

Article

Solid-State Transformations in Inner Coordination Sphere of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ as a Route to Access Catalytically Active Co-Fe Materials

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Abstract: Thermal decomposition of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ in argon atmosphere, at a low heating rate ($3^\circ/\text{min}$), and in large amounts of the initial complex (~ 0.1 mole), has been studied. It was possible to distinguish four decomposition steps upon heating: In the temperature range of $50\text{--}100^\circ\text{C}$ —the loss of crystal water; $100\text{--}190^\circ\text{C}$ —stability region of dehydrated complex; $230\text{--}270^\circ\text{C}$ —the range of stability of intermediate phase with the formula $\text{CoFe}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2$; $270\text{--}350^\circ\text{C}$ —thermal decomposition of the intermediate with the formation of metallic products and further air oxidation with the formation of $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$. Catalytic properties of thermolysis products were tested in the decomposition reaction of H_2O_2 (inactive), oxidation of acetone (average activity), and decomposition of ammonium perchlorate (highly active).

Keywords: double complex salts; coordination sphere; catalyst; single-source precursor; thermal decomposition

1. Introduction

Iron group metals (Fe, Co and Ni) were considered as a base to access of polymetallic catalysts. Their activity and selectivity can be drastically improved by the addition of other transition elements. The active part of these catalytic systems is a disordered, mainly amorphous, oxide-metal nanostructured layer covering a support [1]. The morphology and stability of polymetallic catalysts strongly depends on the preparation routine and the nature of the precursor. Thermal activation, treatment with an alkaline or acid solutions, with further washing or impregnation, may be used to improve catalytic properties of iron-base catalysts [1,2].

Double complex salts (DCS), containing coordination cation and coordination anion, have been proposed as promising, single-source precursors for polymetallic and oxide materials, with promising catalytic activity [3]. Previously we investigated double complex salts with a general formula $[\text{M}^1(\text{A})_6][\text{M}^2\text{X}_6]$, where $\text{M}^1, \text{M}^2 = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$; $\text{A} = \text{NH}_3, \text{en}/2, \text{tn}/2, \text{ur}$ (En—diaminoethane; Tn—1,3-diaminopropane; Ur—urea), $\text{X} = \text{CN}^-, \text{C}_2\text{O}_4^{2-}/2$, as precursors of bimetallic catalysts [4–7]. Their thermal decomposition products were tested as catalysts for H_2O_2 decomposition [4], gas-phase oxidation of ethanol and acetone [5,6], as well as in the solid-state decomposition of NH_4ClO_4 [7]. It has been shown, that thermal decomposition products prepared by thermolysis in a hydrogen flow are active in decomposition of H_2O_2 . Nevertheless, ethanol oxidation and NH_4ClO_4 decomposition can be catalyzed by thermal decomposition products in the air. In the most tested samples of these

catalysts, residual carbon was detected. It should be noted that a mechanism of carbon formation in the thermal decomposition of carbon, containing double complex salts in a solid state is still unclear.

The chemical $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ is a precursor for a mixed Co-Fe-containing catalyst. It is sufficient due to its relative low thermal stability and absence of any toxic components as products of its thermal decomposition [8]. Gaseous products can be overall removed from the solid products of its thermal decomposition. The chemical $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ is an example of carbon, containing double complex salts, which in some conditions does not form carbon as an admixture to its solid thermal decomposition products. These products do not belong to the most catalytically active series. The chemical $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ is a member of a broad family of isostructural and isomeric salts $[\text{M}^1(\text{NH}_3)_6][\text{M}^2(\text{C}_2\text{O}_4)_3] \cdot n\text{H}_2\text{O}$ with $\text{M}^1 = \text{Co}, \text{Ir}$; $\text{M}^2 = \text{Fe}, \text{Cr}$. Salts are poorly soluble in water, insoluble in organic solvents, as well as air and water stable. The crystal structure of isostructural analogous salt $[\text{Ir}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ (CSD 1865520) (ICSD, Fachinformationszentrum Karlsruhe, B-76344 Eggenstein-Leopoldshafen, Germany; e-mail crysdata@fiz-karlsruhe.de) has been solved and refined using a single-crystal X-ray diffraction. Isoformular salt $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ is isostructural and crystallizes in the hexagonal system with $a = b = 12.55(2)$, $c = 20.65(5)$ Å at room temperature (Figure 1). The structure can be considered as a close packing of cationic and anionic hexagonal layers. The island structure consists of isolated octahedral $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations, octahedrally coordinated $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$. The geometric characteristics of cations and anions in the crystal structure are similar to the values characteristic for other salts such as $[\text{M}^1(\text{NH}_3)_6]\text{Cl}_3$ or $\text{K}_3[\text{M}^2(\text{C}_2\text{O}_4)_3]$ [9].

