

## Some aspects of thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

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### Abstract

$\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  decomposition in air and in helium was studied using TG, DTA and MS and FTIR analyses. It was found that the dehydration phase of reaction is not complete. Remaining water occluded in the pores of nickel oxalate is not liberated until the decomposition of oxalate ions starts. The residual water takes part in reaction of the basic nickel carbonate formation. The basic nickel carbonate decomposition is a source of traces of nickel oxide stated in the final product of decomposition along with metallic nickel. It was found that the double peak endothermic DTA signal which accompanies decomposition of nickel oxalate results from changing of the microscopic mechanism of reaction.

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### 1. Introduction

Thermal decomposition  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  has been studied for many years. In the extensive reports on thermal decomposition of oxalates [1,2] the number of references concerning this process are cited. Despite the numerous works and publications on thermal decomposition of nickel oxalate dihydrate this reaction still remains the subject of investigations.

There are several effects that accompany this reaction which still have no clear explanation and give rise to many controversies. One of them is incomplete dehydration process and an inability to obtain anhydrous compound. The possibility of obtaining anhydrous nickel oxalate was discussed in several works. In paper [3] Authors stated that dried nickel oxalate can take up to 15% of original water on storing on air and that this water can be completely removed about 250 °C. Authors of Ref. [4] stored dehydrated nickel oxalate at 200 °C in the desiccator over  $\text{P}_2\text{O}_5$  for 2 years to remove residual water. After this time nickel oxalate re-absorbed 15% of water. Dehydration of nickel oxalate dihydrate in the dynamic vacuum led to the compound

of composition 99.2%  $\text{NiC}_2\text{O}_4$  and 0.8%  $\text{H}_2\text{O}$  [5]. The residual water was considered as the occluded water [6,7]. All the results quoted indicate that complete dehydration of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  to obtain anhydrous nickel oxalate cannot be achieved. However, in other papers full dehydration of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  was stated and the kinetics of decomposition of anhydrous nickel oxalate was determined [8].

The second unexplained effect related to nickel oxalate decomposition in inert atmosphere is the complex DTA/DSC peak corresponding to oxalate ions degradation. The complexity of DTA or DSC curve, manifested by a shoulder on the peak, was pointed out in many works [2,5–7,9–11]. The same shape shows the DTG curve [9]. The different explanations of this effect were given. It was supposed to be connected with the phase transition of nickel at Curie point [7,9] or with the formation of solid intermediate [8]. The secondary reaction of nickel with residual water was indicated as the cause of complex DTA signal in Ref. [5]. In Ref. [12] three stage mechanism of decomposition of  $\text{NiC}_2\text{O}_4$  was proposed and the differences in the particular reactions rate were assumed to be responsible for the complex DTA curve.

And finally there are still controversies concerning the primary and secondary reactions occurring during  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  decomposition. In most experiments performed in air NiO was

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claimed to be the primary product of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  decomposition. However, Authors of Refs. [10,13] suggest that the primary product of decomposition is Ni and NiO forms in result of secondary oxidation of nickel by oxygen. Almost everybody agrees that decomposition of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in inert atmosphere leads to the formation of Ni and  $\text{CO}_2$ , however some Authors suggest that Ni forms due to the reduction of the primary product NiO by CO in secondary reaction [14]. During decomposition in the atmosphere of  $\text{CO}_2$  metallic Ni was found as the product of  $\text{NiC}_2\text{O}_4$  decomposition by Authors of Ref. [10] whereas in paper [15] the final product of decomposition was NiO.

The objective of this work is to present new results concerning mentioned effects which shall throw some light on these controversial points in thermal decomposition of nickel oxalate dihydrate.

## 2. Experimental

### 2.1. Preparation of nickel oxalate

Nickel oxalate dihydrate was prepared by the reaction of nickel nitrate(V) with oxalic acid in aqueous solution at about  $65^\circ\text{C}$  for 4 h (all chemicals were of analytical grade Polskie Odczynniki Chemiczne S.A.). pH 4.0 of the mixture was maintained with ammonia and hydrochloric acid to avoid precipitation of nickel hydroxide. Next, crystalline precipitate was filtered, washed with dilute oxalic acid and finally with an absolute alcohol. The product obtained was dried at  $50^\circ\text{C}$  on air.

### 2.2. Experimental techniques

Thermal decomposition measurements were performed with an apparatus that enabled simultaneous recording of TG and DTA signals (SDT 2960 TA INSTRUMENTS). The samples of mass from the range 6 to 20 mg were heated in a standard platinum sample pan. The experiments were carried out in dynamic flow of helium (99.999%) or synthetic air ( $<15$  ppm  $\text{H}_2\text{O}$ ). The gas flow rate was  $0.1 \text{ dm}^3 \text{ min}^{-1}$  and the volume of thermoanalyzer was  $0.06 \text{ dm}^3$ .

