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Thermal decomposition of nickel nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$, in comparison to $Co(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$

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Abstract

The thermal decomposition of $Ni(NO_3)_2 \cdot 6H_2O$ (**1**), $Ca(NO_3)_2 \cdot 4H_2O$ (**2**) and nitryl/nitrosyl nitrato nickelate(II), $NO_2/NO[Ni(NO_3)_3]$ (**3**), was investigated by thermogravimetric measurements with quasi-isothermal conditions and compared to $Co(NO_3)_2 \cdot 6H_2O$. The respective decomposition processes of **1** and **2** differ from each other showing that at one hand anhydrous $Ca(NO_3)_2$ was obtained whereas anhydrous nickel dinitrate has not be formed due to redox and condensation reactions. Instead basic nickel compounds have been formed. In reducing atmosphere nickel metal can be obtained. Anhydrous $Ni(NO_3)_2$ results by the thermal degradation of nitryl/nitrosyl nitrato nickelate. FT-Raman spectra have been of help in the judgement of the decomposition processes.

Keywords: $Ni(NO_3)_2 \cdot 6H_2O$; $Ca(NO_3)_2 \cdot 4H_2O$; $NO_2/NO[Ni(NO_3)_3]$; Thermochemistry

1. Introduction

Metal nitrates (hydrates) are most popular precursor components for the preparation of oxidic and metallic materials with wide spread properties as e.g. high surface catalysts, ceramics, semiconductors, gas sensors and high temperature superconductors [1–9]. The widely used procedures thereby are the thermal degradation/decomposition of metal nitrates as well as chemical vapor deposition (CVD) methods. The actual decomposition processes often depend very much upon the experimental conditions employed as for example heating rate, amount and packing of starting material, kind and pressure of the gas atmosphere, gas flow rate, melting/formation of a hydrate melt, and others more.

Dependent on the applied preparation procedures thereby, different decomposition reactions and mechanisms result and are disputed for the thermal degradation *respective* decomposition [3,10–18]. Different routes of thermal decomposition especially of transition metal nitrate hydrates in form of consecutive reactions are outlined in a series of papers of A. Malecki and co-workers [12–14,17] including the formation of HNO_3, NO, NO_2 and O_2 as well as the formation of hydroxide nitrate hydrates, hydroxide nitrates, basic nitrates and oxides dependent on experimental conditions inclusive formation of hydrate melts. In some cases anhydrous metal nitrates can be obtained as intermediates (e.g. barium, calcium, cadmium and cobalt nitrate) [14,19,20] whereas in other cases basic oxo- or hydroxo-nitrates are formed (e.g. copper, nickel and manganese compounds) [2,6,8,13,15,17,21–23]. In a continuation of our investigation of the thermal decomposition of cobalt(II)nitrate hexahydrate [20] we investigated the title nitrates, especially in relation to their decomposition reactions and chemism.

2. Experimental

2.1. Substances and methods

Commercial nickel nitrate hexahydrate (Fluka, puriss. p.a.) and calcium nitrate tetrahydrate (Fluka, puriss. p.a.) (Fluka, purum p.a.) were used as received. $NO_2/NO[Ni(NO_3)_3]$ was prepared out of $NiCl_2$ and N_2O_5 according to ref. [24].

The thermogravimetric (TG) measurements have been performed with a thermobalance (Sartorius, type 4201) in which the sample compartment is separated and kept magnetically in

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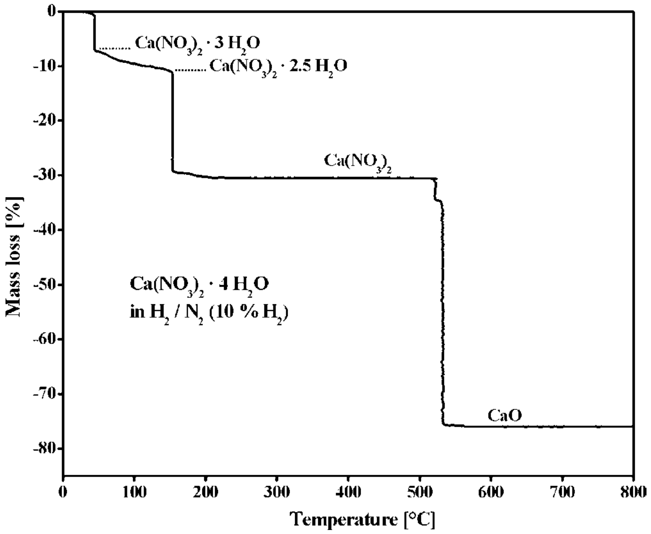

Fig. 1. Thermal decomposition (TG) of calcium nitrate tetrahydrate in H_2/N_2 (10% H_2) atmosphere with indicated degradation steps/stages. Loading: 150 mg; heating rate between the quasi-isothermal steps: 0.6 K min^{-1}.

