Journal of Thermal Analysis, Vol. 42 (1994) 1155-1165

CHARACTERIZATION OF THE DECOMPOSITION COURSE OF NICKEL ACETATE TETRAHYDRATE IN AIR

G. A. M. Hussein[*], *A. K. H. Nohman and K. M. A. Attyia*

Chemistry Department, Faculty of Science, Minia University, El-Minia 61519, Egypt

(Received December 14, 1993)

Abstract

Thermogravimetry, differential thermal analysis, X-ray diffractometry and infrared spectroscopy showed that $Ni(CH_3COO)_2 \cdot 4H_2O$ decomposes completely at 500°C, giving rise to a mixture of Ni^o and NiO. The results revealed that the compound undergoes dehydration at 160°C and melts at 310°C. The water thus released hydrolyses surface acetate groups, acetic acid being evolved into the gas phase. At 330°C, the anhydrous acetate is converted into $NiCO_3$, releasing CH_3COCH_3 into the gas phase. The carbonate subsequently decomposes (at 365°C) to give $NiO_{(s)}$, $CO_{2(g)}$ and $CO_{(g)}$. On further heating up to 373°C, a mixture of Ni^o and NiO is formed. Other gas-phase products were detected at 400°C, viz. CH_4 and $(CH_3)_2CH=CH_2$, which were formed in surface reactions involving initial gas-phase products. Non-isothermal kinetic parameters (A and ΔE) were calculated on the basis of temperature shifts experienced in the various decomposition processes as a function of heating rate (2–20 deg·min^{-1}).

Keywords: nickel acetate tetrahydrate, kinetics

Introduction

A number of studies have been published [1–6] on the thermal decomposition of nickel acetate, most of which focused on the reaction stoichiometry, and on the influence of temperature on the product distribution and nature. These studies were performed mostly in a N_2 atmosphere and/or in vacuum. However, studies in air, the nature of the gaseous products evolved and the interfacial chemical reactivity have received little attention.

The interest in nickel acetate decomposition is due, in part, to its possible utilization as a means of obtaining finely-divided NiO for catalytic purposes [7–11] and the manufacture of Ni^o-containing alloys [12]. Studies in N_2 demon-

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[*] Author to whom correspondence should be addressed.

0368–4466/94/ $ 4.00

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strated the formation of a basic salt as an intermediate (at 118°C) and a mixture of nickel carbide and metallic Ni° as final product (at 320°C). The isothermal kinetic study in N_2 by Galwey *et al.* [6] furnished evidence of an autocatalytic reaction, in which acetate anion breakdown is promoted by the predominant solid product (viz. nickel carbide). Towards the end of the reaction, and increasingly at higher temperatures, the nickel metal produced by Ni_3C decomposition effectively accelerates the reaction.

In contrast, Baraldi [4] has shown that the acetate undergoes dehydration at 85°C, and the subsequent decomposition in air proceeds at 162–230°C, to give a final product of NiO, with no basic salt as intermediate. In vacuum, the dehydration occurs at 80°C, an intermediate basic slat is formed at 195°C, and the decomposition takes place at 200–300°C, eventually giving a mixture of Ni° and NiO.

Dorémieux [2] characterized the steps involved in the pyrolysis of nickel acetate tetrahydrate and observed a change in the decomposition mechanism at 320°C. On heating, nickel acetate tetrahydrate loses water, with concurrent partial conversion to a basic salt and the evolution of some acetic acid. On continued heating, the constituent anion breaks down to yield CO_2, CO, acetic anhydride, acetone and a residue containing both nickel carbide and nickel metal [3].

The present investigation explores the thermal decomposition course of nickel acetate tetrahydrate in air and the chemical reactivity at the gas/solid interfaces thus established. Thermal events in the decomposition were monitored by thermogravimetry and differential thermal analyses. They were characterized by X-ray and infrared (IR) spectroscopic analysis of the solid and gas-phase products at certain selected temperatures. Non-isothermal kinetic parameters (A and ΔE) were determined for the decomposition pathways, using known methods.

