

THERMAL DECOMPOSITION STUDY OF SELECTED ISOPOLYMOLYBDATES

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The thermal decomposition of ammonium trimolybdate $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, anilinium trimolybdate $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ and anilinium pentamolybdate $(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ in air and nitrogen has been investigated. The decomposition of molybdates was studied *in situ* by powder X-ray diffraction. Moreover, results of TG, as well as scanning microscopy studies, are presented. It was found that during thermal treatment in air phases of MoO_x type are obtained, while thermal treatment in nitrogen leads to obtaining a mixture of Mo_yC_z and Mo_pN_q . It is worth noting that even though chemical decomposition and formation of new compounds took place, in some cases needle-like or plate-like shapes of crystallites were preserved during thermal treatment.

Keywords: molybdates, powder X-ray diffraction, thermal decomposition

Introduction

Thermal treatment of chemical compounds, due to thorough mixing on the atomic level, can yield as a result compounds with compositions which are difficult to obtain using classical methods of ‘annealing of reagents’. Through thermal decomposition of metal-organic compounds or thermal decomposition of heavy metals embedded in polymers, groundwork ‘pre-ceramic’ materials can be obtained. With further treatment they can yield carbides, borides and nitrides. The thermal decomposition process depends on many variables, such as the composition of a given chemical compound, the rate of heating or the atmosphere surrounding a sample.

The thermal decomposition of molybdates can yield molybdenum trioxide MoO_3 and partially reduced molybdenum oxide MoO_{3-x} , which can be used as catalysts. These oxides are also very useful as exemplary systems of more composed systems (molybdenum oxides with additional compounds, e.g. Bi, W, V, Cu) [1].

The catalytic activity of these materials depends on their real structure (the quantity and type of defects), their composition and size of particles. These features are dependent on the kind of precursor treatment [2]. The results of thermal treatment of ammonium trimolybdate, anilinium trimolybdate and anilinium pentamolybdate in air and in nitrogen are presented in this paper.

Experimental

The sample of ammonium trimolybdate was obtained according to the procedure described in [3].

Synthesis of anilinium trimolybdate [4]: to a boiling solution of $\text{H}_2\text{MoO}_4\cdot\text{H}_2\text{O}$ (0.01 M) in 150 mL of water, a stoichiometric amount of aniline was added. The solution was slowly cooled and left for crystallisation at room temperature. Precipitated after about 4 months white fibrillar crystals were filtered off, washed with ethanol and dried in air.

Synthesis of anilinium pentamolybdate: to a boiling solution of $\text{H}_2\text{MoO}_4\cdot\text{H}_2\text{O}$ (0.01 M) in 150 mL of water, 0.02 M of anilinum hydrochloride dissolved in a small amount of water was added. The solution was boiled for 24 h; next, very fine grey-blue crystals were filtered off and washed with a small amount of a 50% water–alcohol mixture.

The XRPD investigations were performed using a Philips X’Pert Pro powder diffractometer and a reaction chamber XRK 900 (Anton Paar). The measurements were performed at temperatures of 25, 220, 400, 500, 600, 700, 800, 850 and 900°C. The atmospheres were selected in order to obtain an oxidizing environment (air) and a neutral environment (nitrogen). The XRD patterns were taken in 2Θ range from 5.0 to 100°, step size 0.025° 2Θ . The X-ray radiation source was a Co tube.

The thermogravimetric measurements were carried out, within the range of 25–700°C, using a Mettler Toledo TGA/SDTA 851° microscale. The sample was heated at a constant speed of 10°C min^{-1}

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in the air atmosphere, and after that in the argon atmosphere with a flow of 80 mL min^{-1} .

Scanning microscopy studies were performed using a JEOL JSM-5410 microscope and HITACHI S-4700 with EDS microanalysis in the Scanning Microscopy Laboratory of Biological and Geological Science of Jagiellonian University.

Results and discussion

The powder diffraction method was applied in order to test crystallinity and purity of the samples. The crystalline phases were identified with the use of PDF-2 [5] and PDF-4 [6] databases. The phases identified in the processes of thermal decomposition of ammonium trimolybdate, anilinium trimolybdate and anilinium pentamolybdate in air and in nitrogen are listed in Table 1. After thermal decomposition experiments, obtained products were investigated by chemical analysis. Results of chemical analysis supplemented the XRPD indications.

