

Effect of Mechanochemically Synthesized CuI on the Thermal Decomposition Kinetics of Ammonium Nitrate

L. Mussapyrova^{1,2}, D. Muktaly¹, A. Batkal¹, K. Kamunur^{1,2*}

¹Al-Farabi Kazakh National University, Al-Farabi Ave., 71, Almaty, Kazakhstan

²Institute of Combustion Problems, Bogenbay Batyr Str., 172, Almaty, Kazakhstan

ARTICLE INFO

Received
25.05.2026

Received in revised form
28.07.2026

Accepted
11.08.2026

Keywords:

mechanochemical
synthesis; copper(I)
iodide(CuI); thermal
decomposition; catalytic
effect; activation energy

ABSTRACT

In this work, the catalytic effect of copper (I) iodide (CuI) synthesized by a mechanochemical method on the thermal decomposition of ammonium nitrate (NH_4NO_3) was studied. CuI was obtained by ball milling $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KI at 300–400 rpm for 60–120 min. The results of X-ray phase analysis showed that CuI, with high phase purity, formed after 120 min of processing. The composite systems were prepared based on NH_4NO_3 by adding 1, 3, and 5 wt.% CuI. DSC analysis was carried out in the temperature range of 25–500 °C and at heating rates of 5–20 °C·min⁻¹. While for pure ammonium nitrate the main thermal decomposition was observed at ~282 °C, the appearance of a pronounced exothermic peak at ~276 °C in the presence of CuI indicated an earlier reaction onset. In addition, it was found that the deepening of the endothermic effect at ~300 °C is associated with the intensive release of gaseous products. According to the results of kinetic analysis, the activation energy for pure NH_4NO_3 is in the range of 101.27–113.48 kJ·mol⁻¹, while with the introduction of 5 wt.% CuI, this value decreases to 81.37–94.59 kJ·mol⁻¹. In the second reaction stage, the activation energy decreases from 188.73 kJ·mol⁻¹ to 159.71 kJ·mol⁻¹. The observed decrease in activation energy is consistent with a mechanism reported in the literature involving $\text{Cu}^+/\text{Cu}^{2+}$ redox cycling and the possible formation of reactive radicals. The results show that CuI synthesized by the mechanochemical method significantly affects the thermal decomposition kinetics of ammonium nitrate, thereby decreasing the reaction energy barrier and increasing the system's overall reactivity.

1. Introduction

Currently, the regulation of the thermal decomposition mechanisms of oxidizers is considered one of the most important scientific directions to increase the efficiency of energy materials and pyrotechnic compositions [1–3]. Among the oxidizers widely used for this purpose, ammonium nitrate holds a special place, as it has a high oxygen balance and is relatively safe [4, 5]. Nevertheless, ammonium nitrate has several disadvantages, in particular its high hygroscopicity, insufficient thermal stability, and the onset of decomposition at relatively high temperatures. These factors limit the effectiveness of this compound in energy systems to some extent.

In recent years, research has focused on using various catalysts to reduce the thermal decomposition temperature of ammonium nitrate and increase

the reaction rate [6–10]. In this regard, special attention is paid to the effectiveness of transition-metal compounds. It has been found that copper-based nanostructured materials, including oxides and ferrites, can reduce the decomposition temperature of ammonium nitrate and reduce the activation energy [11–12]. In addition, it has been shown that the formation of metal-nitrate-type intermediates, catalyzed by a catalyst, affects the reaction mechanism and increases the intensity of gaseous product formation [13].

One of the compounds that has received special attention in this direction is copper(I) iodide (CuI). Its high electrical conductivity, stable crystal structure, and the presence of active surface centers make this compound a promising material for use in catalytic processes [14–16]. In particular, the mechanochemical preparation of CuI increases particle dispersion

*Corresponding author: K. Kamunur; E-mail address: kkamunur@gmail.com

and enhances their reactivity. Mechanochemical synthesis, which is carried out without a solvent or with a small amount of solvent, is an energy-efficient and environmentally safe method that has become widespread in recent years [17]. Nevertheless, it cannot be said that the effect of mechanochemically prepared CuI particles on the thermal decomposition of ammonium nitrate has been fully studied. In particular, systematic data on changes in the reaction's kinetic parameters in the presence of CuI, modifications to the decomposition mechanism, and the formation of gaseous products remain insufficient [18-19].

Accordingly, the present study aims to synthesize CuI via a mechanochemical method, investigate its structural and morphological characteristics, and comprehensively evaluate its effect on the thermal decomposition behavior of ammonium nitrate. The findings of this study provide a scientific basis for improving the performance of ammonium nitrate-based energetic systems and for the rational design of new catalytic additives. Previous studies have suggested that copper-containing catalysts accelerate the thermal decomposition of ammonium nitrate through electron transfer via the $\text{Cu}^+/\text{Cu}^{2+}$ redox cycle and the formation of reactive intermediates. However, this catalytic pathway has mainly been inferred from indirect experimental observations and has not been sufficiently verified for mechanochemically synthesized CuI. Therefore, the present study focuses on evaluating the catalytic effect of CuI via thermal and kinetic analyses, while the mechanistic interpretation is discussed based on prior literature.

2. Materials and methods

2.1. Initial materials

Chemical compounds with analytical purity $\geq 99\%$ were used as starting reagents in the study. Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was used as a source of copper, and potassium iodide (KI) was used as a source of iodide ions. Ammonium nitrate (NH_4NO_3) was chosen as the oxidizing agent for thermal studies. All reagents used were obtained from commercial suppliers and used without further purification. Samples were stored in a dry environment and protected from moisture until the start of the experiment.

2.2. Mechanochemical Synthesis of CuI

CuI particles were synthesized by the mechanochemical method in a planetary ball mill. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KI were used in a stoichiometric ratio for the reaction. The mixture was placed in a steel drum with steel balls with a diameter of 5–10 mm and subjected to mechanical processing.

