

Synthesis and Thermal behaviors of 1, 8-Dihydroxy-4, 5-Dinitroanthraquinone Nickel Salt

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Abstract. A novel energetic combustion catalyst, 1, 8-dihydroxy-4, 5-dinitroanthraquinone nickel salt (DHDNENi), was firstly synthesized by the process of metathesis reaction in a yield of 91%, and its structure was characterized by IR, element analysis, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The thermal behavior and non-isothermal decomposition reaction kinetics of DHDNENi were studied by means of different heating rate differential scanning calorimetry (DSC). The kinetic equation of major exothermic decomposition reaction for DHDNENi is obtained. The self-accelerating decomposition temperature (TSADT) and critical temperature of thermal explosion (Tb) are 574.4K and 593.4K, respectively. The thermal stability of DHDNENi is good.

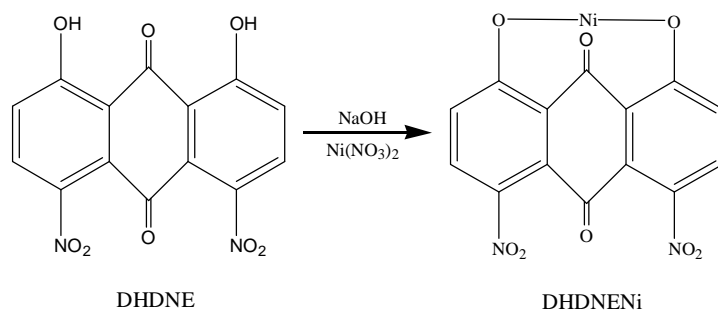
1. Introduction

Combustion catalyst as a ballistic modifier is an important ingredient in solid rocket propellant [1-3]. These are generally metal salts of carboxylic acids, and salts of aromatic carboxylic acids are found effective as combustion catalysts [4-8]. However, the carboxylic acid moiety in these salts is inert and does not contribute to the energetic [9-11]. In other hand, most combustion catalyst was organic lead compounds, the toxicities of lead compounds have attracted people's much more attention in these decades, and new kinds of combustion catalysts replacing lead compounds need to be found [12-14]. Nickel compounds, with their catalytic effect close to lead compounds, have been used as eco-friendly combustion catalysts documented in many literatures.

1, 8-dihydroxy-4, 5-dinitroanthraquinone (DHDNE) was an energetic compound with acidity. The structure contains acid group, energetic group and more carbon content. So it could be used as the intermediate to synthesize energetic combustion catalyst. In this paper, the structure of nickel salt of 1, 8-dihydroxy-4, 5-dinitroanthraquinone (DHDNENi) was designed and synthesized, a kind of new metal salt of 1, 8-dihydroxy-4, 5-dinitroanthraquinone, can be used as a green energetic combustion catalyst to modify combustion performance of solid propellants. The studies on the thermal behaviors and catalysis are a very important starting point for the selection, application and exploitation of DHDNENi. To the best of our knowledge, there is no report about it.

The aim of this work is to use the acidity of DHDNE synthesizing DHDNENi (scheme 1), and gain the thermolysis kinetics of DHDNENi under static state by means of differential scanning calorimetry (DSC) at different heating rate [15-17].





Scheme 1. Synthetic routes of DHDNENi.

2. Results and discussion

2.1. Structural analysis of DHDNENi

2.1.1. The RSFTIR spectrum of DHDNENi at room temperature. The RSFTIR spectrum of DHDNENi at room temperature is shown in figure 1. The antisymmetric and symmetric stretching vibration absorptions of C-NO₂ bonds ($\nu_{\text{as}}(\text{C-NO}_2)$ and $\nu_{\text{s}}(\text{C-NO}_2)$) are at 1548 and 1311 cm⁻¹, the $\nu_{\text{as}}(\text{-C=O})$ peak at 1684cm⁻¹.

