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Thermal decomposition of ammonium molybdates

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Abstract

The thermal behavior of ammonium molybdates, i.e. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (**1**) and $(\text{NH}_4)_2\text{MoO}_4$ (**2**), was studied in inert (N_2) and oxidizing (air) atmospheres by TG/DTA-MS, XRD, FTIR and SEM. The thermal decomposition sequence of **2** had similarities to **1**; however, there were significant differences as well. When both of them were annealed, NH_3 and H_2O were released parallel, and in air the as-evolved NH_3 was burnt partially into NO and N_2O . In both atmospheres, while **1** decomposed in four steps, the thermal decomposition of **2** involved 5 steps. In the case of **1**, the intermediate products were $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$, $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$ and h- MoO_3 . In contrast, the decomposition intermediates of **2** were

$(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$ and h-MoO_3 . By both **1** and **2**, the final product was dominated by o-MoO_3 , accompanied with small amount of Mo_4O_{11} in N_2 , which was absent in air. Most decomposition steps were endothermic, except for the last step around $400\text{ }^\circ\text{C}$, where crystallization from the residual amorphous phase had an exothermic heat effect. In addition, the combustion of NH_3 also changed the DTA curve into exothermic in some cases. The morphology of the final products was characterized by $1\text{-}5\text{ }\mu\text{m}$ sheet-like particles, except for annealing **2** in N_2 , when $0.5\text{-}1\text{ }\mu\text{m}$ thick and $5\text{-}10\text{ }\mu\text{m}$ long needle-shaped particles were detected.

1. Introduction

Ammonium molybdate tetrahydrate or ammonium heptamolybdate, i.e. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (**1**) is widely used for the preparation of molybdenum oxides, reduced molybdenum oxides, mixed molybdenum oxides or supported molybdenum oxide catalysts, and it can be also a precursor for molybdenum carbide or molybdenum metal. MoO_x catalysts have applications in various catalytic reactions, e.g. partial oxidation for light alkenes, hydrotreating, hydrodenitrogenation, or hydrodesulfurisation [1-5]. Molybdenum carbide is also applied as a catalyst for e.g. hydrogenation reactions [6-7]. Metallic molybdenum offers excellent mechanical, thermal and electrical properties and good corrosion resistance which makes it attractive for electronics, metallurgical, aerospace and electrical industries [8].

The structure of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ is composed of monomers of seven distorted, edge-sharing, molybdenum-oxygen octahedra. The thermal behavior of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ has been studied in a great number of papers [9-38]. The role of decompositions conditions (e.g. atmosphere, heating rate, presence of dopants, influence of possible support materials) have been investigated in detail. The reason for this increased interest is that the various MoO_x materials, molybdenum carbide and molybdenum metal can be easily obtained by the thermal treatment of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, and their application properties depends strongly on the structure, composition and morphology of the products, which are then determined by the circumstances of the annealing of the precursor [39].

However, there is another ammonium molybdate, i.e. $(\text{NH}_4)_2\text{MoO}_4$ (**2**), called ammonium orthomolybdate, which has a much simpler structure and composition [40]. It is mostly used as a corrosion inhibitor and can be also an intermediate to gain Mo from its ores [40]. Interestingly, the thermal behavior of $(\text{NH}_4)_2\text{MoO}_4$ has not been studied in detail yet, to the best of our knowledge. In order to use it also as a possible precursor for MoO_x compounds, it is important to obtain information about its thermal properties.

Hence, in this study our aim was to explore the thermal decomposition of $(\text{NH}_4)_2\text{MoO}_4$, and also study the thermal properties of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ for comparison. Thus, the annealing of the two materials was studied both in inert (N_2) and oxidizing (air) atmospheres. The thermal events were followed by simultaneous thermogravimetry and differential thermal analysis (TG/DTA) and also by evolved gas analysis performed by mass spectrometer (EGA-MS) coupled on-line to the TG/DTA device. The changes in morphology, structure and bonds were investigated by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and infrared spectroscopy (FTIR), respectively.

2. Experimental

The $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (**1**) and $(\text{NH}_4)_2\text{MoO}_4$ (**2**) samples were obtained from Sigma-Aldrich, and they were used as received.

SEM images were recorded by a JEOL JSM-5500LV scanning electron microscope.

Powder XRD patterns were measured on a PANalytical X'pert Pro MPD X-ray diffractometer using Cu K_α radiation.

FTIR spectra were obtained by an Excalibur Series FTS 3000 (Biorad) FTIR spectrophotometer in the range of $400\text{-}4000\text{ cm}^{-1}$ in KBr pellets.