Synthesis parameters:

- rotation speed: 300–400 rpm
- processing time: 60–120 min
- ball/powder ratio: 10:1

As a result of the mechanochemical effect, a redox-exchange reaction occurs, Cu^{2+} ions are reduced to the Cu^+ state, and the CuI phase is formed. The obtained powder was washed with water, dried in vacuum, and used for further analysis

2.3. Structural and morphological analysis of mechanochemically synthesized CuI

Modern analytical methods were used to characterize the structural and morphological properties of Copper(I) iodide samples synthesized by mechanochemical synthesis. To determine the phase composition and crystal structure, an X-ray diffractometer (XRD) DW-XRD-27mini ($\text{CuK}\alpha$ radiation source) was used. Based on the diffractograms obtained, the sample's crystalline phases were identified, and its structural features were evaluated. The morphology and particle sizes of the samples were studied using a scanning electron microscope (SEM), Thermo Scientific Phenom XL G2 Desktop SEM. In addition, energy-dispersive X-ray spectroscopy (EDX) was used to determine the elemental composition and distribution. The results of the comprehensive analysis enabled assessment of the structural integrity, morphological features, and the consistency of the elemental composition of the synthesized CuI materials.

2.4. Preparation and thermal analysis of NH_4NO_3 -CuI composite mixtures

Model compositions based on ammonium nitrate were prepared by mechanical mixing. NH_4NO_3 was used as the main oxidant, and mechanochemically synthesized Copper(I) iodide was added to it in different amounts (1, 3, and 5 wt.%). The mixtures were mixed until a uniform distribution of the components was ensured on an agate plate, and then stored in hermetic containers. The thermal properties of the prepared composite systems were studied by differential scanning calorimetry (DSC). The analysis was carried out over the temperature range of 25–500 °C at heating rates of 5, 10, 15, and 20 °C min^{-1} in a nitrogen atmosphere. Based on the DSC

curves obtained, the onset and maximum decomposition temperatures, the nature of the exothermic effects, and the reaction stages were determined. To ensure the reproducibility of the experimental results, all mechanochemical synthesis procedures, DSC measurements, and kinetic analyses were performed at least three times independently under identical experimental conditions. The reported values correspond to the average of repeated measurements, and good agreement across independent experiments confirmed the reproducibility of the results. The experimental uncertainty in the measured thermal parameters was estimated to be $\pm 2^\circ\text{C}$, and the relative experimental error did not exceed 5%.

2.5. Calculation of kinetic parameters

The Kissinger method was used to estimate the thermal decomposition kinetics. The activation energy was calculated from the maximum temperatures measured at different heating rates [20].

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \text{const} \quad (1)$$

where: β – heating rate; T_p – exothermic peak temperature; E_a – activation energy; R – universal gas constant.

The kinetic parameters obtained allow us to quantitatively assess the effect of the CuI catalyst on the decomposition of ammonium nitrate.

3. Results and Discussion

3.1. Structural and Morphological Characterization of CuI

The structural and morphological characteristics of Copper(I) iodide materials synthesized by mechanochemical methods are the primary determinants of their physicochemical properties and catalytic activity in energy systems. In particular, the phase composition, degree of crystallinity, particle size distribution, and surface morphology directly affect the material's reactivity and the characteristics of its interactions with oxidizing components.

It is known that the mechanochemical synthesis process contributes to the formation of highly dispersed particles and an increase in structural defects, which, in turn, can enhance the material's surface activity [21]. In this regard, a comprehensive study of the crystal structure and micromorphological features of the obtained CuI samples is important for explaining their characteristics during

subsequent thermal processes. The phase composition of the synthesized material at different stages of ball-mill synthesis of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ system is shown in Fig. 1.

Figure 1 shows the X-ray phase composition of the samples obtained as a result of mechanochemical treatment of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ system for different times. Although the formation of the CuI phase as the main product was observed during grinding for 60 min (a), the presence of additional reflexes belonging to the K_2SO_4 and K_3OI phases in the diffractogram indicates that the reaction is not completely completed and by-products are retained in the system. This indicates that the interaction between the solid phases is incomplete due to the lack of mechanical action and that complex reaction pathways occur, accompanied by partial oxidation of iodide ions. When the grinding time is increased to 120 min, the reflexes of the CuI phase (b) become clearly dominant, and the intensity of foreign phases decreases significantly, which is explained by the increase in mechanochemical activation, the increase in the degree of particle crushing and the deeper course of the reaction. However, the preservation of weak traces of potassium-containing phases indicates that their complete conversion is not ensured solely by mechanical processing. In this regard, the obtained powders were further purified by leaching with water, since potassium salts are highly soluble in water, whereas CuI is insoluble in water. The X-ray phase analysis of the purified copper iodide is shown in Fig. 2.

Figure 2 shows the X-ray phase composition of the product purified by water leaching after mechano-

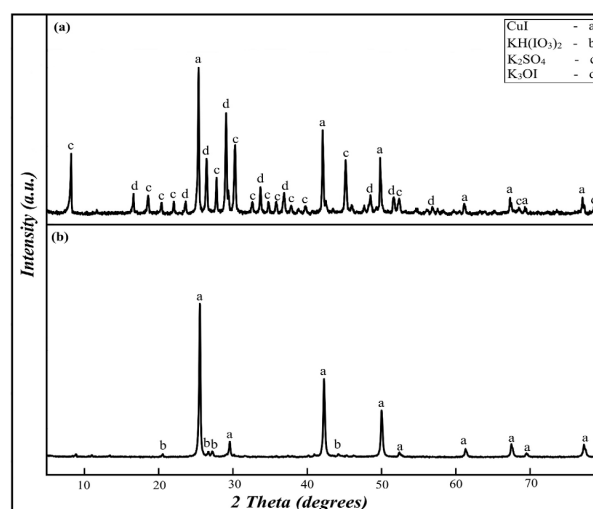


Fig. 1. X-ray phase composition of products obtained from the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ system at different rotation times in a ball mill: (a) 60 min; (b) 120 min.

