample was recorded at different heating rates of 4, 7, and 10 °C/min. Arrhenius parameters for the thermal decomposition reaction of CuCr2O4 nanocomposite was calculated using Kissinger's model (Equation 1). Activation energy of tested samples was calculated using Ozawa's model (Equation 2).

$$\log \beta = -0.4567 \left(\frac{E}{R}\right) \frac{1}{T_P} \qquad (2)$$

3. Results and discussion

3.1 Characterization of copper chromite nanoparticles

TEM micrographs of synthesized copper chromite's particles demonstrated spheres of 45 nm. Copper chromite particles demonstrated high quality particles (Figure 1).

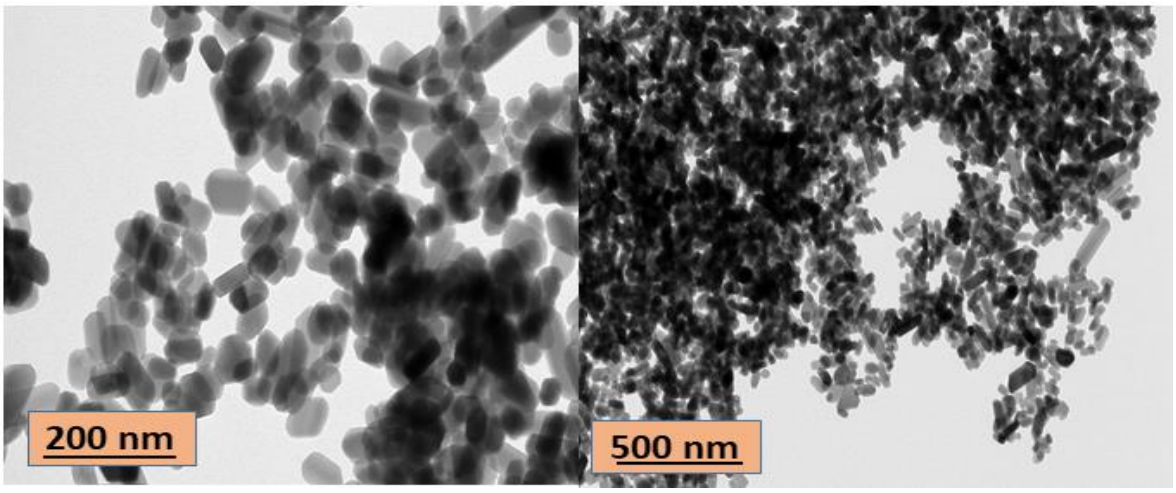

Figure 1. TEM of micrographs of copper chromite particles.

3.2 Characterization of AN nanocomposite

Morphology of starting AN and copper chromite/AN nanocomposite was investigated using SEM. While virgin AN demonstrated polydisperse particles 80 µm. copper chromite/AN demonstrated monodispersed particle of 5 µm. Uniform dispersion of copper and chromium elements within AN matrix was verified via elemental mapping. It is obvious that good distribution of copper chromite particles was accomplished (Figure 2).

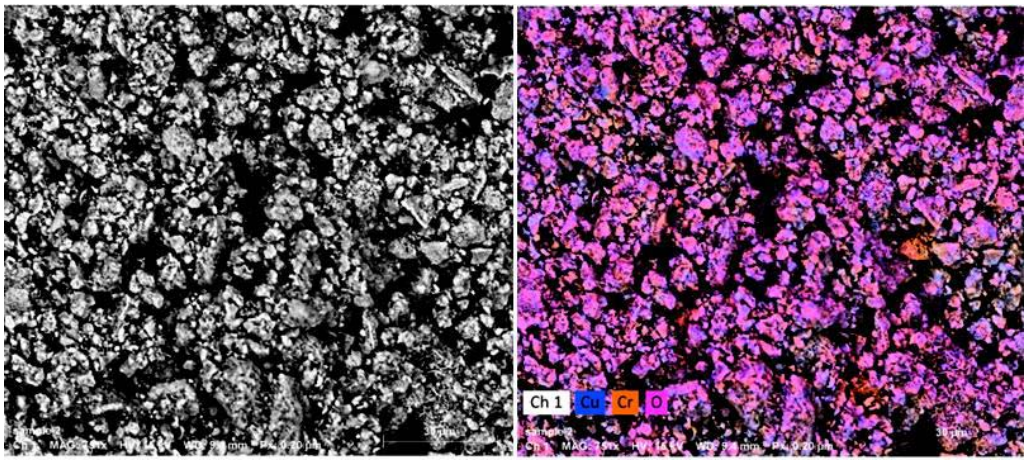

Figure 2. Elemental mapping of AN nanocomposite.