The thermal decomposition of the samples was studied by a TG/DTA-MS apparatus, which consisted of an STD 2960 Simultaneous TGA/DTA (TA Instruments Inc.) thermal analyzer and a Thermostat GSD 200 (Balzers Instruments) quadrupole mass spectrometer. On-line coupling between the two parts was provided through a heated ($T = 200^\circ\text{C}$) 1 m 100% methyl deactivated fused silica capillary tube with inner diameter of 0.15 mm. A mass range between $m/z = 1 - 200$ was monitored by scan mode. During the measurements an open platinum crucible, a heating rate of $10\text{ }^\circ\text{C min}^{-1}$, sample sizes of 5 – 6 mg and flowing air (130 ml min^{-1}) were used.

3. Results and discussion

Characterization of 1

According to SEM images (Fig. 1a) sample **1** consisted of irregularly shaped $10\text{-}50\text{ }\mu\text{m}$ aggregated particles. The sample was made up only by $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (ICDD 27-1013), and there were no impurities detected in the X-ray powder diffractograms (Fig. 2). In the FTIR spectrum (Fig. 3) the

bands below 1000 cm^{-1} were assigned to various Mo-O lattice vibrations, characteristic to polymolybdates [41]. The N-H and O-H deformation bands of ammonium ions and water appeared at 1400 and 1630 cm^{-1} , respectively; while the O-H and N-H stretching vibrations were detected at 3135 and 3570 cm^{-1} [42-43].

Thermal decomposition of 1 in N₂

The first decomposition step was observed between 25 - $180\text{ }^{\circ}\text{C}$, and it was accompanied by an endothermic heat effect (Fig. 4). NH_3 and H_2O were released parallel. Due to their evolution the intensity of the N-H and O-H bands in the FTIR spectrum decreased to some extent. The initial crystal structure changed completely and a new polymolybdate phase, i.e. $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ (ICDD 37-0381) appeared (93.3 and 93.2% theoretical and measured remaining mass), as evidenced by XRD and FTIR. In the second decomposition step (180 - $270\text{ }^{\circ}\text{C}$) in an endothermic reaction again NH_3 and H_2O evolved, and the $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ phase transformed into $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$ (ICDD 11-4665) (88.9 and 88.7% theoretical and measured remaining mass). The N-H and O-H FTIR peaks reduced in intensity considerably and the Mo-O lattice vibration region was also modified.

In the third, endothermic decomposition step (270 - $370\text{ }^{\circ}\text{C}$) the parallel evolution of NH_3 and H_2O continued, and the O-H and N-H bands in the infrared spectrum disappeared almost completely. The crystal structure changed and a mixture of two phases was present. Traces of hexagonal molybdenum oxide, i.e. h- MoO_3 (ICDD 21-0569) were observed, but besides this phase already orthorhombic molybdenum oxide, i.e. o- MoO_3 (ICDD 12-8070) also appeared, which was the main component at this temperature.

In the last step (370 - $400\text{ }^{\circ}\text{C}$) in a slightly exothermic reaction the amount of o- MoO_3 increased (81.5 and 81.2% theoretical and measured remaining mass). The h- MoO_3 phase disappeared and a partially reduced molybdenum oxide, i.e. Mo_4O_{11} (ICDD 89-8980) formed, which was responsible for the lower measured remaining mass than the theoretical value for MoO_3 . FTIR also revealed the formation of molybdenum oxide [44].

At the end of the annealing the morphology changed significantly compared to the starting material (Fig. 1b). At $700\text{ }^{\circ}\text{C}$ the product was built up by 1 - $5\text{ }\mu\text{m}$ particles and sheets.

Thermal decomposition of 1 in air

The first two steps of the thermal decomposition of **1** in air were similar to those in N₂. From the starting material in the first endothermic step (25-180 °C) NH₃ and H₂O were released (Fig. 5) and (NH₄)₈Mo₁₀O₃₄ formed (Fig. 6). Then between 180 and 270 °C this phase transformed into (NH₄)₂Mo₄O₁₃ in an endothermic reaction, accompanied by the release of NH₃ and H₂O. In the FTIR spectra (Fig. 7) the changes were also very similar to those in air; the most remarkable was the decrease of the intensity of the N-H and O-H vibrations, and as the crystal structure changed, the lattice vibration region below 1000 cm⁻¹ was modified. The only significant difference was that in air in the first decomposition step a small amount of the as-released NH₃ was oxidized thermally to NO. Due to the elevated temperature, in the second decomposition step a larger portion of the as-evolved NH₃ was burnt, and besides NO also N₂O was detected as combustion product. Although the oxidation of NH₃ is an exothermic process [45-47], still the endothermic heat effect of the decomposition of the solid phase was dominant on the DTA curve; thus, here again an intense endothermic DTA peak was observed at 234 °C.