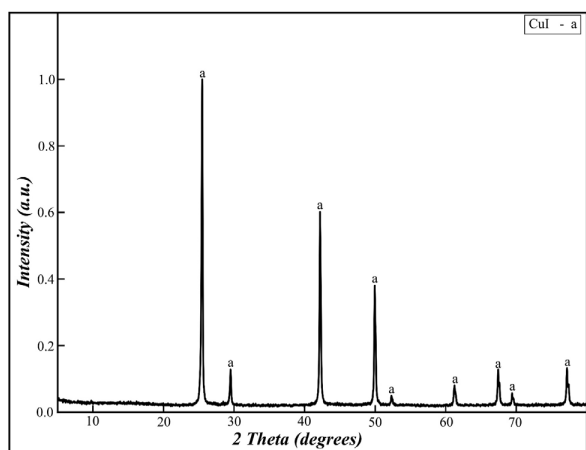


Fig. 2. XRD pattern of purified CuI after water washing.

chemical synthesis. The preservation of reflections characteristic only of the CuI phase in the diffractogram, and the complete disappearance of additional potassium-containing phases such as $\text{KH}(\text{IO}_3)_2$, K_2SO_4 , and K_3OI observed in previous samples, confirm the high efficiency of the purification process. This is explained by the high solubility of potassium salts in water and their ease of separation from the solid phase, whereas the insolubility of CuI allows its structure to be preserved. In addition, the high in-

tensity and clarity of the diffraction peaks indicate that the material is well-crystallized and that the structure formed during mechanochemical treatment is not destroyed. The results show that combining mechanochemical synthesis with subsequent water leaching is an effective method for obtaining CuI with high phase purity from the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ system.

Figure 3 shows the morphological and elemental characteristics of CuI samples obtained by the mechanochemical method in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ system. SEM analysis allows us to determine the particle structure and changes during processing, while EDX analysis allows us to assess the compositional purity of the product obtained from the synthesis.

Figure 3 presents the morphological and elemental characteristics of CuI samples synthesized by the mechanochemical method in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ system. The obtained SEM micrographs (3a) show that the initial product is finely dispersed, consisting of particles of various sizes, agglomerated and has a rough surface structure, which is explained by the simultaneous processes of particle crushing and re-aggregation under the influence of high-energy impacts during mechanochemical treatment. In the sample after water treatment (3b), the morphology

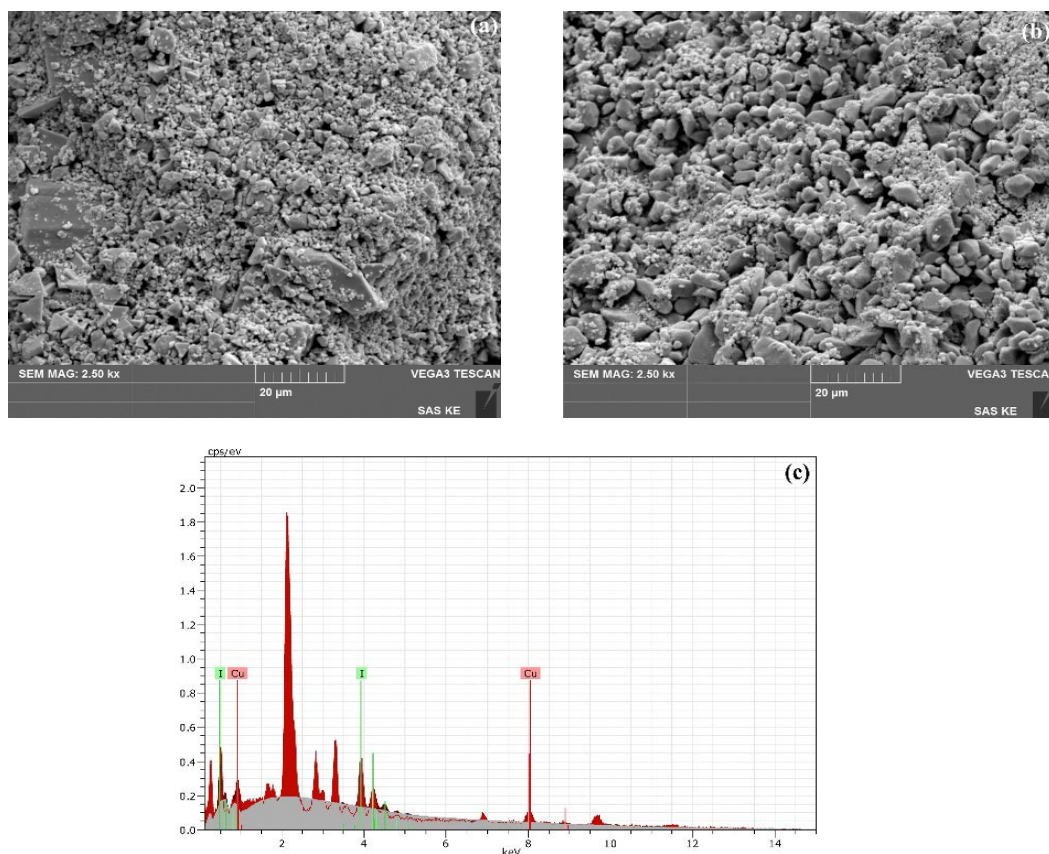


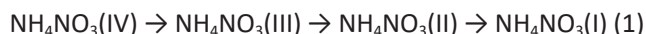
Fig. 3. Micromorphology and elemental composition of CuI samples obtained by mechanochemical synthesis in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ system: (a) synthesized CuI; (b) water-purified CuI; (c) EDX spectrum.

of the particles is somewhat clarified, the disintegration of large agglomerates and the formation of a relatively homogeneous structure are observed, which is associated with the removal of side reaction products (e.g., soluble salts). In addition, after surface cleaning, the particle shape becomes clearly visible, and porosity increases. The EDX spectrum (3c) confirms the presence of Cu and I as the main elements, which proves the formation of the CuI phase. The absence of pronounced peaks of foreign elements in the spectrum indicates that the synthesis was carried out with relatively high purity. Overall, the results indicate that the mechanochemical method is effective for synthesizing CuI, and that the subsequent water treatment stage plays an important role in increasing the structural homogeneity and purity of the product.