3.3 Thermal behaviour of virgin ammonium nitrate

Decomposition enthalpy and thermal behavior of virgin AN was investigated to virgin AP using DSC. Virgin AP demonstrated exothermic reaction with total decomposition enthalpy of -733.0 J/g. AN demonstrated total decomposition enthalpy of +1734.9 J/g. this means strong endothermic oxidizer decomposition (Figure 3).

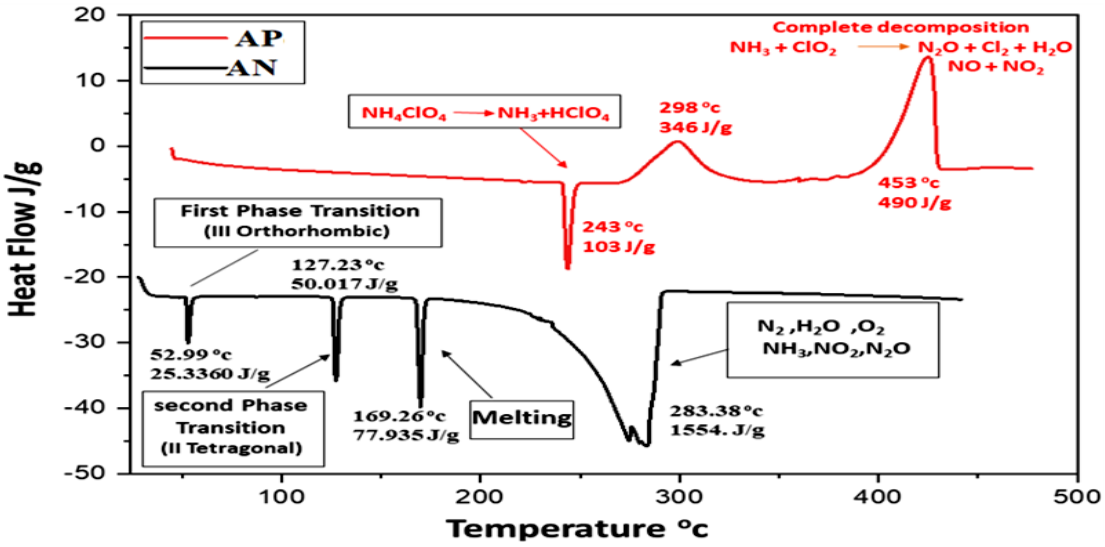

Figure 3. Thermal behavior of virgin AN to virgin AP.

AN demonstrated multiple endothermic peaks over the temperature range 25 °C to 350 °C. AN did not demonstrate any exothermic decomposition peaks. The crystallographic transformations IV → II and II → I could withstand the two endothermic peaks at 53 and 127 °C, respectively. The endothermic peak at

169.26 °C corresponds to the melting of AN. The strong endothermic peak at 283 °C was correlated to decomposition of AN. It is obvious that AN decomposes endothermically with total heat of +1707 J/g.

3.4 Thermal behaviour of catalyzed AN

The impact of copper chromite 3 wt % on AN thermal decomposition and decomposition enthalpy was investigated DSC. Copper chromite experienced significant change on AN thermal decomposition. Catalyzed AN demonstrated exothermic total decomposition enthalpy of -1492 J/g compared with total endothermic decomposition of 1707 J/g for virgin AN (Figure 4).