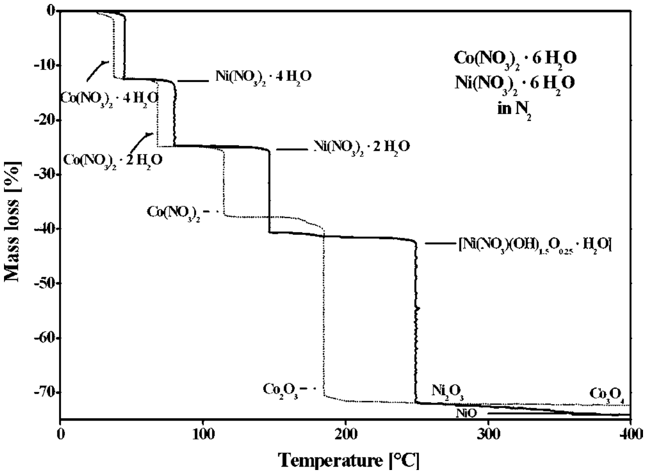

Fig. 2. Thermal decomposition (TG) of nickel(II)nitrate hexahydrate (full line) in comparison to cobalt nitrate hexahydrate (dotted/broken line) (c.f. ref. [20]) in N_2 atmosphere up to 400 °C with indicated degradation steps/stages. Sample loading: 150 mg; heating rate between the quasi-isothermal steps: 0.6 K min^{-1}. The different behavior of both nitrates is seen in the third step *respective* stage.

suspension (Magnetic Suspension Balance). By a computer-based driving, the heating rate is controlled by relative mass loss in response to the sample decomposition allowing so-called quasi-isothermal conditions [25]. This method is in effect comparable to the "Dynamic Rate Controlled Method" [26]. With the mentioned thermobalance also thermal decomposition reactions evolving corrosive gases as e.g. HNO_3, NO_X, Cl_2, etc., can be pursued as well as it is possible to work in different atmospheres. The method's efficiency is outlined for some effects of the thermal degradation of $Co(NO_3)_2{\cdot}6H_2O$ [20].

The TG measurements were done in a flowing gas atmosphere of N_2 *respective* H_2/N_2 (10% H_2). The choice of the applied atmosphere was made in order to evaluate a possible influence on partial decomposition steps.

3. Results and discussion

3.1. Thermal decomposition of calcium nitrate tetrahydrate, $Ca(NO_3)_2{\cdot}4H_2O$

The slow thermal decomposition of $Ca(NO_3)_2{\cdot}4H_2O$ (**2**), shown in Fig. 1, reveals the stepwise formation of distinct hydrates, anhydrous calcium nitrate and finally calcium oxide, CaO. This decomposition course is typical for nitrates with hard-oxidable *respective* unoxidable cations as alkali, alkaline earth, Cd^{2+}, Pb^{2+}, Zn^{2+} and others. The used atmosphere, here H_2/N_2 (10% H_2), has no influence on it. The corresponding experimental details and thermo-analytical characters including the chemical reactions are summerized in Table 1 and indicated in Fig. 1, respectively. Nevertheless, high sample loading and dense packing may hinder the leaving of water and cause the formation of side-products, too. Such effects we discussed for Co $(NO_3)_2{\cdot}6H_2O$ in ref. [20]. The insignificant "step" in the mass loss curve between $Ca(NO_3)_2$ and CaO (Fig. 1) could be caused by short electronic net pertubation.