3.2. Thermal decomposition behavior and thermokinetic analysis of ammonium nitrate-CuI compositions

This section comprehensively considers the features of thermal decomposition of ammonium nitrate-based systems in the presence of CuI and their kinetic characteristics. The aim is to determine the effect of CuI addition on the thermal stability of Ammonium Nitrate (AN), decomposition stages and reaction rate. In this regard, the thermal characteristics of the systems were evaluated by DSC analysis, and the temperature parameters of the main exothermic and endothermic processes (T_{onset} , T_{max} , T_{offset}) were determined. In addition, based on the experimental data obtained, the reaction kinetics were analyzed and the laws of the decomposition process at different heating rates (β) were studied. The features of thermal decomposition of ammonium nitrate-based systems in the presence of CuI are shown in Fig. 4.

Figure 4 shows the typical DSC curves for the AN and AN–CuI systems, illustrating their thermal behavior. The endothermic peaks observed in the low-temperature region (~56 °C and ~131 °C) are associated with polymorphic phase transitions in ammonium nitrate. These transitions result from the rearrangement of the crystal lattice without changing the chemical composition. These transformations are expressed as follows [3] (1):



Therefore, these processes are considered as structural changes accompanied by heat absorption. In the presence of CuI, a slight change in peak tem-

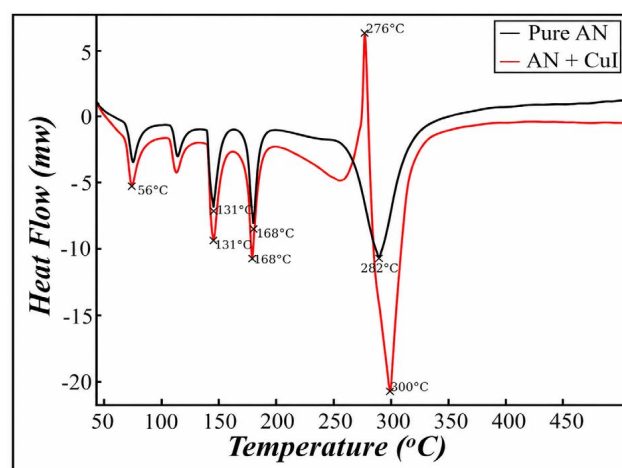


Fig. 4. DSC curves of pure AN and AN–CuI compositions.

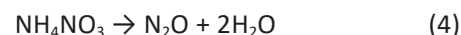
perature and intensity indicates that the mixture's crystal lattice stability is affected to some extent. The endothermic effect observed at ~168 °C is associated with the melting of ammonium nitrate [3]:



At this stage, the substance transitions from solid to liquid, and the prerequisites for further thermal decomposition of the system are established. In the high temperature region (~250–300 °C), the main thermal decomposition processes of AN occur. In the first stage, ammonium nitrate can dissociate into ammonia and nitric acid [5]:



Then the main decomposition reaction occurs [5]:

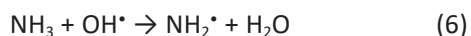


For pure AN, this phenomenon manifests itself as an endothermic effect observed around ~282 °C and is also accompanied by the release of gaseous products.

In the AN–CuI system, the thermal characteristics change significantly. In particular, the appearance of a pronounced exothermic peak in the region of ~276 °C indicates the catalytic effect of CuI. Based on previous literature, the catalytic effect of CuI may be attributed to electron transfer via the $\text{Cu}^+/\text{Cu}^{2+}$ redox couple, which could facilitate the formation of reactive intermediates during ammonium nitrate decomposition. Although this mechanism is consistent with the observed decrease in decomposition temperature and activation energy, it has not been directly verified in the present work and should therefore be regarded as a proposed reaction pathway. A possible catalytic pathway proposed in previous studies can be described as follows [22]:



According to Xu et al. [11], Cu-containing catalysts promote the homolytic decomposition of nitric acid, leading to the formation of NO₂-containing radical intermediates. The exact radical generation pathway was not directly investigated in the present work and is therefore discussed only as a literature-supported mechanism.



The formation of reactive intermediates such as NH₂^{*}, O^{*}, and OH^{*} has been proposed in previous studies as a possible consequence of Cu⁺/Cu²⁺-mediated electron transfer. This proposed mechanism is consistent with the experimentally observed decrease in decomposition temperature and activation energy. However, the formation of these radical species was not directly verified in the present study. In addition, the deep endothermic peak observed in the region of ~300 °C is clearly enhanced in the AN-CuI system. This phenomenon is associated with an increase in the intensity of the main decomposition reaction and the rapid release of gaseous products. The deepening of the endothermic effect indicates an increase in mass transfer and gas evolution in the system. The results suggest that the CuI additive modifies the thermal decomposition behavior of

ammonium nitrate. The decrease in the reaction onset temperature and activation energy is consistent with the proposed catalytic mechanism, although the formation of intermediate reactive species was not directly verified in this study. It should be emphasized that the present study provides indirect evidence for the catalytic action of CuI, based solely on DSC measurements and kinetic analysis. No in situ spectroscopic, electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), or other direct techniques were employed to verify the Cu⁺/Cu²⁺ redox cycle or the formation of radical intermediates during ammonium nitrate decomposition. Therefore, the proposed catalytic mechanism should be regarded as a literature-supported interpretation rather than an experimentally confirmed reaction pathway.

The Kissinger and Ozawa–Flynn–Wall methods were used to estimate the kinetic parameters. The main focus of the analysis was on how the activation energy (*E_a*) changes. Based on this, it was possible to characterize the catalytic effect of CuI and assess its impact on the reaction. The temperature parameters (*T_{onset}*, *T_{max}*, *T_{offset}*) of the AN and AN–CuI systems at different DSC heating rates are given in Table 1.