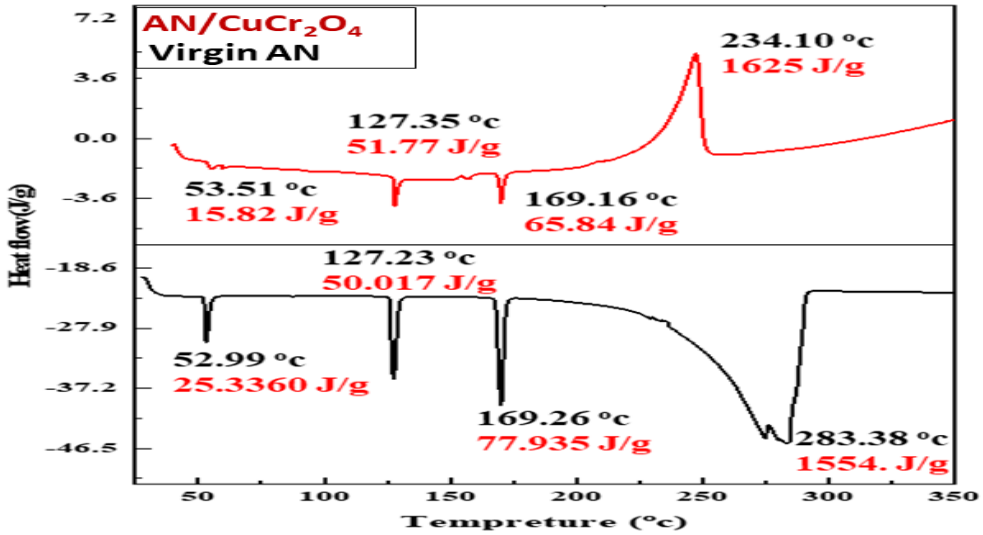

Figure 4. Impact of copper chromite on AN decomposition

Copper chromite demonstrated significant impact on AN main decomposition reaction. AN decomposition was completely changed from strong endothermic reaction of +1554 J/g to strong exothermic reaction of -1625 J/g. AN decomposition can be summarized in the following main steps. Chromium ion can expose different oxidation states and could induce different catalytic condensed phase reactions. The catalytic effect of copper chromite could be ascribed to the facile reaction of chromium ion with the decomposition reactants. This condensed phase reaction could facilitate AN decomposition, and could boost the decomposition enthalpy (Figure 5).

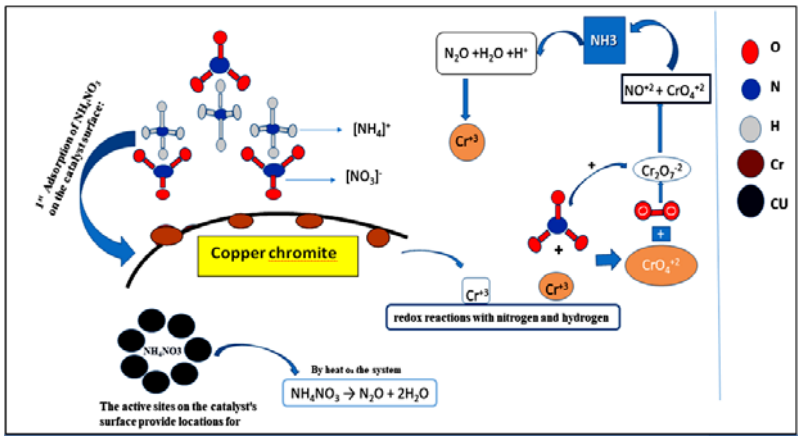

Figure 5. Schematic for catalytic effect of chromium ion on AN

Catalytic effect of copper chromite can be summarized in the following steps:

- Excess nitrate ions (NO^{-3}) can oxidize Cr^{+3} ion to chromate ions $Cr_2O_4^{+2}$.
- The chromate ions ($Cr_2O_4^{+2}$) can further react with O_2 to form dichromate ions ($Cr_2O_7^{-2}$).
- Nitrate ions react with $Cr_2O_7^{-2}$ ions to produce nitrite ions (NO^{+2}) and $Cr_2O_4^{+2}$.