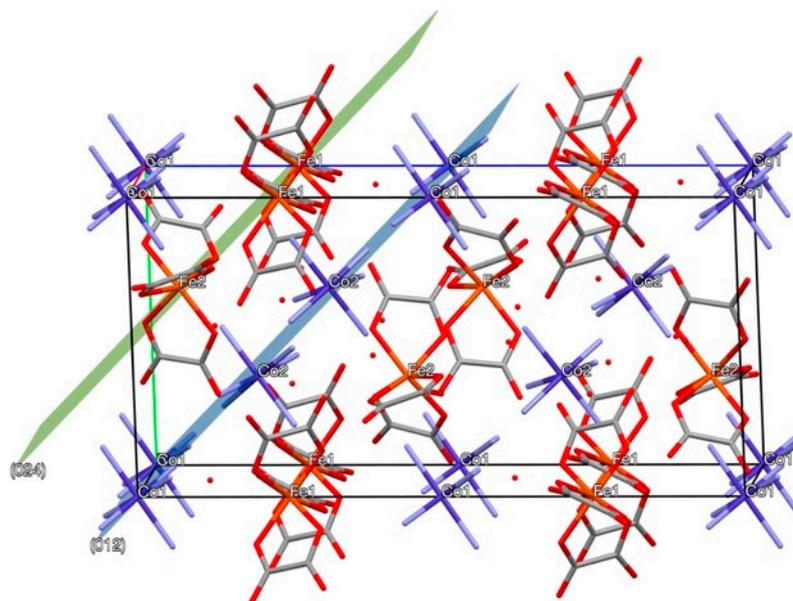


Figure 1. General view of the unit cell in the crystal structure of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ along the hexagonal axis a . Crystallographic planes (0 1 2) and (0 2 4) correspond to $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ hexagonal layers.

As a general trend, thermal decomposition in a hydrogen atmosphere proceeds in one step, and the process of thermal degradation in an inert atmosphere can have several separate stages [10], which is the reason we settled on an inert atmosphere. The thermal decomposition in the inert atmosphere (helium, argon, or nitrogen flow) is a solid-phase process in the inner coordination sphere of cations and anions, i.e., all products of their thermolysis are formed due to the interaction of the central ions with ligands coordinated to them. It is important, that thermal decomposition of double complex salts can be characterized as a ligand exchange and interaction between central metallic ions and ligands. The detailed understanding of thermal analysis curves and volatile thermolysis products

should be accompanied by material balance analysis to be able to understand how inner coordination spheres change with heating. Special large-scale experiments are necessary to address whose issues.

Double complex salts with Co and Fe, such as $[\text{CoA}_6][\text{M}(\text{C}_2\text{O}_4)_3] \cdot 3(4)\text{H}_2\text{O}$ ($A = \text{NH}_3, \frac{1}{2}\text{en}$; $M = \text{Fe}, \text{Cr}$) were investigated in much detail [11,12]. Thermal decomposition of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ in air results in the formation of an oxide mixture below 275 °C. Thermal decomposition in the inert atmosphere results in a formation of a mixture of oxides and CoFe nano-dispersive alloy. Thermal decomposition in a hydrogen flow results in the formation of pure single-phase CoFe alloy. Water, ammonia, CO, and CO₂ are the main gaseous products of its thermal decomposition. In the temperature range 250–300 °C, the formation of an intermediate phase has been proposed [11]. Nevertheless, intermediate phases were never isolated and investigated to obtain their exact composition and properties.