The DSC results shown in Table 1 show the dependence of the thermal decomposition parameters of the AN and AN-CuI systems on the heating

Table 1. Thermal parameters of the DSC curves of pure AN and AN–CuI compositions at different heating rates

Sample	β, (Heating rate, °C·min ⁻¹)	Thermal Decomposition					
		1 st Step			2 nd Step		
		<i>T_{onset}</i>	<i>T_{offset}</i>	<i>T_{max}</i>	<i>T_{onset}</i>	<i>T_{offset}</i>	<i>T_{max}</i>
Pure AN	5	225.4	276.3	267.3	-	-	-
	10	238.1	294.1	277.2	-	-	-
	15	239.5	307.9	288.5	-	-	-
	20	250.3	315.5	296.3	-	-	-
AN with 1 wt.% CuI	5	222.9	259.3	235.5	263.2	286.5	281.1
	10	239.1	262.8	246.3	269.9	298.4	292.3
	15	247.4	268.1	254.7	271.5	299.4	296.1
	20	248.0	268.7	263.1	272.8	305.2	297.7
AN with 3 wt.% CuI	5	243.5	278.2	262.8	287.8	313.7	298.2
	10	257.4	287.9	273.3	278.9	317.1	306.3
	15	260.4	290.6	284.7	294.1	322.2	313.6
	20	273.8	293.2	292.8	297.8	324.7	318.2
AN with 5 wt.% CuI	5	213.6	242.1	231.8	243.6	275.3	301.1
	10	219.8	247.8	242.4	248.3	293.5	315.7
	15	235.7	265.6	251.9	265.7	298.3	319.4
	20	246.7	270.7	263.1	271.6	298.6	322.1

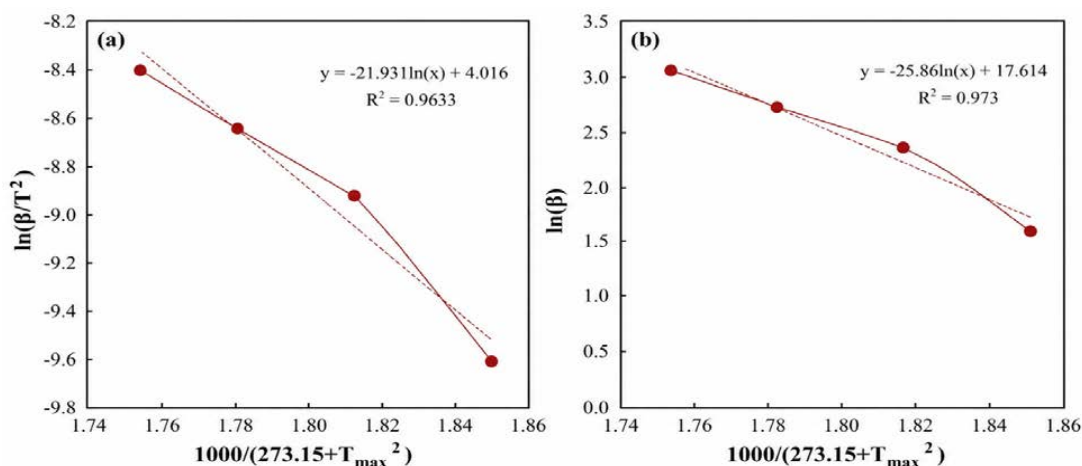


Fig. 5. Kissinger (a) and Ozawa (b) plots of a pure AN.

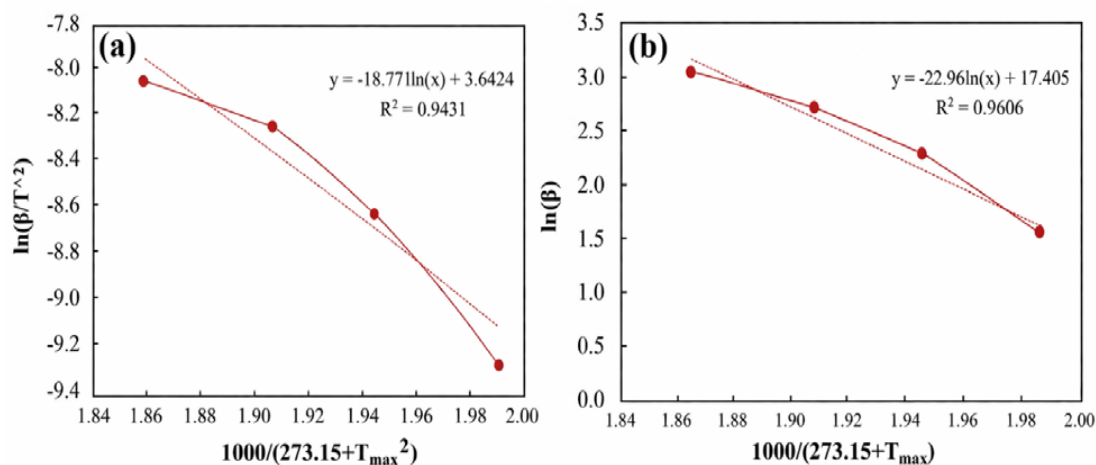


Fig. 6. Kissinger (a) and Ozawa (b) plots of an AN-CuI composite systems.

rate. Using these temperature results, kinetic parameters were determined based on the Kissinger and Ozawa-Flynn-Wall methods.

In order to determine the kinetic characteristics of the studied systems, the $\ln(\beta/T^2) - 1/T$ and $\ln(\beta) - 1/T$ dependences were constructed, and Kissinger and Ozawa plots were obtained, respectively (Figs. 5-6). Based on the slope angles of the obtained linear dependences, the activation energy values were calculated and compared with the value of the initial ammonium nitrate.