The products of long-term 'pre-ceramic' thermal treatment at higher temperatures were the focus of this project; thus, the compounds obtained in the range of $0\text{--}100^\circ\text{C}$ were not investigated in detail. In addition, in control studies it was established that annealing of anilinium pentamolybdate in the temperature of 100°C continuing even for several months causes no changes in the diffraction patterns.

The character of changes taking place in the samples of the investigated isopolymolybdates was also studied by scanning electron microscopy. The SEM images of ammonium trimolybdate, anilinium trimolybdate and anilinium pentamolybdate, before and after annealing in nitrogen, were recorded. These images are presented in Figs 7–9, respectively.

Investigation of thermal treatment of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ in air

On the basis of powder diffraction patterns it was found that during thermal treatment of ammonium trimolybdate in air, four stages of sample decomposition occur. In first stage anhydrous $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$ [7] is created, (measurement was performed in different conditions (λ , kV), so that not presented in the Fig. 1). The second stage in which the phase of $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$ appeared was observed at a temperature of 220°C . At a temperature range of $400\text{--}700^\circ\text{C}$ MoO_3 was detected. In the last stage, at a temperature of 800°C , molybdenum oxide Mo_4O_{11} was obtained (Table 1). The powder diffraction patterns of ammonium trimolybdate annealed in air are presented in Fig. 1.

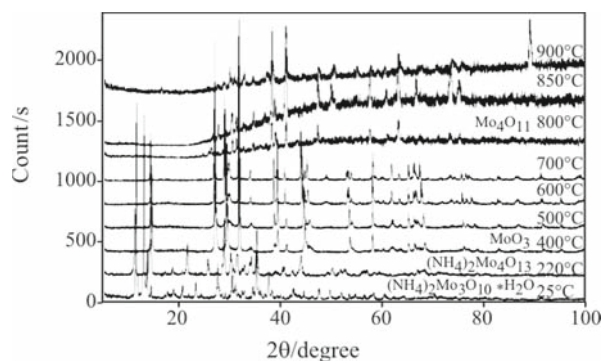


Fig. 1 Powder diffraction patterns of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ annealed in the air

Investigation of thermal treatment of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ in nitrogen

The powder diffraction patterns recorded during the thermal decomposition of ammonium trimolybdate in nitrogen are presented in Fig. 2. With the rise of temperature, ammonium trimolybdate hydrate disappears and a new phase of ammonium trimolybdate (about 120°C), next ammonium tetramolybdate in 220°C is observed. After that, the decomposition of ammonium tetramolybdate was observed, and at a temperature range of $400\text{--}700^\circ\text{C}$ a mixture of phases of molybdenum oxides MoO_3 , MoO_2 and Mo_4O_{11} was detected. At a temperature of 800°C only one phase, namely molybdenum oxide(IV) MoO_2 , was present (Table 1).

Thermal decomposition of ammonium hepta-, di- and octamolybdates in static air, helium and reducing atmosphere has already been investigated [8, 9]. During the thermal decomposition of ammonium trimolybdate, like in the case of other ammonium molybdates, ammonium octamolybdate was formed at a temperature about 200°C . In contrast to the decomposition of ammonium heptamolybdate neither amorphous nor hexagonal MoO_3 (or similar phases) were observed. Partial reduction of MoO_3 can be attributed to its reaction with the decomposition products (NH_3 and H_2O),

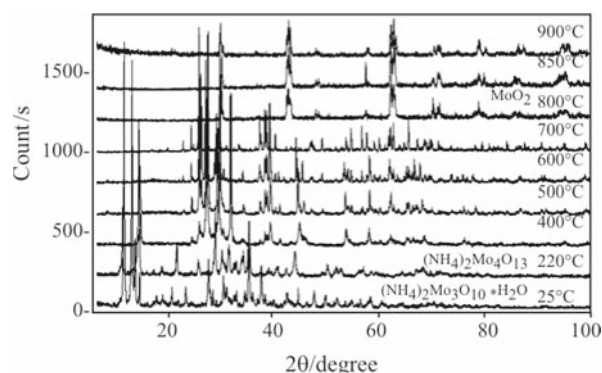


Fig. 2 Powder diffraction patterns of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ annealed in nitrogen