Here, we present a detailed study of the thermal decomposition of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ in an inert atmosphere (argon flow). It is a model system for an in-depth study of more complex cases of the formation of carbon-containing single-source precursors for catalytically active systems. A key crystalline intermediate was isolated and studied using thermal analysis, infrared (IR) spectroscopy, and powder X-ray diffraction. Gram-scale experiments allowed us to isolate homogeneous air-stable samples and investigate their catalytic activity in model reactions. The catalytic properties of nano-structured bi-metallic powders, which do not contain carbon, were characterized in oxidation-reduction reactions.

2. Materials and Methods

A total of 400 g of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ was synthesized by mixing aqueous solutions of equivalent amounts of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ (both were synthesized according to [13]). Elemental compositions of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, as well as intermediate products were confirmed by elemental analysis (C, Co, Fe). For the elemental analysis, the compounds were dissolved in a concentrated HCl water solution. The metal concentrations were further determined by atomic absorption spectrometry using an AAnalyst-400 spectrometer. Carbon was analyzed using an ELTRA CS-2000 C,H,N automatic analyzer. An elemental analysis of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, wt %: C—13.5, Co—11.0, Fe—10.4. Calculated, wt %: C—13.46, Co—11.02, Fe—10.44.

A powder X-ray diffraction (PXRD) study was performed using a Shimadzu XRD 6000 diffractometer (room temperature, $\text{CuK}\alpha$ radiation, graphite mono-chromator). IR spectra were collected on a Nicolet 6700 FT-IR spectrometer in KBr tablets. Characteristic absorption maxima in the IR spectrum, cm^{-1} : 3547, 3469 ν (OH), 3301, 3195 ν (NH), 1707, 1679 ν (C = O), 1396 ν (CO) + ν (CC), 1323, 899, 854 ν (CO) + $\bar{\alpha}$ (OC = O), 795 ρ (OH₂), 532 ν (MO) + ν (CC), 482 δ_{cyclo} + $\bar{\alpha}$ (OC = O).

Specific surface areas were measured using a Tristar 3020 unit. Samples for specific surface area measurements (Table 1) were prepared in a tubular quartz reactor inserted into a tubular Nabertherm RT 50-250/11 furnace.

Thermal gravimetric (TG) curves were obtained using a NETZSCH STA 409 PC/PG (7–10 mg powdered samples were heated in argon flow with heating rates of 3, 5 and 10°/min in a temperature range of 20–1000 °C). Corresponding TG curves for $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ and an intermediate sample I-1 are presented in Figure 2. Scanning electron microscopy images were obtained using a SEM-Leo 420 microscope (Figure 3).

Intermediate products were isolated after heating $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ up to 250 (I-1) and 260 °C (I-2) in argon flow in a quartz vessel using a THERMODAT 1955 programmable furnace with a heating rate of 3°/min. Products were tempered at final temperature for an hour and cooled naturally during 24 h. White condensate, from a stream of gaseous products, was collected in a vessel with Raschig rings cooled by ice (0 °C), NH₃, and CO₂ were collected in two coupled Drexel flasks with HCl and NaOH water solutions. Details are given in Table 2.

Catalytic tests were performed using 0.1 g thermolysis products II-1, II-2, III and IV. The reactions mentioned above were used to test the catalytic properties of the products. The 1-decomposition of

hydrogen peroxide occurred in an aqueous solution in the presence of a solid sample [4]. The first order rate constant has been determined using the residual concentration of H_2O_2 . The 2-gas-phase oxidation of acetone with oxygen in a current of air, the speed of which was determined by the amount of CO_2 formed per unit time [5,6]. The 3-solid-phase decomposition of ammonium perchlorate with an additive of 1% of the catalyst to be tested, the efficiency of which was determined by lowering the temperature of complete decomposition of NH_4ClO_4 [7].