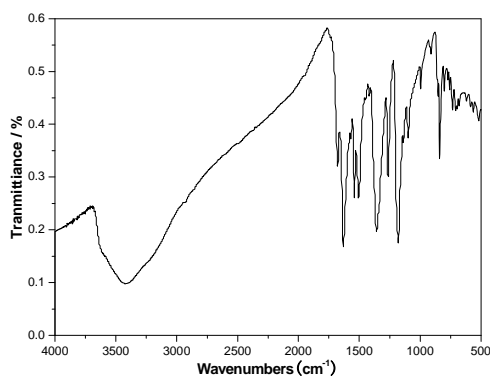


Figure 1. RSFTIR spectrum of DHDNENi at room temperature.

2.1.2. The TG curve of DHDNENi. The TG curve for DHDNENi is shown in figure 2. TG curve shows the mass loss process of DHDNENi is divided into two stages. The first stage begins at about 360K and completes at 553K with a mass loss of 12.8%, and the second stage begins at 586K and completes at 606K with a mass loss of 71.4%. The mass residue ratio is 15.8%. We can deduce that the structure of DHDNENi may contain three crystals water, and the main component of the residue is NiO and some hydrocarbon polymer.

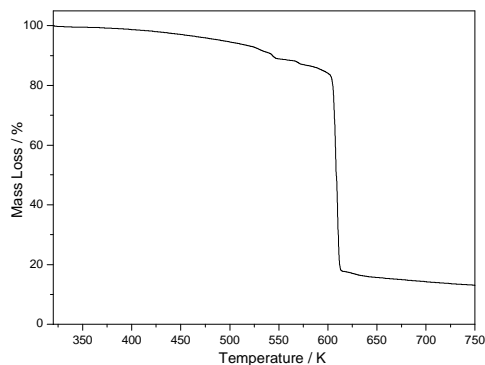


Figure 2. TG curve for the title compound at a heating rate of 10K min^{-1} .

2.1.3. Elemental analysis and X-ray fluorescence of DHDNENi. The elemental analysis can test the content of organic elements (C, H, N, O, et al), and the X-ray fluorescence tests the content of metal. The results of elemental analysis and X-ray fluorescence are C 38.10, H 2.275, N 6.33, O 39.99 and Ni 13.30, respectively.

According to the results of RSFTIR, TG, elemental analysis and X-ray fluorescence, the molecular formula of DHDNENi is can be deduced, and it is $\text{C}_{14}\text{H}_4\text{N}_2\text{O}_8\text{Ni} \cdot 3\text{H}_2\text{O}$.

2.2. The thermal decomposition behavior of DHDNENi under static N_2 gas condition. The typical DSC curve (figure 3) indicates that thermal behavior of DHDNENi present one stage. The stage is an obvious exothermic decomposition process. The extrapolated onset temperature and peak temperature of the process are 575.1K and 659.7K at the heating rate $10.0\text{K} \cdot \text{min}^{-1}$, respectively.

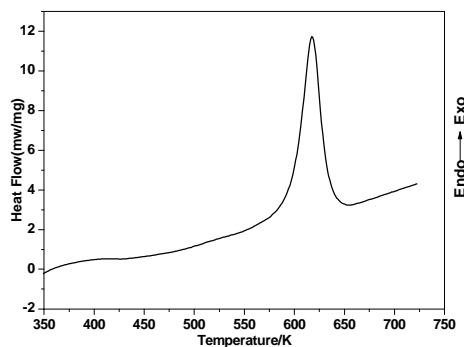


Figure 3. DSC curve for the title compound at a heating rate of 10K min^{-1} .

2.3 Non-isothermal decomposition kinetics of DHDNENi. In order to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the two main exothermic decomposition reactions for the title compound, a multiple heating method (Kissinger's method [18] and Ozawa's method [19]) was employed as follows:

Kissinger's equations:

$$\ln \left(\frac{\beta}{T_p^2} \right) = \ln \frac{AR}{E} - \frac{E}{R T_p} \quad (1)$$

Ozawa's equations:

$$\log \beta + \frac{0.4567E}{RT_p} = C \quad (2)$$

where T_p is the peak temperature (K), β is the linear heating rate (K min⁻¹), E is the apparent activation energy (kJ mol⁻¹), A is the pre-exponential constant (s⁻¹), R is the gas constant (J mol⁻¹ K⁻¹) and C is a constant.