Table 1 Phases obtained by thermal decomposition of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$, $(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ in oxidizing atmosphere (air) and in nitrogen

Compound	Atmosphere	Temperature /°C	Identified phase	PDF
$(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$	air	25	$(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$	83-0421
		100	$(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$	[7]
		220	$(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$	80-0757
		400–700	MoO_3	05-0508
		800–900	Mo_4O_{11}	86-1269
$(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$	N_2	25	$(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$	83-0421
		220	$(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$	80-0757
		400–700	MoO_3	80-0347
			Mo_4O_{11}	72-0448
			MoO_2	01-0615
800	MoO_2	01-0615		
$(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$	air	25	$(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$	49-2407
		220	amorphous	–
		400–700	MoO_3	05-0508
		800	MoO_2	02-0422
$(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$	N_2	25	$(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$	49-2407
		220–600	amorphous	–
		700–850	Mo_2C	15-0457
			Mo_2N	25-1368
			$\text{Mo}_{0.42}\text{C}_{0.58}$	36-0863
			Mo_{18}C_7	02-1127
			Mo_{18}C_7	02-1127
		900	Mo_2N	25-1368
$(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$	air	25–220	$(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$	48-2500
		400–500	MoO_3	80-0347
			Mo_4O_{11}	72-0448
			MoO_2	78-1073
		600	Mo_4O_{11}	05-0338
		700–900	MoO_2	78-1072
$(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$	N_2	25–220	$(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$	48-2500
		700–900	$\text{Mo}_{0.42}\text{C}_{0.5}$	36-0683
			Mo_{16}N_7	23-1256
			Mo_2C	77-0720

particularly due to the fact that our experiments were carried out in ‘static air’, or very slow flow of N_2 .

Investigation of thermal treatment of $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ in air

The powder diffraction patterns recorded during annealing of anilinium trimolybdate at a temperature

of 220°C indicate changes connected with amorphisation of the sample. Similar behaviour was observed in case of thermal decomposition of Co, Ni, Cu and Zn trimolybdates [10].

The formation of a new crystalline phase starts at a temperature of 400°C. At a temperature of 800°C another change in the diffraction pattern is observed. Comparison of the obtained patterns with the PDF

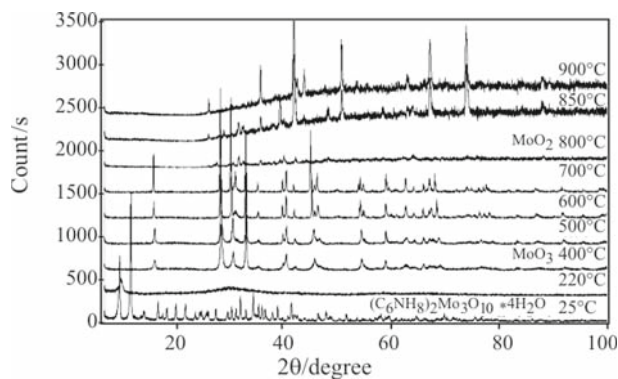


Fig. 3 Powder diffraction patterns of $(C_6NH_8)_2Mo_3O_{10} \cdot 4H_2O$ annealed in air

database indicates that during the thermal decomposition of anilinium trimolybdate in air, molybdenum oxide(VI) MoO_3 was created at a temperature of $400^\circ C$, and molybdenum oxide(IV) MoO_2 at a temperature of $800^\circ C$ (Table 1). The powder diffraction patterns of anilinium trimolybdate annealed in air are presented in Fig. 3.