It must be mentioned that N₂O and NO formation might be also the consequence of NH₄NO₃ intermediate formation and decomposition to some extent. Such phenomenon was observed in case of other ammonium salts of other oxometallates (e.g. permanganates, vanadates, etc.), when the metal oxide type intermediates could catalyze the oxidation reaction [48-52].

In contrast to inert atmosphere, in air in the third step (270-350 °C) the (NH₄)₂Mo₄O₁₃ phase transformed only into o-MoO₃. The absence of h-MoO₃ at the end of the third decomposition step is explained by annealing in oxidizing atmosphere. Due to annealing in air, besides NH₃ and H₂O, also NO and N₂O were detected, similar to the second decomposition step.

In the fourth step, similar to N₂ atmosphere, a small exothermic heat effect was observed. However, here in the final solid product only o-MoO₃ was observed without the partially reduced Mo₄O₁₁, in contrast to what was observed in inert atmosphere; thus, here the measured remaining mass was equal to the theoretical 81.5 % value. Before and after the exothermic reaction the solid phase contained o-MoO₃, and the only difference was that the sample became more crystalline at the end of the fourth step. Hence, the exothermic heat effect is explained by the further crystallization of o-MoO₃ from the residual amorphous part of the sample at 350 °C.

The morphology of the final product was characterized again by 1-5 μm particles, however, here their size was even smaller than in N₂, and most of them were sheet-like.

Characterization of 2

Sample **2** was built up by 1-10 μm particles, which were aggregated into much larger blocks (Fig. 8a). Thus, the particles size of sample **2** was much smaller than that of **1**. The sample consisted of only $(\text{NH}_4)_2\text{MoO}_4$ (ICDD 12-2248) with no impurities. The FTIR spectrum was similar to **1**; however, in **2** the O-H deformation vibration band (1630 cm^{-1}) was more intense compared to the N-H deformation peak (1400 cm^{-1}). The Mo-O vibration region below 1000 cm^{-1} was also somewhat different, corresponding to the difference in the crystal structures of **1** and **2**.

Thermal decomposition of 2 in N₂

Though the structure and composition of **2** was quite simple, nevertheless its thermal decomposition was quite complex, which is in contrast to e.g. $(\text{NH}_4)_2\text{WS}_2$, which has similar structure, and its thermal behaviour is not complicated, and involves only few decomposition steps and intermediates [53].

The mass loss (17.6 %) in the first decomposition (25-200 $^{\circ}\text{C}$) step of **2** in N_2 (Fig. 11) was much larger than in the case of **1**. Similarly, NH_3 and H_2O were released parallel in an endothermic reaction, and in the FTIR spectrum the intensity of the N-H and O-H peaks decreased to some extent. The intermediate sample after the first decomposition step consisted of different phases, compared to **1**, i.e. $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$ (ICDD 09-9568) and a small amount of $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ (ICDD 12-7094) were detected at 200 $^{\circ}\text{C}$ in the case of annealing **2** in N_2 .

In the second decomposition step (200-230 $^{\circ}\text{C}$), accompanied with a small evolution of NH_3 and H_2O and 0.7 % mass loss, in an endothermic reaction the $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ content of the sample at 200 $^{\circ}\text{C}$ transformed into $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$. Thus, the sample at 230 $^{\circ}\text{C}$ contained only $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$ (82.3 and 81.7 % theoretical and measured remaining mass).

The third decomposition step (230-280 $^{\circ}\text{C}$) was also characterized by a small mass loss (2.4 %). Here again NH_3 and H_2O were detected as gaseous decomposition products. The sample at 280 $^{\circ}\text{C}$ contained only $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$ (80.1 and 79.4 % theoretical and measured remaining mass), which was also the only constituent of the intermediate sample at 270 $^{\circ}\text{C}$ during the thermal decomposition of **1** in N_2 . Therefore, from this stage the thermal behavior of **2** has become similar to **1**.

Accordingly, sample **2** almost completely lost its NH_4^+ and H_2O content at 370 $^{\circ}\text{C}$ in an endothermic reaction, and hence the N-H and O-H deformation and stretching FTIR peaks basically disappeared. As the main constituent of the intermediate sample at 370 $^{\circ}\text{C}$ o-MoO₃ was detected; in addition, traces of h-MoO₃ were also present.

Then, in the final decomposition step (370-420 $^{\circ}\text{C}$) the h-MoO₃ disappeared, the o-MoO₃ became more crystalline accompanied by an exothermic heat effect (exothermic DTA peak at 400 $^{\circ}\text{C}$) and also the

Mo₄O₁₁ phase was detected to some extent, just as in the case of **1**. Accordingly, the remaining was a bit lower (73.3 %) than what expected for pure MoO₃ (73.5 %)

In contrast to **1**, the morphology of the final decomposition product of **2** was dominated by needle like particles, which were 0.5-1 μm thick and 5-10 μm long (Fig. 8b).