Experimental

Nickel acetate tetrahydrate

Nickel acetate (NiAc), $Ni(CH_3COO)_2{\cdot}4H_2O$, was a 99.9% pure product of Hayashi Chemical Industries (JAPAN). Its calcination products were obtained by heating at 150, 270, 300 and 500°C for 1 h, in a static atmosphere of air. The calcination temperatures were chosen on the basis of the thermal analysis results (see below). Prior to examination, these materials were kept dry over P_2O_5. For the sake of simplicity, the calcination products are indicated in the text by NiAc, followed by the calcination temperature in parenthesis. Thus, NiAc(300) means the decomposition product of NiAc at 300°C.

Thermal analyses

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed by heating at various rates ($\theta=2$, 5, 10 and 20 deg·min^{-1}) up to 500°C in a dynamic atmosphere of air (20 ml·min^{-1}), using an automatically recording Shimadzu (Model 30H) analyzer (Japan). Typically, 15–20 mg portions of the test sample were used for the TG, and highly-sintered α-Al_2O_3 was the reference material for the DTA measurements.

X-ray diffractometry (XRD)

XRD analysis of NiAc and its calcination solid-phase products was carried out with a model JSX-60PA Jeol diffractometer (Japan) equipped with a source of Ni-filtered CuK_α radiation. For identification purposes, the diffraction patterns obtained (I/I^0 *vs.* d-spacing (Å)) were matched with relevant ASTM standards.

Infrared spectroscopy (IR)

IR analysis of NiAc and its calcination (gas and solid-phase) products was carried out over the frequency range 4000–300 cm^{-1}, at a resolution of 5.3 cm^{-1}, with a model 580B Perkin-Elmer spectrophotometer (U.K.). The solid-phase spectra were taken of thin (20 mg·cm^{-2}), lightly loaded (1%) KBr-supported discs of the test samples. IR gas-phase spectra were taken of the atmosphere surrounding a 0.5 g portion of NiAc, with heating for 10 min at various temperatures (100–400°C) in a specially designed IR cell [13] equipped with KBr windows. Prior to analysis, the cell was evacuated at 10^{-3} torr for 5 min. In all cases, the cell background spectrum was ratiod out, using an on-line Perkin-Elmer Data Station (Model 3500).

Non-isothermal kinetic analysis of thermoanalytical data

From the resultant thermoanalytical curves, the temperatures (T_{max}) at which mass-variant (TG) and invariant (DTA) processes are maximized were determined as a function of the heating rate (θ) applied. The kinetic activation energy (ΔE, in kJ mol^{-1}) was then calculated for each process by plotting $\log\theta$ *vs.* $1/T_{max}$, according to the following relationship [14]:

$$\Delta E = -R/(b \text{ d} \log\theta/d(1/T)) \tag{1}$$

where R is the gas constant (=8.31 J mol^{-1}·deg^{-1}), θ is the heating rate (deg·min^{-1}), and b is a constant (0.457).

Calculation of the frequency factor (A, in sec^{-1}) of the mass-variant processes was carried out by assuming first-order kinetics, using the following equation [15]:

$$\log(-\log(1 - C/T^2) = \log AR/\Delta E - \Delta E/2.303\, RT \qquad (2)$$

where C is the fraction decomposed and T is T_{max}.