Investigation of thermal treatment of $(C_6NH_8)_2Mo_3O_{10} \cdot 4H_2O$ in nitrogen

The diffraction patterns recorded during the process of annealing of anilinium trimolybdate in nitrogen indicate changes in the investigated sample leading to formation of four different phases (or mixtures of phases). Starting from 220 to $600^\circ C$ only amorphous phase exists. Between 700 and $900^\circ C$ molybdenum nitride (Mo_2N) and molybdenum carbides (Mo_2C , $Mo_{18}C_7$, $Mo_{0.42}C_{0.58}$) are formed (Table 1). Identification of the obtained compounds is unambiguous and possible only on the basis of the well-defined maxima recorded at a temperature of $800^\circ C$. The diffractograms of anilinium trimolybdate annealed in nitrogen are shown in Fig. 4.

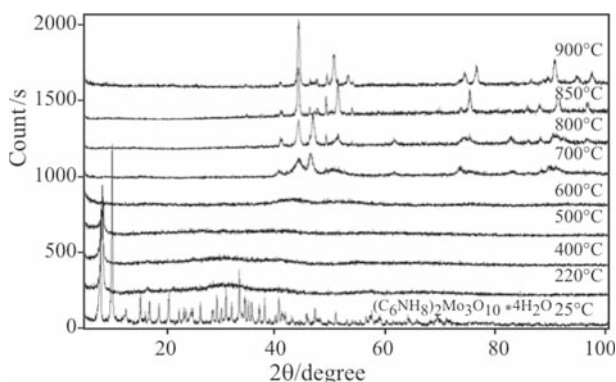


Fig. 4 Powder diffraction patterns of $(C_6NH_8)_2Mo_3O_{10} \cdot 4H_2O$ annealed in nitrogen

Investigation of thermal treatment of $(C_6NH_8)_2Mo_5O_{16}$ in air

On the basis of diffraction patterns of anilinium pentamolybdate annealed in air, four steps connected with the creation of different crystalline phases are observed. The first step occurs at a temperature range of $25\text{--}220^\circ C$, the second step at a range of $400\text{--}500^\circ C$ and the following steps at 600 and $700\text{--}900^\circ C$. In contrast to the decomposition process of anilium trimolybdate, in the case of pentamolybdate no completely amorphous phases were noticed. After the demise of the initial molybdate, the following sequence of oxides: (MoO_3 , Mo_4O_{11}), (MoO_2 , Mo_4O_{11}) was observed. The final product of thermal decomposition is MoO_2 (at a temperature of $900^\circ C$) (Table 1). The diffractograms of anilinium pentamolybdate annealed in an oxidising atmosphere are presented in Fig. 5.

Investigation of thermal treatment of $(C_6NH_8)_2Mo_5O_{16}$ in nitrogen

The thermal decomposition of $(C_6NH_8)_2Mo_5O_{16}$ can be divided into two steps: the gradual demise of pentamolybdate (up to a temperature of $400^\circ C$) and the forming of a new phase starting at a temperature

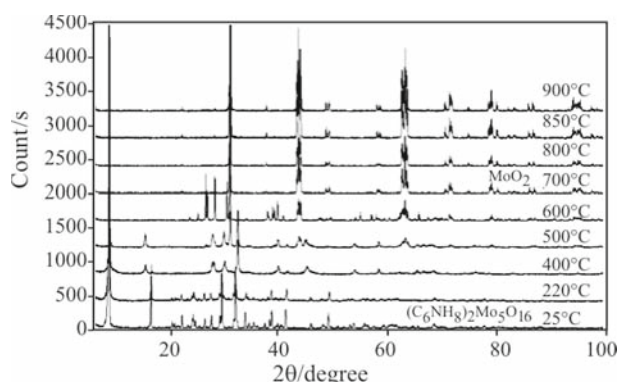


Fig. 5 Powder diffraction patterns of $(C_6NH_8)_2Mo_5O_{16}$ annealed in air

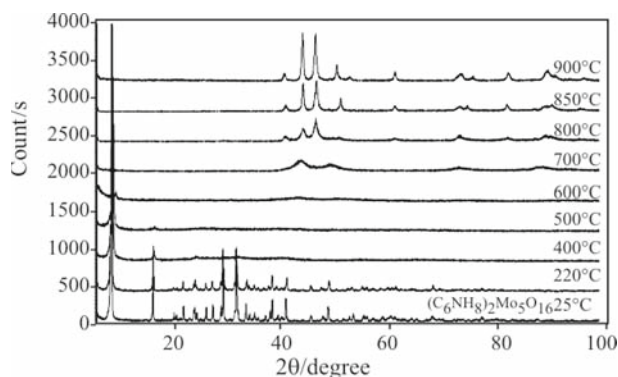


Fig. 6 Powder diffraction patterns of $(C_6NH_8)_2Mo_5O_{16}$ annealed in nitrogen