Thermal decomposition of 2 in air

The thermal decomposition of **2** in air was a combination of the thermal behavior of **2** in N₂ and the thermal decomposition of **1** in air.

In the first decomposition step (25-205 °C), NH₃ and H₂O was released parallel and also small amount of NO was detected (Fig. 12). The mass loss (15.8 %) was similar as in N₂, and the formed crystalline phases were also similar, i.e. (NH₄)₂Mo₃O₁₀ and (NH₄)₂Mo₂O₇ (Fig. 13). The intensity of the N-H and O-H stretching and deformation modes decreased to some extent, and there were also changes in the Mo-O vibration region below 1000 cm⁻¹, according to the change in the crystalline structure (Fig. 14).

In the second (205-230 °C) and third decomposition (230-270 °C) steps NH₃ and H₂O evolved (endothermic DTA peaks at 214 and 242 °C, respectively), and at 270 °C the solid sample was composed of mostly (NH₄)₂Mo₄O₁₃.

In the fourth decomposition step (270-370 °C) the sample transformed into o-MoO₃. Here the combustion of the as-released NH₃ was so intensive that the DTA peak started as endothermic (endothermic DTA peak at 317 °C) due the decomposition of the solid materials, but then it changed into exothermic at the second part of the decomposition step (exothermic DTA peak at 343 °C). The XRD pattern of the intermediate obtained at 325 °C showed traces of h-MoO₃, but by the end of this step these peaks disappeared.

In the last decomposition step the amorphous part of the sample transformed into o-MoO₃ in an exothermic reaction (small exothermic DTA peak at 420 °C) and hence the XRD peaks of this phase became stronger and narrower, and FTIR also showed the characteristic bands of the o-MoO₃ phase.

Unlike the annealing of **2** in N₂, the morphology of the final product of **2** in air was built up again by sheet-like particle of 1-5 μm (Fig. 8c), similar to when **1** was annealed in N₂ and air.

4. Conclusion

The thermal decomposition of (NH₄)₆Mo₇O₂₄·4H₂O (**1**) and (NH₄)₂MoO₄ (**2**) were studied extensively in inert (N₂) and oxidizing (air) atmospheres by TG/DTA-MS, XRD, FTIR and SEM.

1 decomposed in four steps in N₂, where NH₃ and H₂O were released parallel. The intermediate products were (NH₄)₈Mo₁₀O₃₄, (NH₄)₂Mo₄O₁₃ and h-MoO₃, while the final sample was dominated by o-MoO₃, accompanied with a small amount of the partially reduced Mo₄O₁₁ phase. In air the as-released NH₃ was oxidized thermally into NO and N₂O. Due to the oxidizing atmosphere the only final product was o-MoO₃. The hexagonal molybdenum oxide phase (h-MoO₃) and the partially reduced molybdenum oxide (Mo₄O₁₁) in air were not observed.

The thermal decomposition sequence of **2** had similarities to **1**; however, there were significant differences as well. In addition, though the structure and composition of **2** was quite simple, its thermal decomposition was complex. In N₂ the decomposition intermediates were (NH₄)₂Mo₃O₁₀ and (NH₄)₂Mo₂O₇ in the first two steps in contrast to **1**, where only (NH₄)₈Mo₁₀O₃₄ observed as a decomposition intermediate in this region. Then at 270-280 °C (NH₄)₂Mo₄O₁₃ was a common intermediate for both **1** and **2**. The final product was o-MoO₃ together with a small amount of Mo₄O₁₁, similar to **1**. The thermal decomposition of **2** in air was a combination of the thermal behavior of **2** in N₂ and the thermal decomposition of **1** in air. The decomposition intermediates were the same as for **2** in N₂, i.e. (NH₄)₂Mo₃O₁₀, (NH₄)₂Mo₂O₇, (NH₄)₂Mo₄O₁₃ and h-MoO₃, and the final product was highly crystalline o-MoO₃ without the presence of Mo₄O₁₁. Similar to the decomposition of **1** in air, the as-evolved NH₃ was burnt partially into NO and N₂O.

In the case of both **1** and **2**, most decomposition steps were endothermic. An exception was the last step for both phases (around 400 °C), where the increase in the crystallinity of the samples through the formation of o-MoO₃ from the residual amorphous phase at the end of the previous step had exothermic heat effect. In addition, the combustion of NH₃ was so intensive that, when **2** was annealed in air, after 330 °C the DTA curve changed from endothermic into exothermic.

While **1** consisted of irregularly shaped 10-50 µm aggregated particles, **2** was built up by 1-10 µm particles. Nevertheless, after annealing **1** in air and N₂ and heating **2** in air the final products were composed of 1-5 µm particles and sheets. In contrast, when **2** was annealed in N₂ at 700 °C, the sample was dominated by 0.5-1 µm thick and 5-10 µm long needle like particles.