The activation energy of the system was calculated using various methods using graphs based on the $\ln(\beta/T^2) - 1/T$ and $\ln(\beta) - 1/T$ dependences, and the relative values are given in Table 2.

The results presented in Table 2 show a clear change in the kinetic parameters of the systems based on ammonium nitrate and CuI. According to the data in the table, the activation energy for pure AN is relatively high, indicating its high thermal sta-

bility. When CuI is introduced, a gradual decrease in the E_a values is observed in the first stage, especially at 5 wt.% CuI. This proves that the catalyst reduces the energy barrier in the initial stage of the reaction and facilitates decomposition. A similar trend is observed in the second stage: with an increase in the CuI content, the activation energy decreases, but its values remain higher than in the first stage. This indicates that the subsequent reactions in the multi-stage decomposition mechanism are more complex. The obtained data show that the CuI catalyst effectively changes the kinetics of the thermal decomposition of ammonium nitrate, reduces the energy barrier of the reaction and increases the reactivity of the system.

4. Conclusion

The study found that copper(I) iodide synthesized by the mechanochemical method exhibits a pro-

Table 2. Relative E_a values of composites calculated by different methods

Composite mixture	1 st Step				2 nd Step			
	$E_a/(kJ \cdot mol^{-1})$	R^2	$E_a/(kJ \cdot mol^{-1})$	R^2	$E_a/(kJ \cdot mol^{-1})$	R^2	$E_a/(kJ \cdot mol^{-1})$	R^2
	Kissinger's Method		Ozawa's Method		Kissinger's Method		Ozawa's Method	
Pure AN	101.27	0.96	113.48	0.97	-	-	-	-
AN with 1 wt.% CuI	96.49	0.97	108.96	0.98	188.73	0.95	196.63	0.96
AN with 3 wt.% CuI	96.13	0.96	108.59	0.97	173.86	0.98	182.55	0.99
AN with 5 wt.% CuI	81.37	0.94	94.59	0.96	159.71	0.94	169.1	0.95

nounced catalytic effect on the thermal decomposition of ammonium nitrate. The CuI samples obtained by processing in the $CuSO_4 \cdot 5H_2O$ and KI system at 400 rpm for 120 min exhibited high dispersion and phase purity. The results of X-ray phase analysis confirmed the complete elimination of foreign phases and the formation of a pure CuI structure. According to DSC analysis, the main decomposition process for pure NH_4NO_3 was observed at $\sim 282^\circ C$, whereas in systems with CuI (~ 1 -5 wt.%), a pronounced exothermic peak at $\sim 276^\circ C$ indicated that the reaction began earlier. In addition, it was found that the endothermic effect at $\sim 300^\circ C$ is associated with the intensive release of gaseous products and an increase in the process intensity. These results indicate that the CuI catalyst alters the thermal decomposition mechanism, shifting the process to a multi-step, highly reactive regime. The results of the kinetic analysis showed that the introduction of CuI significantly decreases the activation energy. In particular, while the activation energy of the first stage for pure NH_4NO_3 is in the range of 101.27 - $113.48\text{ kJ}\cdot\text{mol}^{-1}$, in the presence of 5 wt.% CuI this value decreases to 81.37 - $94.59\text{ kJ}\cdot\text{mol}^{-1}$. In the second stage, a decrease was observed, respectively, from $188.73\text{ kJ}\cdot\text{mol}^{-1}$ to $159.71\text{ kJ}\cdot\text{mol}^{-1}$. The observed decrease in activation energy is consistent with the catalytic mechanism proposed in the literature, involving Cu^+/Cu^{2+} redox cycling and the possible formation of reactive radical species. However, this interpretation is based on indirect experimental evidence, and the proposed reaction mechanism was not directly verified in the present study. Thus, mechanochemically synthesized CuI is an effective catalytic additive for ammonium nitrate-based systems. It reduces the energy barrier of the reaction, reduces the decomposition temperature, and increases the overall reactivity of the system. The results obtained can serve as a scientific basis for the design of new catalytic systems to increase the efficiency of energetic materials and pyrotechnic compositions. Future studies employing in situ spectroscopic techniques and radical detection methods are required to direct-

ly verify the proposed Cu^+/Cu^{2+} redox mechanism and the formation of reactive intermediates during the thermal decomposition of ammonium nitrate in the presence of mechanochemically synthesized CuI.

Author Contributions

Lyazzat Mussapyrova – Methodology, Investigation, Writing – Review & Editing. **Dinara Mukhtaly** – Investigation, Formal Analysis. **Aisulu Batkal** – Methodology, Investigation. **Kaster Kamunur** – Conceptualization, Formal Analysis, Data Curation, Writing – Original Draft, Writing – Review & Editing, Supervision, Project Administration.

Conflict of Interest

The authors declare that they have no conflict of interest.

Funding

This research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant no. BR28712843).

References

[1]. L.Q. Gong, J.J. Jiang, J.H. Gong, Y. Pan, J.C. Jiang. Experimental and numerical simulation study on thermal decomposition model of ammonium nitrate. *Process Safety and Environmental Protection* 171 (2023) 717-725. <https://doi.org/10.1016/j.psep.2023.01.044>.

[2]. Z. Han, S. Sachdeva, M.I. Papadaki, M.S. Mannan. Ammonium nitrate thermal decomposition with additives. *Journal of Loss Prevention in the Process Industries* 35 (2015) 307-315. <https://doi.org/10.1016/j.jlp.2014.10.011>.