Table 1. Results of thermal treatment of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ in argon flow (heating rate $5^\circ/\text{min}$).

Temperature	Residue, wt %	Residual Carbon, wt %	Total Carbon, wt %	S_{BET} m^2/g	V_{Σ} , cm^3/g	Comment
RT	100	13.46	100	-	-	Precursor tubular crystals
300	52.4	13.14	50	29	0.05	
350	41.6	10.3	33	62	0.16	
385	26.1	0.18	<1	45		
400	24.8	0.15	<1	28	0.15	Air stable
400	29.2	0.12	<1	17	0.08	Pyrophoric
450	25.05	0.095	<1	14.5	0.08	Air stable

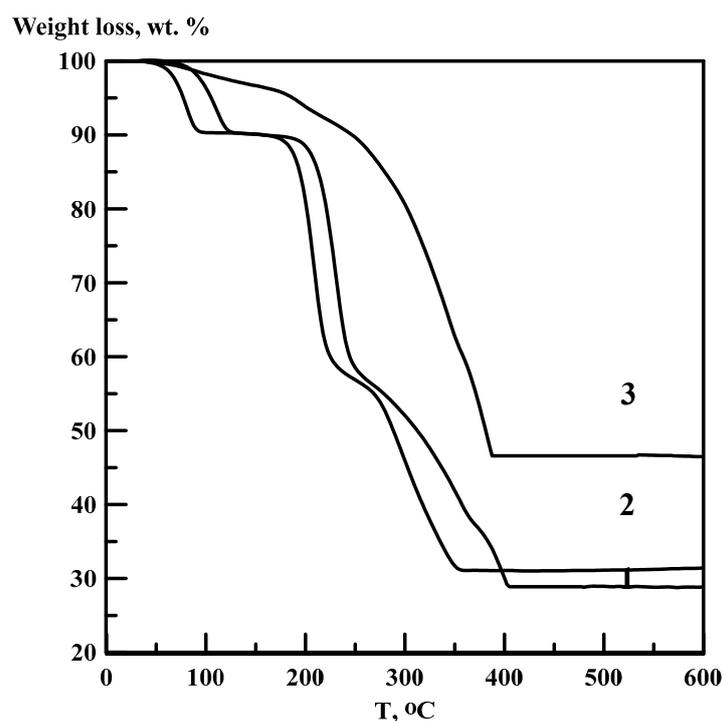


Figure 2. Thermal gravimetric (TG) curves for $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ with heating rate $10^\circ/\text{min}$ (1) $3^\circ/\text{min}$ (2) and TG curve of the intermediate product I-1 (3) (heating rate $3^\circ/\text{min}$).

3. Results and Discussion

3.1. Thermal Decomposition Products

Carbon-containing double complex salts, such as hexacyanoferrate [14], usually form amorphous carbon as a bi-product of their thermal decomposition in an inert atmosphere. Nevertheless, after the thermal decomposition of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ above 385°C , in argon flow, less than 1 wt % of carbon could be detected (Table 1). The product of the thermal decomposition of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, obtained above 400°C , might be pyrophoric on air.

Thermal degradation of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ (Figure 2) already starts below $100\text{ }^\circ\text{C}$, which corresponds to its dehydration (*ca.* 10 wt %). Tubular crystals of initial salt reveal their shape after complete dehydration above $100\text{ }^\circ\text{C}$ (Figure 3). Anhydrous product $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]$ is stable up to $190\text{ }^\circ\text{C}$. Further decomposition contains two sequential steps at $190\text{--}270$ and $270\text{--}350\text{ }^\circ\text{C}$.