The measured values of the extrapolated onset temperature (T_e), peak temperature (T_p) and enthalpy (ΔH_d) of the exothermic decomposition reaction were listed in table 1. The values of T_{e0} and T_{p0} in the stage corresponding to $\beta \rightarrow 0$ obtained by equation (3) were also listed in table 1 [19].

$$T_{(0,e \text{ or } p)i} = T_{(00,e0 \text{ or } p0)} + n\beta_i + m\beta_i^2 \quad i = 1 \sim 4 \quad (3)$$

where n and m are coefficients.

Table 1. The values of T_e , T_p , T_{e0} and T_{p0} of the exothermic decomposition stage for DHDNENi determined from the DSC curves at various heating rates (β).

β (K min ⁻¹)	T_e (K)	T_p (K)	T_{e0} (K)	T_{p0} (K)
5.0	586.3	605.2		
10.0	598.7	618.0	574.4	592.7
15.0	611.6	631.1		

The kinetic parameter values (E and A) determined by Kissinger method and Ozawa method and linear correlation coefficients (r) were listed in table 2. We can see that the apparent activation energy (E) obtained by Kissinger method agrees well with that obtained by Ozawa method, and the linear correlation coefficients are all very close to 1. So, the result is credible.

Table 2. The kinetic parameters obtained by the data in table 1^a.

E_k (kJ mol ⁻¹)	$\log(A/s^{-1})$	r_k	E_o (kJ mol ⁻¹)	r_o
156.1	11.1	0.9998	153.7	0.9999

^a Subscript k, data obtained by Kissinger's method; subscript o, data obtained by Ozawa's method.

By substituting corresponding data (β_i , T_i and α_i , $i=1, 2, 3, \dots$) into equation (2), the values of E for any given value of α (the conversion degree) were obtained and shown in figure 4. We can see that the values of E steadily distribute from 148.1 kJ mol⁻¹ to 1158.1 kJ mol⁻¹ in the α range of 0.3-0.9, and the average value of E is 152.8 kJ mol⁻¹, which is in agreement with that obtained by Kissinger's method and Ozawa's method from only peak-temperature values. So, the values were used to check the validity of E by other methods.

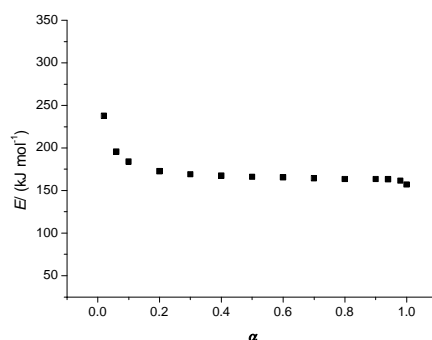


Figure 4. E_a vs α curve for the decomposition reaction of DHDNENi by Ozawa's method.

The four integral equations (Ordinary-integral, MacCallum-Tanner, Šatava-Šesták, Agrawal) were cited to obtained the values of E , A and the most probable kinetic model function ($f(\alpha)$) from each single DSC curve [20].

Forty-one types of kinetic model functions in reference [20] and corresponding experimental data form DSC curve at different heating rates were put into the four equations (Ordinary-integral, MacCallum-Tanner, Šatava-Šesták, Agrawal) for calculating, respectively. The kinetic parameters (E and A), probable kinetic model function and linear correlation coefficient (r) are presented in table 3. We can see that their values of E and $\lg A$ obtained by the five equations agree well with each other, and the mean value is close to that obtained by Kissinger method and Ozawa method. So, we can conclude that the most probable kinetic model function of the exothermic decomposition reaction is classified as

$f(\alpha) = 2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$, Jander equation ($n=1/2$) (No.13), and

$G(\alpha) = [- \ln(1-\alpha)]^{1/2}$, according to the unanimity rule of calculation results to each model equation.