[3]. R. Kazemshoar-Duzdüzani, A. Mousaviazar, K. Ghani. Effect of Covalent Organic Framework COF-43 on the Thermal Decomposition and Phase Transition of

- Ammonium Nitrate. Chemical Engineering Journal Advances (2026) 101101. <https://doi.org/10.1016/j.cej.2026.101101>.
- [4]. P. Priyananda, A.M. Djerdjef, N. Paris, B.S. Hawkett. A Study on Preventing Thermal Runaway of Contaminated Ammonium Nitrate Prill in Bulk Storage. *Propellants, Explosives, Pyrotechnics* (2026) e70130. <https://doi.org/10.1002/prep.70130>.
- [5]. S. Chaturvedi, P.N. Dave. Review on thermal decomposition of ammonium nitrate. *Journal of Energetic Materials* 31 (2013) 1-26. <https://doi.org/10.1080/07370652.2011.573523>.
- [6]. Q. Lu, Y. Hu, J. Yang, H. Yang, L. Xiao, F. Zhao, et al. Thermal decomposition mechanism of ammonium nitrate on the main crystal surface of ferric oxide: experimental and theoretical studies. *Langmuir* 40 (2024) 2198-2209. <https://doi.org/10.1021/acs.langmuir.3c03158>.
- [7]. T. Ketegenov, R. Nadirov, B. Teltayev, B. Milikhat, B. Kalmuratova, H. Keiichi, K. Kamunur. The effect of CuO on the thermal behavior and combustion features of pyrotechnic compositions with AN/MgAl. *Sustainability* 16 (2024) 1488. <https://doi.org/10.3390/su16041488>.
- [8]. M. Atamanov, Z. Yelemessova, A. Imangazy, K. Kamunur, B. Lesbayev, Z. Mansurov, Q.L. Yan. The catalytic effect of CuO-doped activated carbon on thermal decomposition and combustion of AN/Mg/NC composite. *The Journal of Physical Chemistry C* 123 (2019) 22941-22948. <https://doi.org/10.1021/acs.jpcc.9b05094>.
- [9]. P.N. Dave, R. Sirach. Catalytic performance of nano-sized cobalt copper ferrite on thermal decomposition of ammonium nitrate. *Chemical Physics Impact* 6 (2023) 100155. <https://doi.org/10.1016/j.chphi.2022.100155>.
- [10]. P.N. Dave, R. Sirach. Thermal decomposition of ammonium nitrate (AN) in the presence of the optimized nano-ternary transition metal ferrite CoNiZnFe₂O₄. *Energy Advances* 1 (2022) 690-696. <https://doi.org/10.1039/D2YA00146B>.
- [11]. Z.X. Xu, G.S. Xu, X.Q. Fu, Q. Wang. The mechanism of nano-CuO and CuFe₂O₄ catalyzed thermal decomposition of ammonium nitrate. *Nanomaterials and Nanotechnology* 6 (2016) 1847980416681699. <https://doi.org/10.1177/1847980416681699>.
- [12]. Z. Cheng, J. Yin, X. Chu, T. Yang, Y. Gao, H. Zhong, L. Zhang. Synthesis of an Fe/Al composite nanocatalyst with improved catalytic stability for ammonium perchlorate decomposition. *Journal of Materials Science* 58 (2023) 9446-9458. <https://doi.org/10.1007/s10853-023-08632-y>.
- [13]. D. Halder, S. Sen, S. Roy. Recent advances in mechanistic studies and catalyst development for electrochemical nitrate reduction to ammonia. *Communications Chemistry* (2025). <https://doi.org/10.1038/s42004-025-01864-w>.
- [14]. A.C. Fernandez, K.M. Archana. Green synthesis, characterization, catalytic and antibacterial studies of copper iodide nanoparticles synthesized using Brassica oleracea var. capitata f. rubra extract. *Chemical Data Collection* 29 (2020) 100538. <https://doi.org/10.1016/j.cdc.2020.100538>.
- [15]. V. Gottschalch, S. Blaurock, G. Benndorf, J. Lenzner, M. Grundmann, H. Krautscheid. Copper iodide synthesized by iodization of Cu-films and deposited using MOCVD. *Journal of Crystal Growth* 471 (2017) 21-28. <https://doi.org/10.1016/j.jcrysgro.2017.04.033>.
- [16]. M. Jamshidi, J.M. Gardner. Copper (I) iodide thin films: Deposition methods and hole-transporting performance. *Molecules* 29 (2024) 1723. <https://doi.org/10.3390/molecules29081723>.
- [17]. L. Yang, Z. Pan, Z. Tian. Mechanochemical synthesis of solid catalysts and application in catalytic reaction. *ChemCatChem* 16 (2024) e202301519. <https://doi.org/10.1002/cctc.202301519>.
- [18]. B. Sharma, M.K. Rabinal. Ambient synthesis and optoelectronic properties of copper iodide semiconductor nanoparticles. *Journal of Alloys and Compounds* 556 (2013) 198-202. <https://doi.org/10.1016/j.jallcom.2012.12.120>.
- [19]. C. Xu, L. Lv, D. Luo, W. Liu. Synthesis, structure and photoluminescence properties of three copper (I) iodide based inorganic-organic hybrid structures with pyrazine derivatives. *New Journal of Chemistry* 44 (2020) 14103-14107. <https://doi.org/10.1039/D0NJ02364F>.
- [20]. S. Vyazovkin, E. Kissinger. Method in kinetics of materials: things to beware and be aware of. *Molecules* 25 (2020) 2813. <https://doi.org/10.3390/molecules25122813>.
- [21]. P. Chuayplod, D. Aht-Ong. Mechanochemical-assisted heterogeneous surface modification of parawood microcrystalline cellulose and its effect on the properties of polypropylene composites. *World Journal of Engineering* 15 (2018) 719-730. <https://doi.org/10.1108/WJE-03-2017-0056>.
- [22]. A.R.M. Cruz, E.M. Assaf, J.F. Gomes, J.M. Assaf. Active copper species of co-precipitated copper-ceria catalysts in the CO-PROX reaction: An in situ XANES and DRIFTS study. *Catalysis Today* 381 (2021) 42-49. <https://doi.org/10.1016/j.cattod.2020.09.007>.