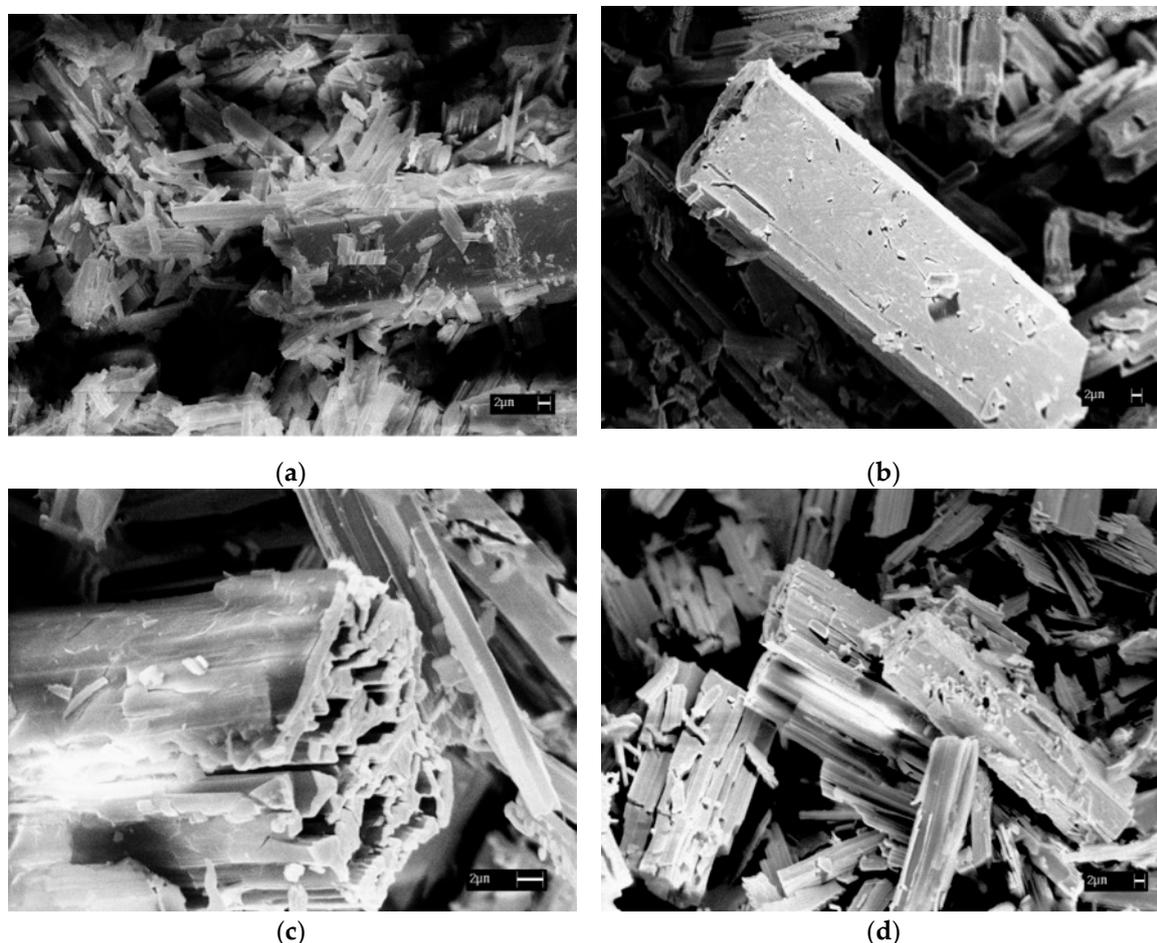


Figure 3. Electronic micrographics of starting $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ single-source precursor (a) and intermediate I-1 (b–d).

For the preparation of intermediate I-1 (60 wt % residual), 75.0 g (0.14 mole) $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ was heated up to $250\text{ }^\circ\text{C}$. White crystalline powder was collected from the inner surface of the furnace, connecting hoses and in the ice-cooled condenser. The powder has high solubility in cold water and can be easily completely dissolved in water. According to IR-spectra, condensed white powder consists of a mixture of ammonium carbonate and ammonium oxalate. According to the weight loss, the intermediate I-1 corresponds to $225\text{ }^\circ\text{C}$ on the TG curve of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ (Figure 2). Repetition experiments at $260\text{ }^\circ\text{C}$ (57 wt % residual) correspond to the intermediate I-2. Both intermediate samples according to their weight loss might have idealised stoichiometry $\text{CoFe}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2$. Further thermal decomposition of the intermediate I-1 (Figure 2) results in a formation of $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$.