of 700°C. In temperature range of 400–700°C only amorphous phases exist. Phase analysis with the use of PDF-2/4 file indicates that at a temperature of 700°C a mixture of molybdenum nitrides and carbides is created (Table 1). The diffractograms of anilinum pentamolybdate annealed in nitrogen are shown in Fig. 6.

TG investigations of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ and $(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ in air and in argon

The results of TG investigations of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ and $(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ in air are presented in Table 2.

During the heating of ammonium trimolybdate in air three decomposition stages (at temperatures ranges of 100–180, 180–250 and 250–400°C) were detected. The first stage was due to dehydration of the investigated compound. The next stage, at a temperature of about 225°C was caused by partial deammonation. From the mass loss data, the molar ratio $(\text{NH}_4)\text{O}/\text{MoO}_3$ of the product was 0.25, as is typical of tetramolybdate. At 340°C a complete further deammonation process was observed.

On the basis of the TG curve of anilinum trimolybdate in air, five decomposition stages were observed. Below 395°C water and the organic part of

the compound are released. These processes are demonstrated in the powder diffraction patterns. The release of the organic part of the compound in air at a temperature up to 395°C leads to amorphisation of the sample (Fig. 3).

Similar results have been obtained and described by Santiago and Martinez [11–13] in the investigations of the thermal decomposition of anilinum octamolybdate dihydrate. Three decomposition steps have been observed. First-dehydration, which takes place up to the temperature about 200°C. The second step corresponds to a very complex decomposition of anilinum cation (200–470°C) in which a series of intermediate organic compounds were obtained. In the last step of decomposition, remaining organic components were removed from the specimen and molybdenum trioxide was formed.

As a result of heating of anilinum pentamolybdate in air, two stages of decomposition of the compound were observed. Both in cases of annealing anilinum trimolybdate and anilinum pentamolybdate, the organic part of the compounds was ‘burnt out’ to the temperature about 400°C, but only heating of anilinum trimolybdate in air does not lead to amorphisation of the sample (Fig. 5).

Interestingly, in contrast to ammonium trimolybdate and anilinum trimolybdate, the decomposition of

Table 2 TG data of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ and $(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ in air

Compound	Temperature	TG mass loss/g mol ⁻¹	TG mass loss/%	Assignment
$(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ 501.94 g mol ⁻¹	(100–180°C)	18.02	3.59	H ₂ O
	(180–250°C)	13.00	2.59	0.5NH ₃ +0.25H ₂ O
	(250–400°C)	39.05	7.78	1.5NH ₃ + .75H ₂ O
Total		70.07	13.96	MoO ₃ is final product
$(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ 708.1476 g mol ⁻¹	(60–120°C)	59.27	8.37	4H ₂ O
	(120–200°C)	24.97	3.50	??
	(200–295°C)	22.02	3.11	?
	(295–395°C)	116.84	16.50	?
	(395–500°C)	63.80	9.01	?
Total		286.90	40.49	loss of 288 g mol ⁻¹ corresponds to decomposition to Mo ₄ O ₁₁
$(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ 923.96 g mol ⁻¹	(295–360°C)	57.38	6.21	?
	(360–520°C)	134.99	14.61	?
Total		192.37	20.81	loss of 188 g mol ⁻¹ if MoO ₃ is final product

??—reaction can not be explained based on XRPD and TG measurement

anilinium pentamolybdate occurs in two steps only. In contradiction to ammonium trimolybdate thermal decomposition of anilinium molybdates can be only qualitatively discussed, particularly due to presence of amorphous phases (Table 2).