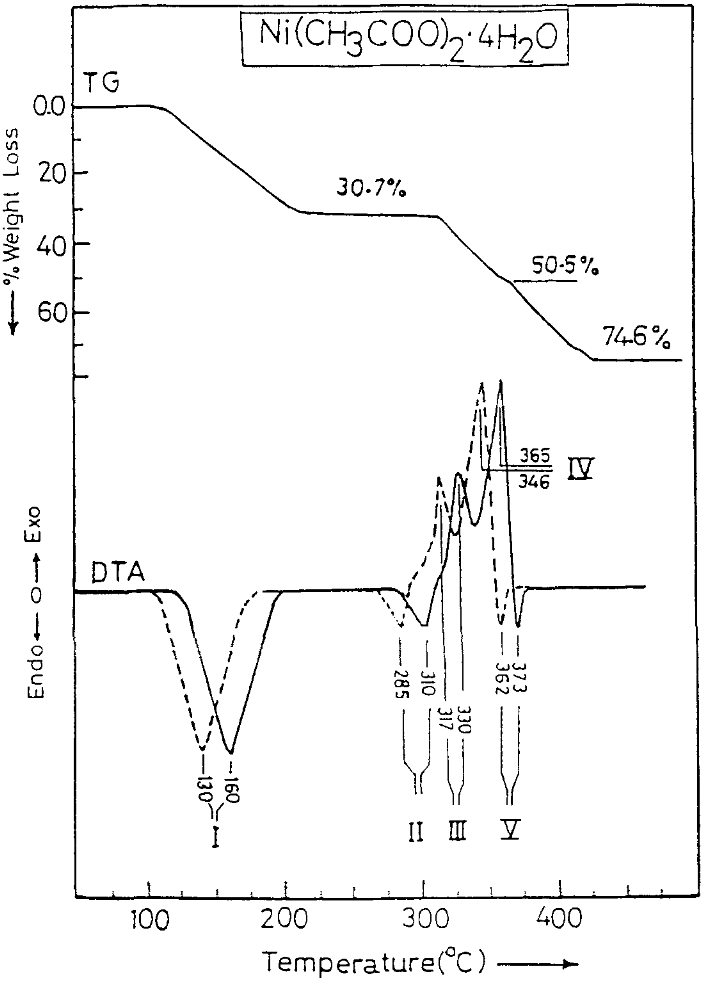

Fig. 1 TG and DTA curves of NiAc, at the heating rates indicated, in a dynamic (20 ml·min^{-1}) atmosphere of air; — 20 deg·min^{-1}, - - - 2 deg·min^{-1}

Results and discussion

TG and DTA curves of NiAc at 20 deg·min^{-1} in a dynamic atmosphere of air are shown in Fig. 1. The results indicate that NiAc suffers five thermal pro cesses: I, T_{max} = 160°C; II, T_{max} = 310°C; III, T_{max} = 330°C; IV, T_{max} = 365°C; and V, T_{max} = 373°C. Processes I, II, and V are endothermic, whereas processes III and IV are exothermic in nature. Moreover, it can be ob-