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6. References

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Figures

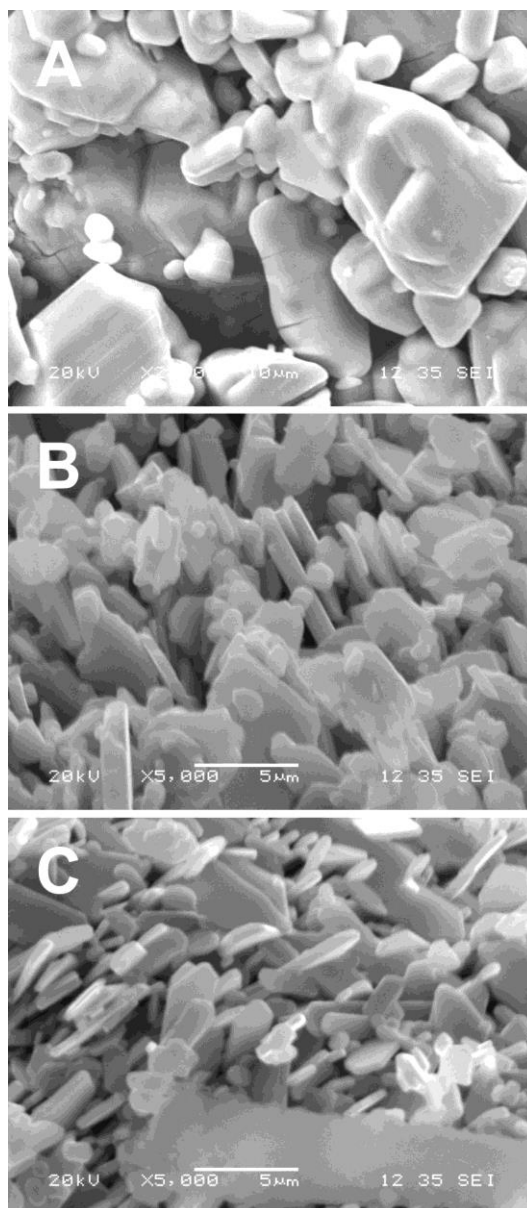


Figure 1. SEM images of (a) **1**; (b) **1** annealed in N₂ at 700 °C; (c) **1** annealed in air at 700 °C