So, the kinetic equation of the exothermic decomposition reaction can be described as:

$$\frac{d\alpha}{dT} = \frac{10^{11.1}}{\beta} 2(1-\alpha)[- \ln(1-\alpha)]^{1/2} \exp(-1.561 \times 10^5 / RT) \quad (4)$$

Table 3. Calculated values of kinetic parameters of decomposition reaction.

β/K min^{-1}	Eq.	$E / \text{kJ mol}^{-1}$	$\lg (A/\text{s}^{-1})$	r
5.0	Ordinary-integral	156.0	11.1	0.9967
	Mac Callum-Tanner	158.7	11.2	0.9971
	Šatava-Šesták	157.9	11.2	0.9971
	Agrawal	156.0	11.1	0.9967
10.0	Ordinary-integral	150.3	10.6	0.9978
	Mac Callum-Tanner	153.1	10.8	0.9981
	Šatava-Šesták	152.7	10.8	0.9981
	Agrawal	150.3	10.6	0.9978
20.0	Ordinary-integral	148.1	10.4	0.9975
	Mac Callum-Tanner	151.1	10.7	0.9979
	Šatava-Šesták	150.9	10.7	0.9979
	Agrawal	148.1	10.4	0.9975
mean		152.8	10.8	

2.4. Self-accelerating Decomposition Temperature (T_{SADT}) and critical temperature of thermal explosion (T_b). The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are important parameters required to insure safe storage and process operations for the energetic materials and then to evaluate the thermal stability. T_{SADT} and T_b can be obtained by equation (5) and equation (6), respectively. So, T_{SADT} and T_b of DHDNENi are 574.4K and 593.4K, respectively. They are all high, indicating that the thermal stability of the title compound is good.

$$T_{\text{SADT}} = T_{e0} \quad (5)$$

where a and b are coefficients.

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O RT_{e0}}}{2R} \quad (6)$$

where E_O is the apparent activation energy obtained by Ozawa method.

3. Experimental

3.1. Synthesis

DHDNENi used in this work was prepared according to the following method: 1,8-dihydroxy-4,5-dinitroanthraquinone (3.30g ,0.01mol) and NaOH (0.84g,0.021mol) were dissolved in 100mL H₂O and the pH was about 8. The reaction mixture was stirred at 60°C for 1 hour, then Ni(NO₃)₂ (2.91g ,0.01mol) dissolving in 20mL H₂O was added into the above reaction solution. The resulting solids were filtered and dried by air. The product obtained is 3.61g, and the yield of 93.3%.

3.2 Experimental instruments and conditions of thermal analysis

DSC measurements were carried out on a Model TA-910 USA instruments. The operation conditions were as follows: heating rates, 2.5K·min⁻¹, 5K·min⁻¹, 10K·min⁻¹ and 20K·min⁻¹; sample mass, 0.5 mg ~1mg; aluminium sample cell; atmosphere, static nitrogen with 0.1MPa.

4. Conclusion

(1) Nickel salt of 1, 8-dihydroxy-4, 5-dinitroanthraquinone (DHDNENi) was synthesized by the process of metathesis reaction, and its structure was characterized by IR, element analysis, TG and DSC.

(2) The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction of DHDNENi obtained by Kissinger's method are 156.1 kJ mol⁻¹ and 10^{11.1} s⁻¹, respectively. The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are 574.4K and 593.4K, respectively.

(3) The thermal behavior and non-isothermal decomposition reaction kinetics of DHDNENi were studied by means of different heating rate differential scanning calorimetry (DSC). The kinetic equation of major exothermic decomposition is

$$\frac{d\alpha}{dT} = \frac{10^{11.1}}{\beta} 2(1-\alpha)[- \ln(1-\alpha)]^{1/2} \exp(-1.561 \times 10^5 / RT)$$

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Acknowledgments

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