This catalytic effect could boost the exothermic decomposition reaction. Furthermore, copper chromite could reduce the activation energy of AN through an alternative reaction pathway with low energy barrier.

3.5 Kinetic study of catalyzed AN

Catalyst could offer superior decomposition enthalpy. Furthermore, it could secure novel decomposition kinetics. Kinetic study was conducted to assess the impact of copper chromite NPs on AN decomposition. Arrhenius parameters for the thermal decomposition reaction for virgin AN, and catalyzed AN were calculated using Kissinger's and Ozawa's methods. Thermal behaviour of each tested sample was investigated at different heating rates of 4, 7, 10 °C using DSC. Thermal behaviour of virgin AN and catalyzed AN at different heating rate is presented in Figure 12.

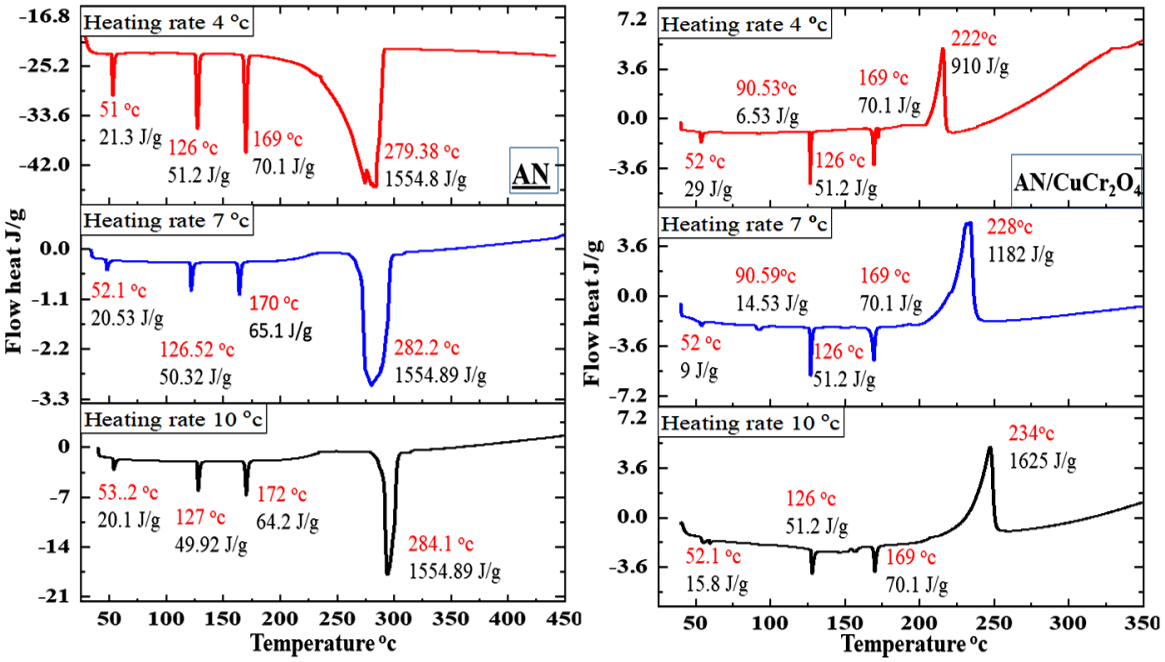

Figure 6. Thermal behaviour of virgin AN and catalyzed AN at different heating rates using DSC

For each heating rate and composition, ln (β/T_p^2) was plotted against ($1/T_p$) and log (β) against ($1/T_p$) according to Kissinger's and Ozawa's models as illustrated in Figure 7.