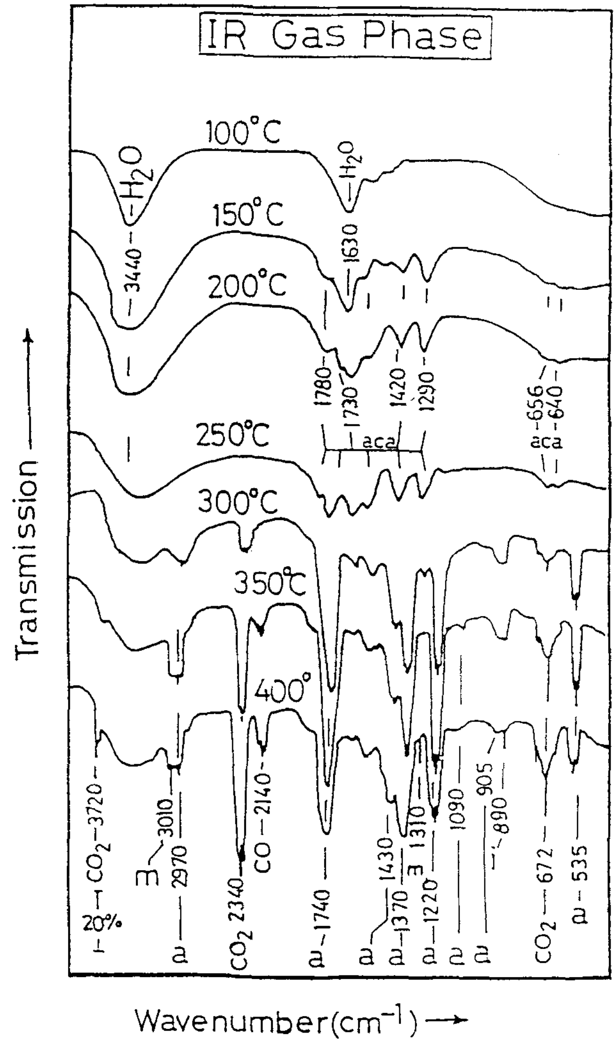

Fig. 2 IR spectra taken at a resolution of 5.3 cm^{-1} from the gas phase surrounding 0.5 g of NiAc being heated (at 10 deg·min^{-1}) to the temperatures indicated for 10 min. Gas-phase decomposition products indicated (*a* = acetone, *aca* = acetic acid, *m* = methane, *i* = isobutene)

served from Fig. 1 that decrease of the heating rate to 2 deg·min^{-1} resulted in low-temperature shifts of the thermal events encountered.

Figure 2 exhibits the IR spectra of the gas phase surrounding NiAc after heating to various temperatures (100–400°C) for 10 min. On the other hand, IR spectra and X-ray powder diffractograms obtained for NiAc and its calcination solid products (at 150–500°C) are shown in Figs 3 and 4, respectively.

Characterization of the thermal processes

Figure 1 reveals that the total loss in mass in process I (30.7%) is close to that expected (28.9%) for the release of four moles of water:

$$Ni(CH_3COO)_2 \cdot 4H_2O \rightarrow Ni(CH_3COO)_2 + 4\ H_2O \qquad (3)$$

The corresponding activation energy is 57.1 kJ·mol^{-1}, which is within the range characteristic of dehydration processes involving loosely bound water molecules (< 60 kJ mole^{-1} [1]). In support of this result, the IR gas-phase spectra at 100 and 150°C (Fig. 2) exhibit bands at 3440 and 1630 cm^{-1}, due respectively to νOH and δHOH [16] of water molecules. However, at 200°C they display additional absorptions due to acetic acid in the gas phase, at 1780, 1730, 1420, 1290, 655 and 640 cm^{-1} [17]; the formation of acetic acid is most probably due to surface acetate hydrolysis [18, 19]. This may explain the slight difference between the observed (30.7%) and the expected (28.9%) mass losses.

The IR spectrum of the solid-phase product at 150°C (Fig. 3) is very similar to that of the parent NiAc, in displaying the diagnostic absorptions of acetate ligands at 1720–635 cm^{-1} [16].

The XR diffractograms of NiAc(150) and NiAc(270) (Fig. 4) indicate an amorphous nature. This suggests that the water molecules are important for the NiAc coherency [20]. It has been reported [20] that, after removal of the water of hydration, nickel carboxylates are largely amorphous. However, there is no evidence in our study for the formation of crystalline $Ni(OH)_2 \cdot Ni(CH_3COO)_2$ or Ni_3C, as was observed in other studies [2, 4, 6] in the same temperature range. This is probably due to the different decomposition atmosphere.

Process II, which maximizes at 310°C, is endothermic and mass-invariant. It is most probably due to fusion of anhydrous NiAc. Other investigators [6] have pointed to the absence of fusion by SEM texture studies of the course of decomposition of NiAc. However, the possibility exists of local and temporary intraparticulate fusion. On testing the melting of NiAc, we observed that at 295°C the material was co-aggregated and then decomposed. ΔE calculated for this process is 108 kJ·mol^{-1}.