IR spectra of I-1 and I-2 are very similar and contain several absorption maxima, cm^{-1} : $3195\text{ v}(\text{NH})$, $1636, 1655\text{ v}_{\text{as}}(\text{C}=\text{O})$, $1313, 799\text{ vs.}(\text{CO}) + \bar{\text{a}}(\text{OC}=\text{O})$, $496\text{ } \delta_{\text{cycle}} + \bar{\text{a}}(\text{OC}=\text{O})$. This indicates the presence of ammonia, carbonyl groups, and cyclic oxalate groups in their structure [15]. All absorption bands in the IR-spectra of initial $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ can be associated with terminal bidentate oxalate groups coordinated to Fe(III) ion, as well as ammonia coordinated to Co(III). Absorption bands in the IR-spectra of I-1 and I-2 can be associated with frequencies of bridged

and cyclic oxalate ligands. For example, bridged tetradentate C_2O_4 -group contains two IR-active C-O valent bands at 1628 and 1345 cm^{-1} and does not contain lines at 1650 and $1250\text{--}1270\text{ cm}^{-1}$, characteristic of terminal chelate oxalate ligands [15].

Intermediate **I-1** is partially soluble in water with the loss of ammonia. After two months on air, **I-1** and **I-2** lose 80 wt % of ammonia. A total of 10.0 g of fresh **I-1** was treated with 150 mL distilled water. Only 1.7 g of **I-1** was dissolved with a formation of water solution of 0.067 g of Co and 0.009 g of Fe. The solid residue after drying has been identified as a mixture of $Co(C_2O_4)_2 \cdot 2H_2O$ and $Fe(C_2O_4)_2 \cdot 2H_2O$ [16,17]. So, the intermediate product $CoFe(NH_3)_2(C_2O_4)_2$ is not water stable and exists in a very narrow temperature interval ($230\text{--}270\text{ }^\circ\text{C}$).

A total of 20.0 g of **I-1** was calcined at $420\text{ }^\circ\text{C}$ in argon flow. A total of 7.5 g of **II-1** (37.5 wt % residual) was obtained. Sample **II-1** is homogeneous, black not pyrophoric powder with specific surface area of about $S = 11.2\text{ m}^2/\text{g}$. A calcination of 20.0 g of **I-2** at $385\text{ }^\circ\text{C}$ results in a residual weight of 8.5 g (**II-2**, 42.5 wt % residual) with a specific surface area of about $S = 17.8\text{ m}^2/\text{g}$ (Table 2). The composition of both samples (**II-1** and **II-2**) can be estimated as $CoFeO_{0.5}$ with 80 wt % of metals. **II-1** and **II-2** are crystalline and can be identified as a mixture of CoFe alloy and $Co_{1.5}Fe_{1.5}O_4$ mixed oxide.

To compare the results of thermolysis of DCS and the intermediate, a weight of 65 g (0.1215 mol) of the original DCS was heated to $370\text{ }^\circ\text{C}$, at a speed of 3 deg/min in the above-described installation with an hourly exposure. When the ampoule was opened, the residue was heated up to more than $100\text{ }^\circ\text{C}$. A residue of 19.95 g (30.7%) was obtained, product III. The specific surface is $12.1\text{ m}^2/\text{g}$, the sample is completely crystalline. According to X-ray phase analysis (Figure 4), it is a mixture of oxides M_3O_4 , (Table 2). Thus, the material burned down, and was, apparently, metal. Repetition of this experiment at $385\text{ }^\circ\text{C}$ under conditions: 60 g (11.22 mmol) in argon gave a residue of 29.5% (17.7 g) of product IV. $S_{sp} = 16.1\text{ m}^2/\text{g}$. When opening the furnace chamber, the material also warmed up, but less than III. The results of the analysis of III and IV, see Table 2. Thermal decomposition of the initial $[Co(NH_3)_6][Fe(C_2O_4)_3] \cdot 3H_2O$ and the intermediate $CoFe(NH_3)_2(C_2O_4)_2$ (**I-2**) finished at the same temperatures, but gave different products (**II-2** and IV, correspondently). Consequently, the initial complex, under continuous heating, yields a more disperse and pyrophoric metallic material in comparison with isolated intermediate, which forms mainly CoFe.