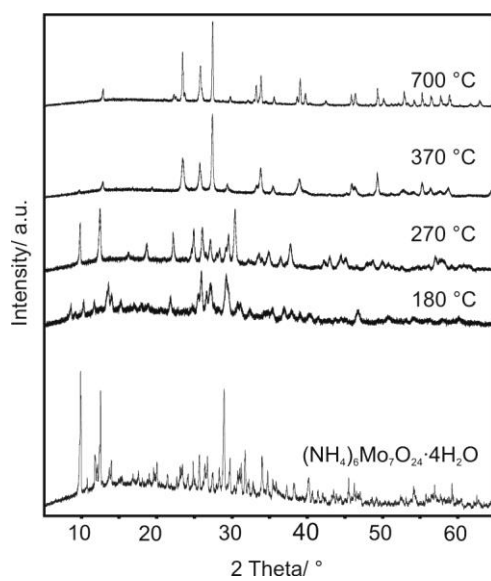


Figure 2. XRD patterns of **1** and its decomposition products in N_2

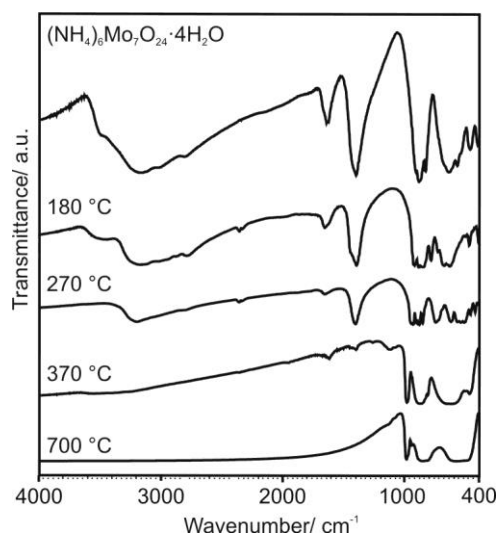


Figure 3. FTIR spectra of **1** and its decomposition products in N_2

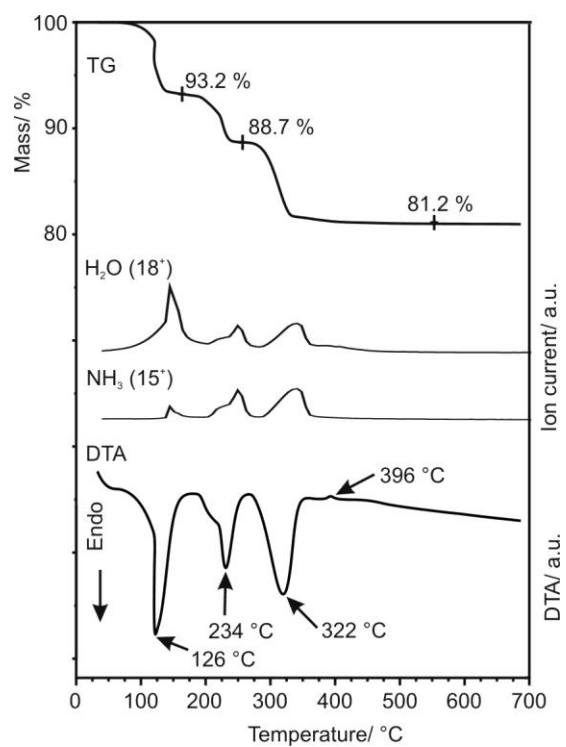


Figure 4. TG/DTA and EGA-MS curves of **1** in N₂

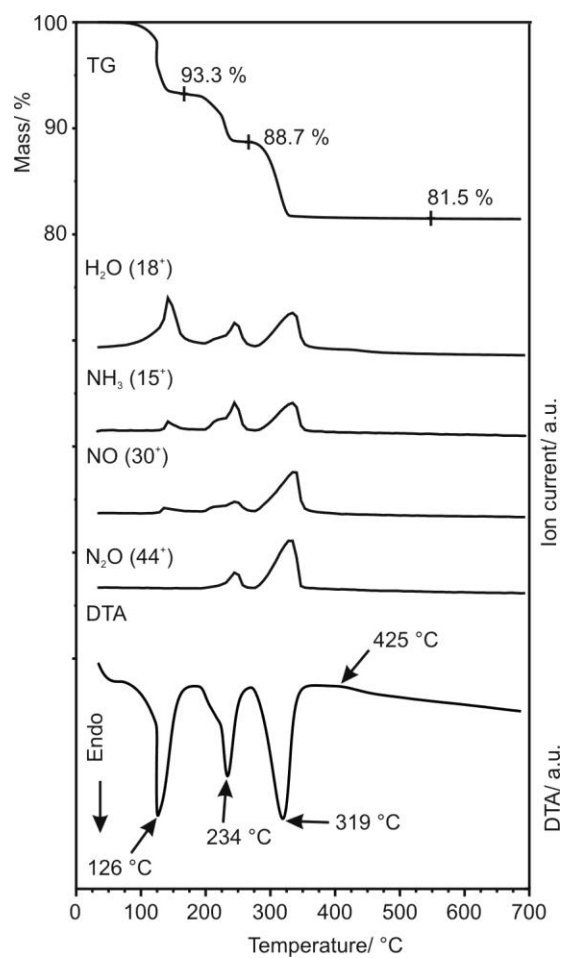


Figure 5. TG/DTA and EGA-MS curves of **1** in air