The DTA and TG curves (Fig. 1) show that the decomposition of NiAc starts immediately after the fusion process, through the two successive exothermic processes III and IV, which are maximized at 330 and 365°C, respectively. The total loss in mass determined for process III is 50.5%, which is close to that expected (52.3%) for the formation of $NiCO_3$. The latter decomposes immediately through process IV, bringing the total mass loss up to ≈71.0%. This is close to that (70.0%) due to the formation of NiO:

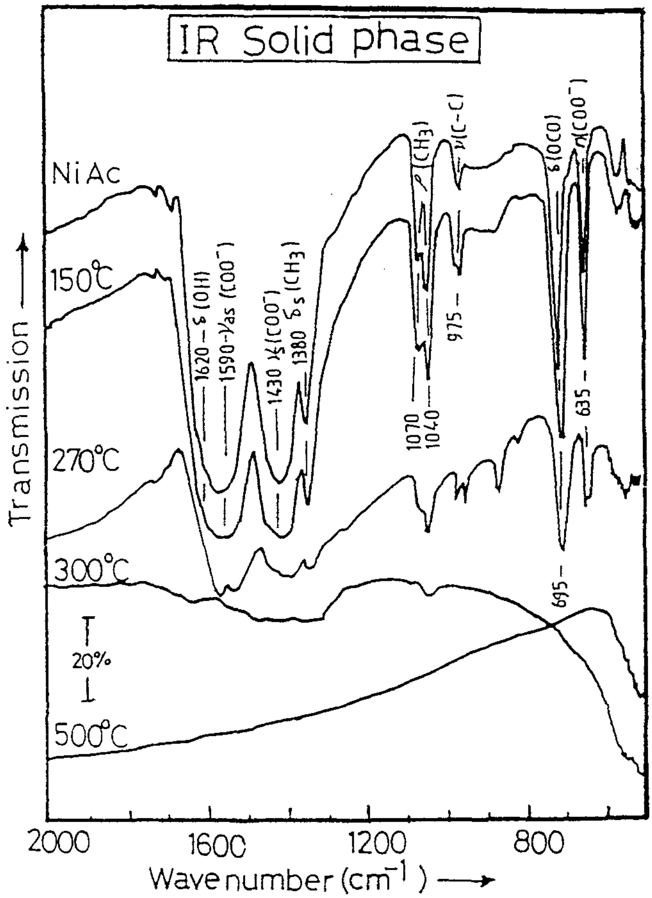

Fig. 3 IR spectra taken at a resolution of 5.3 cm^{-1} from KBr-supported samples of NiAc and its solid decomposition products obtained at the temperatures indicated for 1 h in a static atmosphere of air

$$Ni(CH_3COO)_2 \xrightarrow{III} CH_3COCH_{3(g)} + NiCO_3 \xrightarrow{IV} CO_2 + NiO \quad (4)$$

The IR gas-phase spectra at 300 and 350°C (Fig. 2) can be correlated with the above results, since characteristic absorptions of acetone (at 1740, 1430, 1370 and 1220 cm^{-1}) [15] are displayed therein. Moreover, the gas-phase spectra exhibit absorptions due to minute amounts of CO_2 (at 2340 and 672 cm^{-1}) and CO (at 2140 cm^{-1}) [17].

The IR spectrum of NiAc(300) (Fig. 3) demonstrates the almost complete disappearance of the characteristic band structure of NiAc. In support, the XRD of the same product (Fig. 4) exhibits a pattern identical to that of pure NiO (ASTM 4-835). In turn, these results indicate that neither crystalline Ni_3C nor Ni^0 metal were detected in NiAc(300), in contrast to previous reports [2, 6].