The analysis of gaseous products of decomposition was carried out using a quadrupole mass spectrometer (QMD 300 THERMOSTAR BALZERS) connected on-line with SDT 2960 apparatus by the heated quartz capillary. The mass spectrometer was operated with an electron impact ionizer with energy 0.112 aJ (70 eV). Mass spectra were recorded for  $m/z$  equal to 18, 28, 32 and 44 which correspond to ions:  $\text{H}_2\text{O}^+$ ,  $\text{CO}^+$ ,  $\text{O}_2^+$  and  $\text{CO}_2^+$ , respectively.

CRTA (Constant Rate Thermal Analysis) measurements [16] were performed on an apparatus designed and built in MADIREL Laboratory. This apparatus controls the vacuum pressure signal above the sample at a predetermined constant value. The PID type regulation uses the pressure gauge input to regulate the heating of sample such that the pre-set pressure value, a resultant of vapour from the reaction, is obtained and remains constant until the end of the experiment where there is no more vapour produced by the thermolysis. In experiment the pre-set pressure value was 2 Pa.

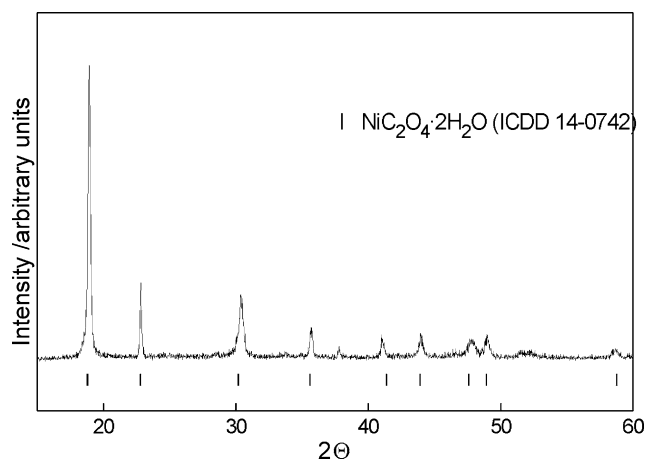


Fig. 1. XRD pattern of the initial sample of nickel oxalate dihydrate.

X-ray diffraction analyses were carried out on Philips X-ray diffractometer using  $\text{Cu K}\alpha$  radiation.

FTIR and HT-DRIFT (High Temperature Diffuse Reflexion Infrared Fourier Transform) spectroscopy measurements were performed on an Equinox 55.

## 3. Results and discussion

The initial sample was analysed for the oxalate ions content by wet analysis and for the nickel content by gravimetric analysis with dimethylglyoxime. Analysis showed that the molar ratio  $\text{Ni}^{2+}/\text{C}_2\text{O}_4^{2-}$  was  $0.97 \pm 0.03$ . X-ray powder diffraction analysis confirmed that the only component of initial sample was  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (ICDD 14-0742) (Fig. 1).

Figs. 2 and 3 show TG/DTA and MS (MS, mass spectrometry) results of thermal decomposition of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  obtained in

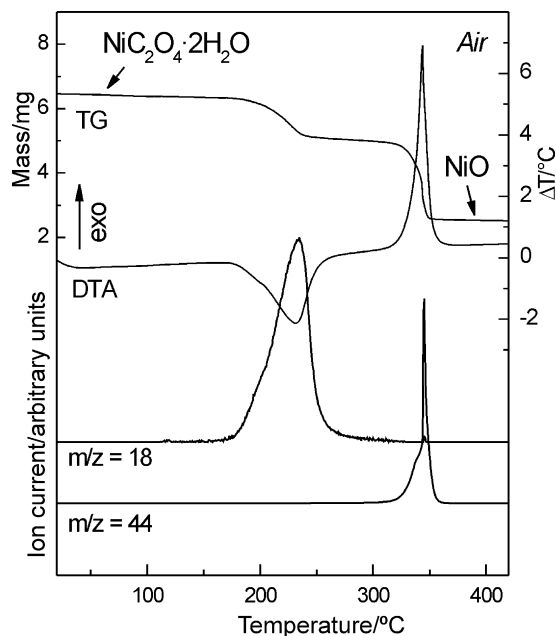


Fig. 2. Thermogravimetric and mass spectrometry results of decomposition of  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in air (heating rate  $\beta = 5^\circ\text{C min}^{-1}$ ).

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