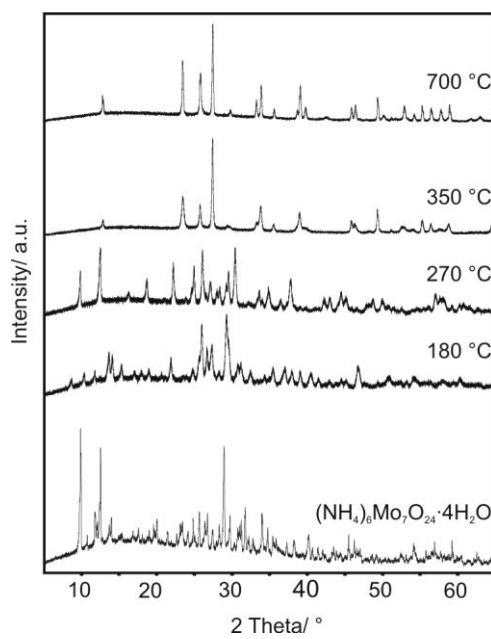


Figure 6. XRD patterns of **1** and its decomposition products in air

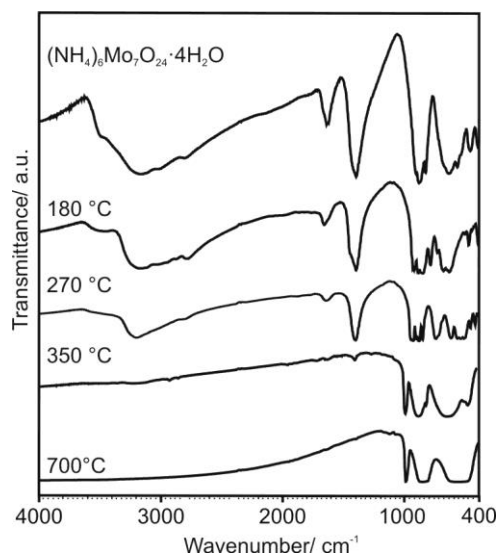


Figure 7. FTIR spectra of **1** and its decomposition products in air

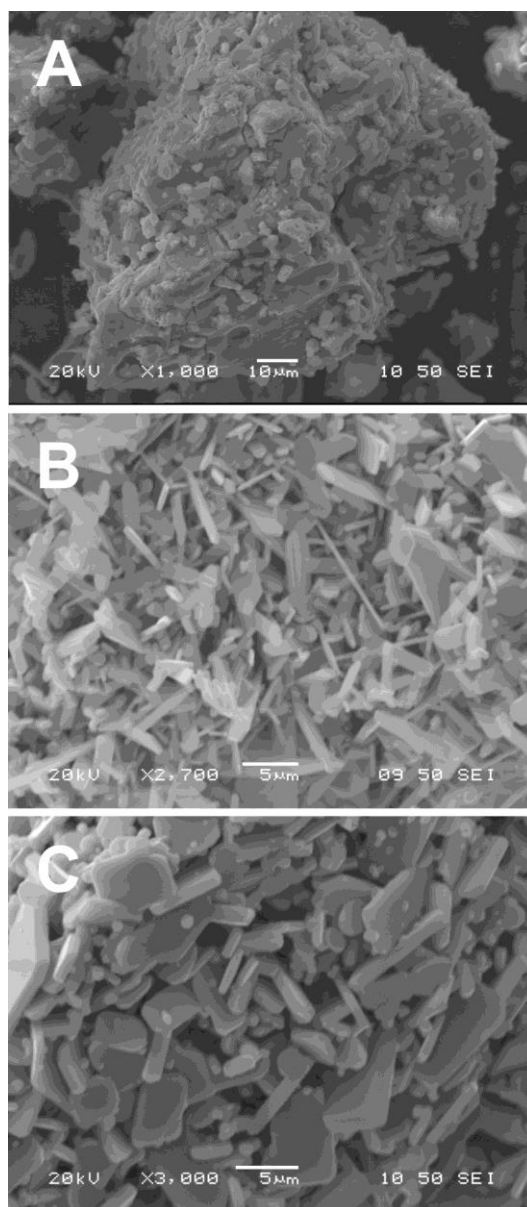


Figure 8. SEM images of (a) **2**; (b) **2** annealed in N₂ at 700 °C; (c) **2** annealed in air at 700 °C