3.2. Thermal decomposition of $Ni(NO_3)_2{\cdot}6H_2O$ in comparison to $Co(NO_3)_2{\cdot}6H_2O$ [20]

In general it is agreed that the thermal degradation/decomposition of nickel(II)nitrate hexahydrate proceeds stepwise and the distinct tetra- and dihydrates are formed if melting *respective* formation of a hydrate melt (m.p. 56.7 °C) is prevented [1–3,6,11,13,17,27–28] (c.f. Fig. 2). Besides this, recently a proof of the existence of the controversial intermediate nickel nitrate salt $Ni(NO_3)_2{\cdot}5.5H_2O$ is claimed [29].

Table 1

Thermal decomposition reactions of $Ca(NO_3)_2{\cdot}4H_2O$ and their characteristics (c.f. Fig. 1)

Reaction/step	T (K)[a]	Δm (%)[b]	
		Experimental	(Calculated)
1. $Ca(NO_3)_2{\cdot}4H_2O = Ca(NO_3)_2{\cdot}3H_2O + H_2O$	318	7.5	(7.63)
2. $Ca(NO_3)_2{\cdot}3H_2O = Ca(NO_3)_2{\cdot}2.5H_2O + 0.5H_2O$	~340	11.2	(11.47)
3. $Ca(NO_3)_2{\cdot}2.5H_2O = Ca(NO_3)_2 + 2.5H_2O$	427	30.3	(30.50)
4. $Ca(NO_3)_2 = CaO + N_2O_5$[c]	805	76.1	(76.25)

[a] Decomposition temperature.

[b] In relation to the starting compound.

[c] *Respective* $2NO_2 + 0.5O_2$.

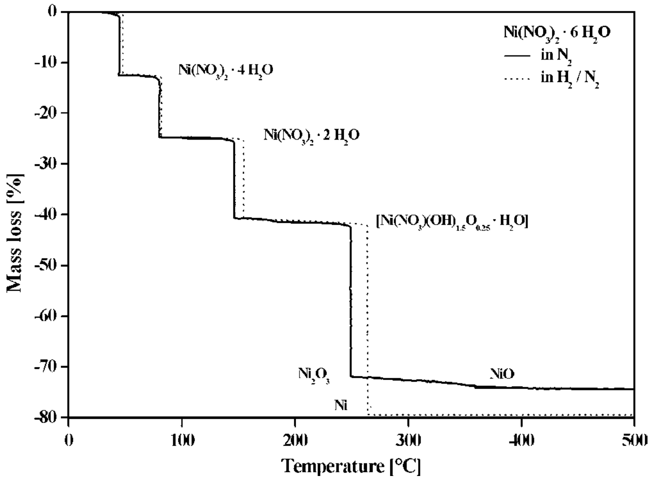

Fig. 3. Thermal decomposition (TG) of nickel(II)nitrate hexahydrate in inert/N_2 atmosphere (full line) and in reducing/H_2/N_2 (10% H_2) atmosphere (dotted/broken line) with indicated degradation steps/stages. Heating rate between the quasi-isothermal steps: 0.6 K min^{-1}.

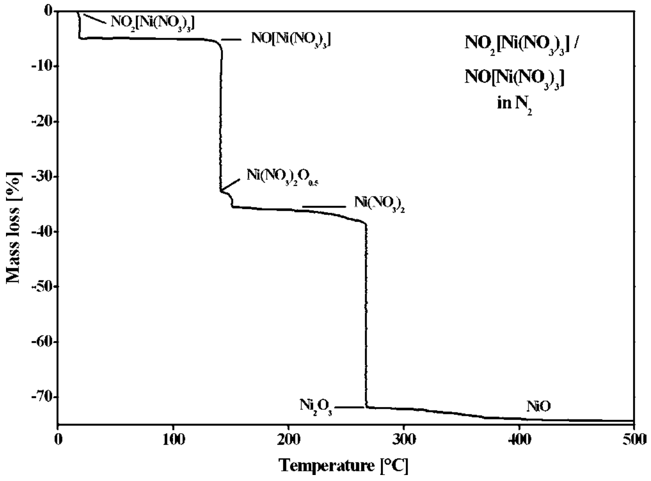

Fig. 4. Thermal decomposition (TG) of nitryl/nitrosyl nitrato nickelate in N_2 atmosphere up to 500 °C with indicated degradation steps/stages. Sample loading: 120 mg; heating rate between the quasi-isothermal steps: 0.6 K min^{-1}.