SEM images of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$, $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ and $(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ before and after annealing in nitrogen

As shown in Figs 7 and 8, ammonium molybdate and anilinium trimolybdate are fibre-like substances. In Fig. 9 images of anilinium pentamolybdate, which forms large, massive and sharp-edged crystalline aggregates, are shown.

SEM images of anilinium trimolybdate (Fig. 8) present the fibrous shape of the crystalline grains of the compound. After heating anilinium trimolybdate in nitrogen the shape of fibres is still the same. Interestingly, the surface of fibres after annealing is not smooth but irregular. The width of the fibres spans a range of 0.35–0.70 μm and the length is over

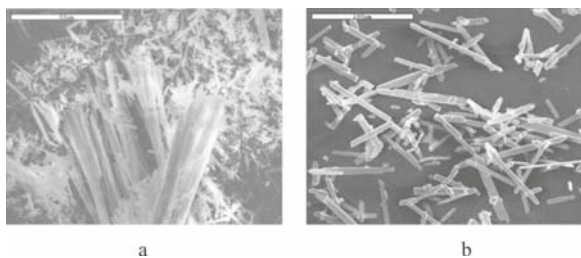


Fig. 7 SEM image of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}\cdot\text{H}_2\text{O}$ a – before and b – after annealing

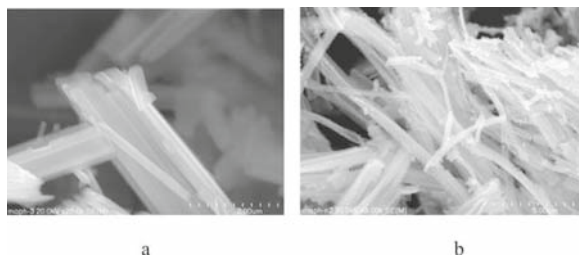


Fig. 8 SEM images of $(\text{C}_6\text{NH}_8)_2\text{Mo}_3\text{O}_{10}\cdot 4\text{H}_2\text{O}$ a – before and b – after annealing in nitrogen

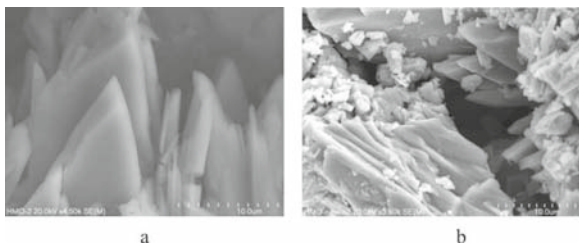


Fig. 9 SEM images of $(\text{C}_6\text{NH}_8)_2\text{Mo}_5\text{O}_{16}$ a – before and b – after heating in nitrogen

14 μm . In the case of ammonium trimolybdate, however, both before and after annealing, well-developed fibres with smooth surfaces are observed.

Conclusions

The aim of the performed investigations was to determine the changes which occur during the thermal decomposition of molybdenum compounds in different atmospheres.

Comparison of the collected diffraction patterns allow us to state that the investigated isopoly-molybdates annealed in a non-oxidising atmosphere decompose into amorphous phases, stable at a wide range of temperatures. The same compounds heated in air create a mixture of crystalline molybdenum oxides. The change of oxidation state from 6+ to lower values can be caused by the reduction of molybdenum by the organic part of a compound.

The results indicate that the decomposition process is strictly connected with the atmosphere surrounding the sample during heating. It was also suggested that the thermal decomposition process can be affected by the rate of introduction of a gas into the reaction chamber [14].

Moreover, the process of decomposition of the examined compounds proceeds as a series of stages leading to new phases or intermediate phases not described thus far. The chemical composition is quite variable under changing thermodynamical conditions with a rise in temperature. Thus the powder diffraction method does not always allow an unambiguous identification of the intermediate products. The analysis is hindered by the fact that the intermediate products create a series of non-stoichiometric phases with very similar diffraction patterns.

The observation that, during the thermal treatment of selected molybdates in the N_2 atmosphere, mixtures of MoO_x , MoC_y and MoN_z are formed and that additionally some features of their original shape are preserved, seems to be of interest for further applications.

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