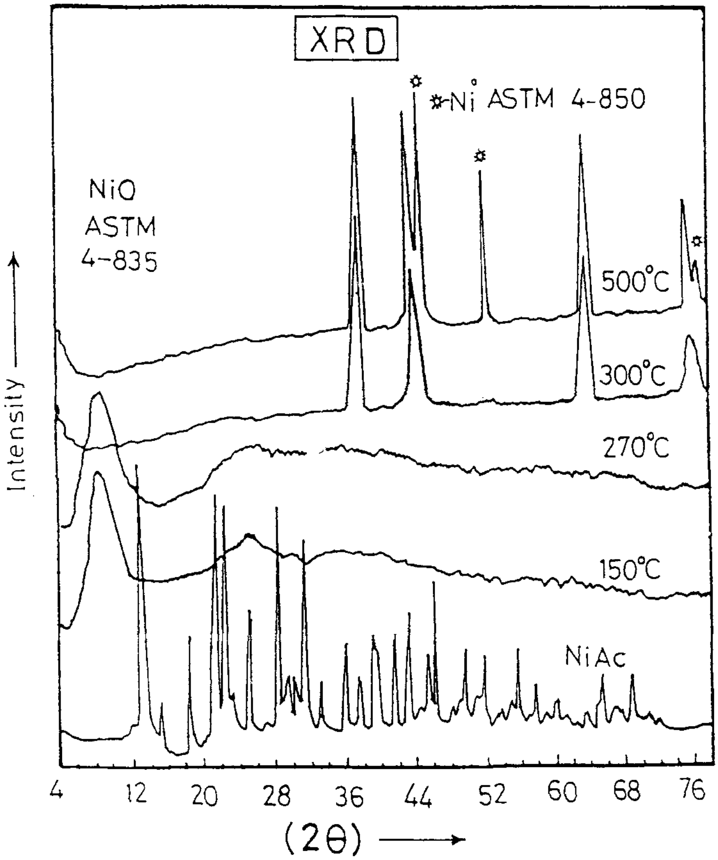

Fig. 4 X-ray powder diffractograms of NiAc and its decomposition products obtained at the temperatures indicated for 1 h in a static atmosphere of air

Galwey *et al.* [6] studied the decomposition of the anhydrous acetate in N_2 atmosphere in the temperature range 317–347°C and detected Ni_3C in the final product. They reported that there is an overlapping in the thermal effects, causing difficulty in interpretation. They also reported different values for the activation energy, depending upon the range of temperature examined, viz. $\Delta E=150\pm8$ kJ·mol^{-1} at 275–305°C, and $\Delta E=80\pm8$ kJ·mol^{-1} at 305–354°C. We found $\Delta E=133.2$ kJmol^{-1} for process III (at 330°C), which is in satisfactory agreement with Galwey *et al.* [6]. This activation energy value is higher than that (84.7 kJ·mol^{-1}) at 365°C for process IV, i.e. $NiCO_3$ decomposition, indicating that process IV is a rapid one.

The DTA curve (Fig. 1) shows that the exothermic process IV is followed by a rapid endothermic effect (process V) maximized at 373°C. This is accompanied by a slight mass loss, which brings the decomposition of NiAc to an end at 74.6% ($\Delta E=90.8$ kJ·mol^{-1}). The X-ray diffractogram of NiAc(500) (Fig. 4) indicates the formation of Ni° metal (ASTM 4-850) besides NiO. The formation of Ni° metal could be attributed to CO-reduction of NiO produced at 300°C, a proposal that might be supported by the fact that NiO is a powerful oxidant for CO [9–11].

Table 1 Non-isothermal kinetic parameters[a] of the processes occurring throughout the decomposition course of NiAc

Process	log A	ΔE/kJ·mol^{-1}
I	12.71	57.1
II	–	108.0
III	17.40	133.8
IV	12.60	84.7
V	17.70	90.8

a) The kinetic parameters for processes I, III, IV and V were calculated from TG data, whereas for process II DTA data were used

The IR spectrum of NiAc(500) (Fig. 3) indicates the complete elimination of the acetate ligands. Additionally the spectrum shows a decrease in the percentage transmission, due, most probably, to a decrease in surface area [21] as a result of Ni° metal formation.