Noteworthy, the third degradation step of the nickel compound differs from this of the cobalt homologue [20] and it results in basic species, and not in anhydrous $Ni(NO_3)_2$!! The statements for the composition of such basic products differ [6,7,21,27]. A homogenous single phase $Ni_3(NO_3)_2(OH)_4$ [$=Ni(NO_3)_2{\cdot}2Ni(OH)_2$] could be characterised recently [7]. The formation of the mentioned basic nickel salt corresponds (at least formal) to an hydrolysis of nitrate and the release of HNO_3 according to

$$3Ni(NO_3)_2{\cdot}2H_2O = Ni_3(NO_3)_2(OH)_4 + 4HNO_3 + 2H_2O$$

corresponding to the calculated mass loss of 57.80%. Such a mass loss could not be detected in the experimental decomposition course (c.f. Figs. 2 and 3).

Otherwise, the nitrate ion has a considerable oxidative power and it is possible that Ni^{2+} can be oxidized to Ni^{3+}, what is indicated in refs. [2,13,17] and proved for $[Ni(NH_3)_6](NO_3)_2$ where the thermal decomposition step of $[Ni(NH_3)_2](NO_3)_2$ is connected with a redox process [30]. It is possible to formulate the ongoing $Ni(NO_3)_2{\cdot}2H_2O$ decomposition reasonably *via* an oxidation step (Table 2, Reaction 3a) followed by a partial condensation (Reaction 3b) with the release of 0.25 equivalents H_2O. The used atmosphere has no influence on the decomposition course, except for the final step, the formation of nickel oxides *respective* elemental nickel (Fig. 3).

Concerning the nickel oxide(s) decomposition we have only checked the existence of NiO (by X-ray diffraction) at the end of the thermal decomposition. It was not tried to obtain and to characterize a Ni_2O_3 sample. In the high-temperature oxide decomposition (Figs. 2–4) the mass loss course proceeds

Table 2
Thermal decomposition reactions of $Ni(NO_3)_2{\cdot}6H_2O$ and their characteristics (c.f. Figs. 2 and 3)

Reaction/step	T (K)[a]	Δm (%)[b]	
		Experimental	(Calculated)
Water separation			
1. $Ni(NO_3)_2{\cdot}6H_2O = Ni(NO_3)_2{\cdot}4H_2O + 2H_2O$	316	12.3	(12.38)
2. $Ni(NO_3)_2{\cdot}4H_2O = Ni(NO_3)_2{\cdot}2H_2O + 2H_2O$	353	24.8	(24.77)
Partial decomposition steps (oxidation and partial condensation)			
3a. $Ni(NO_3)_2{\cdot}2H_2O = Ni(NO_3)(OH)_2{\cdot}H_2O + NO_2$	418	40.6	(40.59)
3b. $Ni(NO_3)(OH)_2{\cdot}H_2O = Ni(NO_3)(OH)_{1.5}O_{0.25}{\cdot}H_2O + 0.25H_2O$	~463	42.0	(42.14)
Decomposition			
4. $Ni(NO_3)(OH)_{1.5}O_{0.25}{\cdot}H_2O = 0.5Ni_2O_3 + HNO_3 + 1.25H_2O$	523	71.8	(71.55)
Oxide decomposition to “NiO”			
5. $3Ni_2O_3 = 2Ni_3O_4 + 0.5O_2$	~523[c]	72.2	(72.47)
6. $Ni_3O_4 = 3NiO + 0.5O_2$	~573[c]	74.0	(74.31)
Reduction with H_2/N_2 (10% H_2) to Ni, from 4			
$3NiO + 3/2H_2 = 3Ni + 3/2H_2O$ (Fig. 3)	~535	79.8	(79.81)

[a] Decomposition temperature.

[b] In relation to the starting compound.

[c] Beginning of reaction.