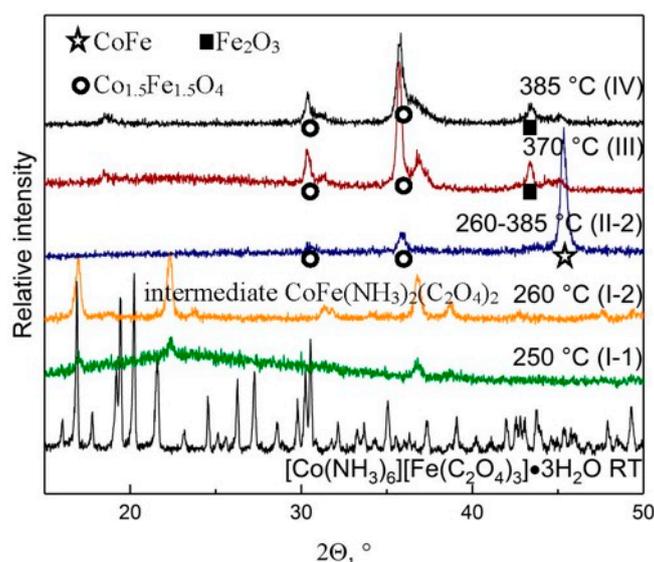


Figure 4. Diffractograms of the precursor salt $[Co(NH_3)_6][Fe(C_2O_4)_3] \cdot 3H_2O$, intermediates **I-III**, and final product **IV**.

Table 2. Results of macroscopic experiments.

Sample	T, °C	Yield, wt %	M.M. Cp.	Content of Elements, at. %			The Released Gas Products, mol/mol DCC		S _{BET} m ² /g	Composition and Properties
				Co	Fe	C	NH ₃	CO ₂		
I-1	250	60.0	321	18.4	17.0	14.9	3.6	0.78	16.8	Light brown, X-ray amorphous Co:Fe:C = 1.03:1:4.08
I-2	260	56.9	304	19.7	19.1	14.5	4.1	0.74	36.5	Light brown Co:Fe:C = 0.98:1:3.53
II-1	420	37.5	120.4	48.1	45.6	0.06	1.1	1.4	11.2	Black, loose Co:Fe:O = 1:1:0.5
II-2	385	42.5	129.2	46.6	46.0	0.14	2.3	2.0	17.8	Black Co:Fe:O = 1:1.04:0.53
III	370	30.7 *	164.2	37.4	35.2	0.06	5.4	3.36	12.1	Black, pyrophoric, according to X-ray analysis Co _{1.5} Fe _{1.5} O ₄ Co:Fe:O = 1:1:2.7
IV	385	29.5*	157.7	39.6	38.5	0.07	5.2	2.8	16.1	Black, pyrophoric Co:Fe:O = 1:1.03:1.55

* After air oxidation.

4. Conclusions

1. Thermal decomposition of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ in argon flow corresponds to four clearly distinguishable stages: (a) Dehydration of the initial complex; (b) anhydrous $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]$ is stable from 100 to 190 °C; (c) further heating results in a formation of $\text{CoFe}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2$ intermediate stable in the temperature interval of 230–270 °C; (d) intermediate phase completely decomposes upon heating below 350 °C.
2. The initial complex, when heated to 370–420 °C, forms a pyrophoric CoFe alloy, which easily forms $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ upon air expose and contains <1 wt % of carbon.
3. Under the same conditions, the intermediate forms a mixture of 80 wt % metals and metal oxides.
4. The final products of thermolysis are catalytically inactive in the decomposition reaction of H_2O_2 , which we explain by the small specific surfaces and the absence of residual carbon.

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