Chemical reactivity at the gas-solid interface

Galwey [6] and Dorémieux [2] investigated the gaseous products by mass spectrometry during the decomposition of NiAc and detected the formation of acetic acid, acetic anhydride, acetone and probably ketene. They also suggested a chemical equation for the formation of CH_4, CO_2 and CO:

$$Ni(CH_3COO)_2 \rightarrow 1.0\,CO_2 + 1\,Ni + 0.6\,C + 0.25\,CO + 0.17\,CH_4$$

The IR spectrum of the gas phase at 400°C (Fig. 2) displays absorption bands characteristic of acetone, CO_2, CO, CH_4 and $(CH_3)_2C=CH_2$. It has been established [18, 19, 22] that the formation of both methane and isobutene in the presence of metal oxide catalysts is due to the involvement of acetone molecules in surface-mediated bimolecular reactions. Acetone is thereby adsorbed and activated for an aldol condensation-like process as follows:

$$\sigma\text{–}(CH_3)_2CO + (CH_3)_2CO_{(g)} + \sigma\text{–}OH^- \rightarrow (CH_3)_2C = CH_{2(g)} + \sigma\text{–}CH_3COO^- \quad (5)$$

where σ = surface, and g = gas.

In the meantime, adsorbed acetone is also activated for a nucleophilic attack by adjacent surface OH to split off a methyl group in the form of CH_4 [21–24]:

$$\sigma\text{–}(CH_3)_2CO + \sigma\text{–}OH^- \rightarrow CH_{4(g)} + \sigma\text{–}CH_3COO^- \quad (6)$$

It should be noted that both reactions (5) and (6) consume acetone, which may explain the decrease in the intensity of the band structure of acetone at 400°C (Fig. 2). The two reactions also produce surface acetate species, which may correlate with the IR observation of carboxylate surface species on NiAc(300) (Fig. 3).

Conclusion

1. In view of the present results and the literature data, it is clear that the decomposition of NiAc is critically controlled by the reaction atmosphere (viz. N_2, air or vacuum).

2. The dehydration of $Ni(CH_3COO)_2 \cdot 4H_2O$ is accompanied by the hydrolysis of surface acetates, which takes place endothermally at 160°C, releasing water and acetic acid into the gas phase.

3. Anhydrous NiAc decomposes through two exothermic processes, maximized at 330 and 365°C, yielding solid-phase NiO and gas-phase acetone and CO_2. Some of the NiO is reduced to Ni^0 metal through an endothermic process, most likely involving a CO-reduction step.

4. The conversion of acetone to methane and isobutene indicates that the gaseous decomposition products observed are not always formed directly in the initial stages, and may be due to interfacial reactions between intermediates.

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The authors wish to express their gratitude to Professor M. I. Zaki (Minia University) for critical reading.

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Zusammenfassung — Mittels TG, DTA, Röntgendiffraktometrie und IR-Spektroskopie wurde die Zersetzung von $Ni(CH_3COO)_2 \cdot 4H_2O$ bei 500°C zu einem Gemisch aus Ni und NiO nachgewiesen. Den Ergebnissen zufolge wird die Verbindung bei 160°C dehydratiert und schmilzt bei 310°C. Durch das auf diese Weise freigesetzte Wasser werden an der Oberfläche befindliche Acetatgruppen hydrolisiert, was zu Essigsäure in der Gasphase führt. Bei 330°C wird das wasserfreie Acetat in $NiCO_3$ umgewandelt, wobei CH_3COCH_3 gasförmig freigesetzt wird. Das Carbonat zersetzt sich anschließend und liefert (bei 365°C) $NiO_{(s)}$, $CO_{2(g)}$ und $CO_{(g)}$. Bei weiterem Erhitzen auf 373°C wird das Gemisch aus Ni und NiO gebildet. Weitere gasförmige Produkte konnten bei 400°C nachgewiesen werden: Wasser, CH_4 und $(CH3)_2CH=CH_2$, die aus den unter Teilnahme der primär gebildeten Gasphasenprodukte verlaufenden Oberflächenreaktionen stammen. Auf der Grundlage der Temperaturverschiebungen, die bei den verschiedenen Zersetzungsprozessen als eine Funktion der Aufheizgeschwindigkeit (2–20 deg·min^{-1}) beobachtet werden, wurden die nichtisothermen kinetischen Parameter (A und ΔE) berechnet.