Table 3
Thermal decomposition reactions of nitryl/nitrosyl nitrato nickelates and their characteristics in N_2 atmosphere (c.f. Fig. 4)

Reaction/step	T (K)[a]	Δm (%)[b]	
		Experimental	(Calculated)
1. $NO_2[Ni(NO_3)_3] = NO[Ni(NO_3)_3] + 0.5O_2$	293	5.0	(5.50)
2. $NO[Ni(NO_3)_3] = Ni(NO_3)_2O_{0.5} + NO + 0.5N_2O_5$	413	32.2	(34.40)
3. $Ni(NO_3)_2O_{0.5} = Ni(NO_3)_2 + 0.25O_2$	~423	38.0	(37.15)
4. $Ni(NO_3)_2 = 0.5Ni_2O_3 + NO_2 + 0.5N_2O_5$	~540	72.0	(71.55)
5. Ni_2O_3 decomposition *via* Ni_3O_4 in NiO	above 593	74.2	(74.31)
The thermal decomposition of $Ni(NO_3)_2$ in H_2/N_2 atmosphere beginning at 255 °C yields elemental nickel			

[a] Decomposition temperature.

[b] In relation to the starting compound.

dawdlingly ending up with NiO. The labels Ni_2O_3 and Ni_3O_4 correspond to the respective mass loss fitting with the experimental ones.

Such an approach will better harmonize with the thermal decomposition of manganese(II)nitrate hydrates for example [22,23] whereat MnO_2 is obviously formed. Unfortunately, the presented thermal decomposition measurements cannot contribute to a solution of the decomposition mechanism by methodical reasons.

3.3. *Thermal decomposition of nitryl/nitrosyl nitrato nickelate ($NO_2/NO)[Ni(NO_3)_3]$*

Since anhydrous $Ni(NO_3)_2$ can not be obtained by thermal dehydration of the title compound under usual conditions as outlined, it can be prepared by thermal decomposition of nitryl/nitrosyl nitrato nickelates, $NO_2/NO\ [Ni(NO_3)_3]$, under milder conditions (Fig. 4, Table 3). The thermal degradation of the nitryl/nitrosyl nitrato nickelate is included here in order to show that anhydrous $Ni(NO_3)_2$ can be obtained in substance and that it has a considerable thermal stability. This so obtained anhydrous nickel dinitrate is characterised by its Raman spectrum (see footnote 3).[3] The Raman frequencies of the nickel(II)nitrate are very similar to those of anhydrous cobalt(II)nitrate [20] and they may also assigned in analogy based on the vibrations of the nitrate unit.

4. Conclusion

The thermal dehydration/degradation of $Ca(NO_3)_2\cdot 4H_2O$ under quasi-isothermal conditions proceeds stepwise *via* distinct hydrates, anhydrous $Ca(NO_3)_2$ and finally CaO. This decomposition course is typical for nitrate hydrates with hard-oxidable mono- and divalent cations (but not for e.g. $Ga(NO_3)_3\cdot 8H_2O$ [31] giving basic intermediates). Contrary to the calcium and cobalt nitrate hydrates [20], the thermal dehydration/decomposition of $Ni(NO_3)_2\cdot 6H_2O$ does not lead to anhydrous $Ni(NO_3)_2$, instead basic intermediate products are formed. In the relevant composition range no distinct phases could be characterised by X-ray diffraction.

Therefore, the reaction mechanism of the thermal decomposition of $Ni(NO_3)_2\cdot 2H_2O$ to basic intermediates either by hydrolysis of nitrate ion or by redox reactions is finally unproved. For further decomposition at higher temperatures the used atmosphere is important, whereas in N_2 nickel oxides and in H_2/N_2 (10%H_2) elemental nickel are formed. Anhydrous nickel nitrate, $Ni(NO_3)_2$, can be obtained in substance by thermal decomposition of nitryl/nitrosyl nitrato nickelate $(NO_2/NO)[Ni(NO_3)_3]$.

At least some contradictory (and non-reproducible) results and findings of the thermal $Ni(NO_3)_2\cdot 6H_2O$ decomposition might be caused by hasty temperature rising *respective* formation of a hydrate melt changing the system drastically by incoupled side reactions and evaporation of volatile species.

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[3] Raman frequencies of anhydrous nickel(II)nitrate, $Ni(NO_3)_2$: *–NO_3 stretchings* 1451w-m, 1383w, 1354w, 1092sh, 1083vs, 1056w; *–NO_3 bendings* 758w, 748w; *lattice vibrations* 208m, 185vw, 160m, 147m, 122sh, 86vw, with s = strong, m = medium, w = weak, v = very, sh = shoulder.

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