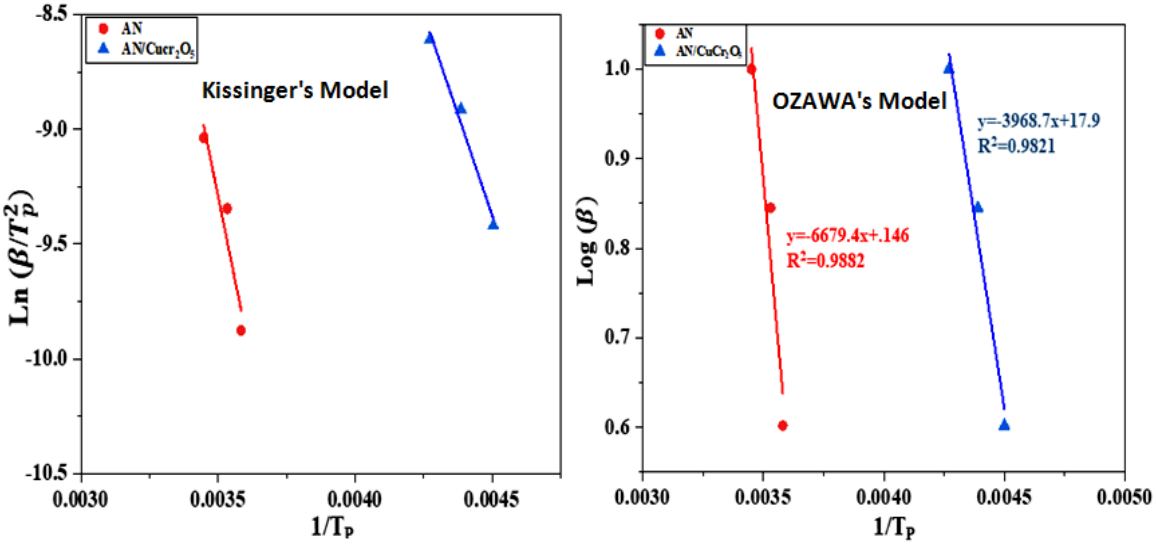

Figure 7. Data correlation line of ln (β/Tp2) against (1/Tp), and log (β) against (1/Tp) for the samples

Kissinger and AZAWA models demonstrated linear regression across the data points yielded a straight line connection. The slope and intercept of the line for each composition were used to compute the activation energy and pre-exponential factors. The kinetic characteristics for each sample are shown in the data listed in Table 1. Virgin AN demonstrated low activation energy compared with virgin AP [11-15]. The integration of copper chromite NPs experienced decrease in AN activation energy by -41.5 %, and -40.6 % using Kissinger and Ozawa models respectively. Firstly, $CuCr_2O_4$ catalyst could absorb the AN reactant onto its surface, this action could weaken the bonds between the NH4+ and NO3- ions and thus facilitating the reaction. Additionally, it is believed that the copper ions within the catalyst play a vital role in reducing the activation energy barrier. Chrome ion can form reactive sites on the catalyst's surface that can interact with the reactants and promote the reaction. Besides, the presence of oxygen within the $CuCr_2O_4$ catalyst can also contribute to the catalytic effect. The oxygen can react with AN to produce nitrogen oxides (NOx), which can then react with the copper ions to form copper nitrate ($Cu(NO_3)_2$). This reaction could generate heat and produce active copper sites that can further promote the decomposition of AN. Moreover, $CuCr_2O_4$ could provide an alternative reaction pathway for AN decomposition with a lower activation energy barrier.

Table 1. Kinetic parameters of virgin AP, virgin AN, catalysed AN

Formulas	**E_a (Kissinger's method) kJ/mol**	**E_a (Ozawa's method) kJ/mol**	**R^2**
AP	103	90.66	0.9907
AN	123.18	121.77	0.968
AN/ $CuCr_2O_5$	72	72.33	0.9984

4. Conclusion

Hydrothermal processing was used to create copper chromite nanoparticles with an average particle size of 45 nm. Copper chromite NPs were effectively integrated into AN matrix. Copper chromite NPs offered novel decomposition enthalpy of AN. Whereas virgin AN demonstrated four endothermic decomposition peaks with total endothermic decomposition of 1708 J/g. Catalyzed AN demonstrated exothermic decomposition with total decomposition enthalpy of -1492 J/g. Copper chromite NPs experienced decrease in AN activation energy by - 41.5 % , and - 40.6 % using Kissinger and Ozawa models respectively. Consequently catalyzed AN could be the green substitute for AP oxidizers for eco-friendly propulsion systems.

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