About the Authors

D. Mukhtaly – Leading Researcher, Institute of Combustion Problems, Almaty, Kazakhstan
E-mail: dinara.mukhtaly@mail.ru
ORCID: <https://orcid.org/0000-0002-1139-5488>

L.A. Mussapyrova – PhD, Leading Researcher, Institute of Combustion Problems, Almaty, Kazakhstan
E-mail: lyazzat.mussapyrova@gmail.com
ORCID: <https://orcid.org/0000-0002-9881-1324>

A.N. Batkal – Researcher, Institute of Combustion Problems, Almaty, Kazakhstan
E-mail: abatkalova@mail.ru
ORCID: <https://orcid.org/0000-0002-2271-6953>

K. Kamunur – PhD, Leading Researcher, Associate Professor, Institute of Combustion Problems, Almaty, Kazakhstan
E-mail: kkamunur@gmail.com
ORCID: <https://orcid.org/0009-0006-0013-1926>

Влияние механохимически синтезированного CuI на кинетику термического разложения нитрата аммония

Л. Мусапирова^{1,2}, Д. Мукталы¹, А. Баткал¹, К. Камунур^{1,2*}

¹Казахский национальный университет им. аль-Фараби, пр. аль-Фараби, 71, Алматы, Казахстан

²Институт проблем горения, ул. Богенбай батыра, 172, Алматы, Казахстан

АННОТАЦИЯ

В данной работе исследовано каталитическое влияние йодида меди(I) (CuI), синтезированного механохимическим методом, на термическое разложение нитрата аммония (NH₄NO₃). CuI получали путем шарового помола CuSO₄·5H₂O и KI при скорости 300-400 об/мин в течение 60-120 мин. Результаты рентгенофазового анализа показали, что после 120 мин обработки формируется CuI с высокой фазовой чистотой. Композиционные системы готовили на основе NH₄NO₃ с добавлением 1, 3 и 5 мас.% CuI. DSC-анализ проводили в температурном диапазоне 25-500 °C при скоростях нагрева 5-20 °C·мин⁻¹. Если для чистого нитрата аммония основное термическое разложение наблюдалось в области ~282 °C, то появление выраженного экзотермического пика при ~276 °C в присутствии CuI свидетельствует о более раннем начале реакции. Кроме того, установлено, что углубление эндотермического эффекта в области ~300 °C связано с интенсивным выделением газообразных продуктов. Согласно результатам кинетического анализа, энергия активации для чистого NH₄NO₃ составляет 101,27-113,48 кДж·моль⁻¹, тогда как при введении 5 мас.% CuI она снижается до 81,37-94,59 кДж·моль⁻¹. На второй стадии реакции энергия активации уменьшается с 188,73 до 159,71 кДж·моль⁻¹. Наблюдаемое снижение энергии активации согласуется с механизмом, описанным в литературе, который включает окислительно-восстановительный цикл Cu⁺/Cu²⁺ и возможное образование реакционноспособных радикалов. Полученные результаты показывают, что CuI, синтезированный механохимическим методом, оказывает существенное влияние на кинетику термического разложения нитрата аммония, снижая энергетический барьер реакции и повышая общую реакционную способность системы.

Ключевые слова: механохимический синтез, йодид меди(I)(CuI), термическое разложение, каталитический эффект, энергия активации

Механохимиялық синтезделген CuI-дың аммоний нитратының термиялық ыдырау кинетикасына әсері

Л. Мусапирова^{1,2}, Д. Мұқталы¹, А. Батқал¹, Қ. Қамұнұр^{1,2*}

¹Әл-Фараби ат. Қазақ ұлттық университеті, әл-Фараби даң., 71, Алматы, Қазақстан

²Жану проблемалары институты, Бөгенбай батыр к., 172, Алматы, Қазақстан

АҢДАТПА

Бұл жұмыста механохимиялық әдіспен синтезделген мыс(I) йодидінің (CuI) аммоний нитратының (NH₄NO₃) термиялық ыдырауына тигізетін каталитикалық әсері зерттелді. CuI CuSO₄·5H₂O мен KI қоспасын 300-400 айн/мин жылдамдықта 60-120 мин бойы шарлы диірменде өңдеу арқылы алынды. Рентгенфазалық талдау нәтижелері өңдеудің 120 мин кейін жоғары фазалық тазалықтағы CuI түзілетінін көрсетті. Композициялық жүйелер NH₄NO₃ негізінде дайындалып, оған 1, 3 және 5 масс.% CuI қосылды. DSC талдауы 25-500 °C температура аралығында және 5-20 °C·мин⁻¹ қыздыру жылдамдықтарында жүргізілді. Таза аммоний нитраты үшін негізгі термиялық ыдырау ~282 °C аймағында байқалса, CuI қатысында ~276 °C шамасында айқын экзотермиялық пиктің пайда болуы реакцияның ертерек басталатынын көрсетті. Сонымен қатар, ~300 °C аймағындағы эндотермиялық эффекттің тереңдеуі газтәрізді өнімдердің қарқынды бөлінуімен байланысты екені анықталды. Кинетикалық талдау нәтижелері бойынша таза NH₄NO₃ үшін активация энергиясы 101,27-113,48 кДж·моль⁻¹ аралығында болса, 5 мас.% CuI енгізілгенде бұл мән 81,37-94,59 кДж·моль⁻¹ дейін төмендейді. Екінші реакция сатысында активация энергиясы 188,73 кДж·моль⁻¹-ден 159,71 кДж·моль⁻¹-ге дейін азаяды. Бақыланған активация энергиясының төмендеуі әдебиеттерде сипатталған Cu⁺/Cu²⁺ редокс-цикліне және реактивті радикалдардың ықтимал түзілуіне негізделген механизммен сәйкес келеді. Алынған нәтижелер механохимиялық әдіспен синтезделген CuI аммоний нитратының термиялық ыдырау кинетикасына елеулі әсер ететінін көрсетеді. Нәтижесінде реакцияның энергетикалық тосқауылы төмендеп, жүйенің жалпы реакциялық қабілеті артады.

Түйін сөздер: механохимиялық синтез, мыс(I) йодиді (CuI), термиялық ыдырау, каталитикалық әсер, белсендіру энергиясы