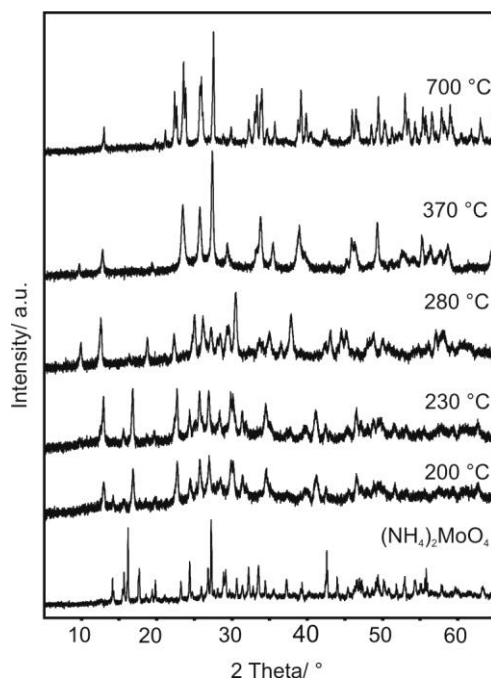


Figure 9. XRD patterns of **2** and its decomposition products in N₂

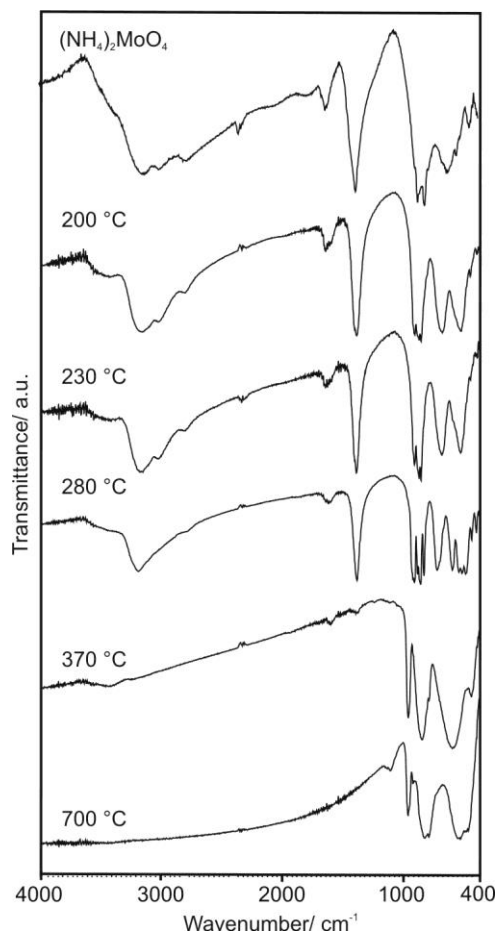


Figure 10. FTIR spectra of **2** and its decomposition products in N₂

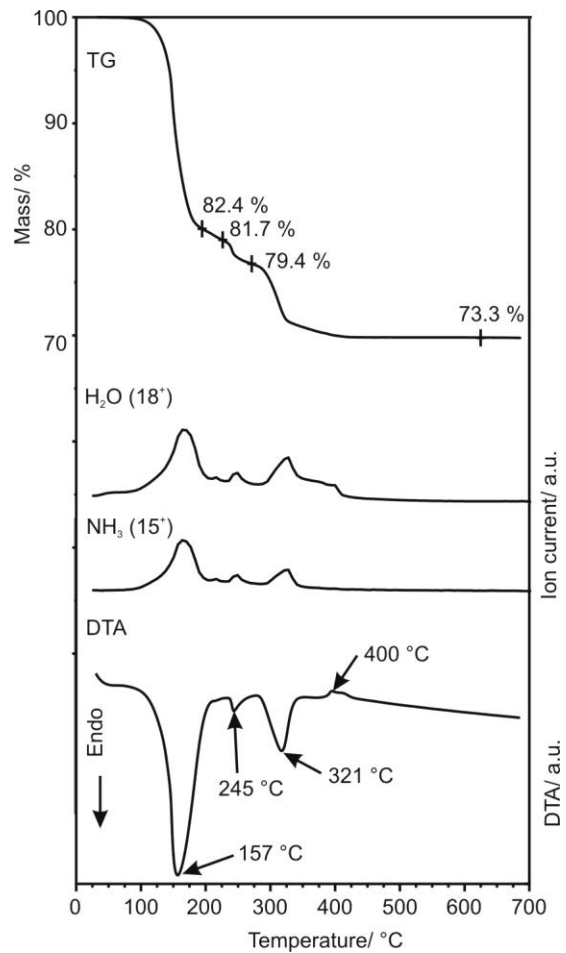


Figure 11. TG/DTA and EGA-MS curves of **2** in N_2

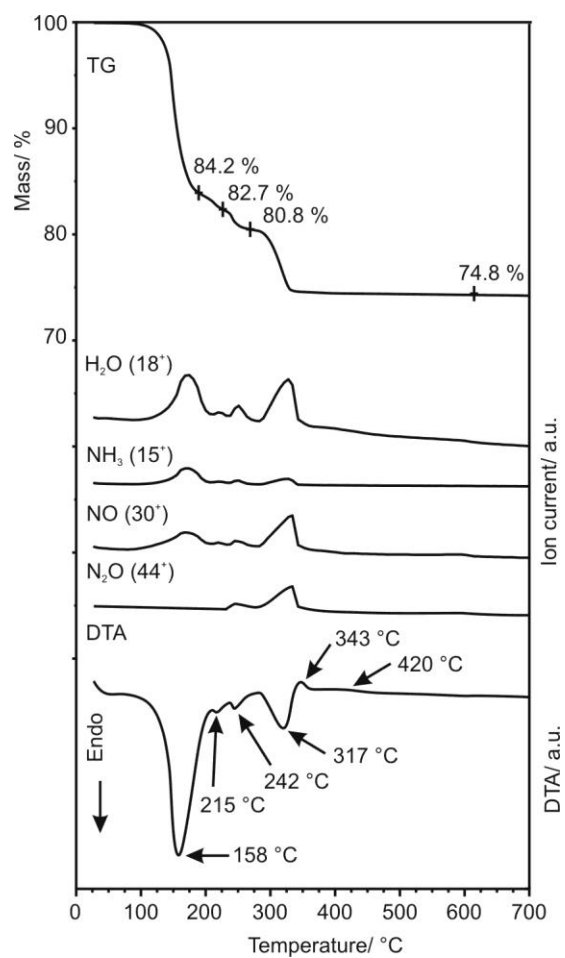


Figure 12. TG/DTA and EGA-MS curves of **2** in air

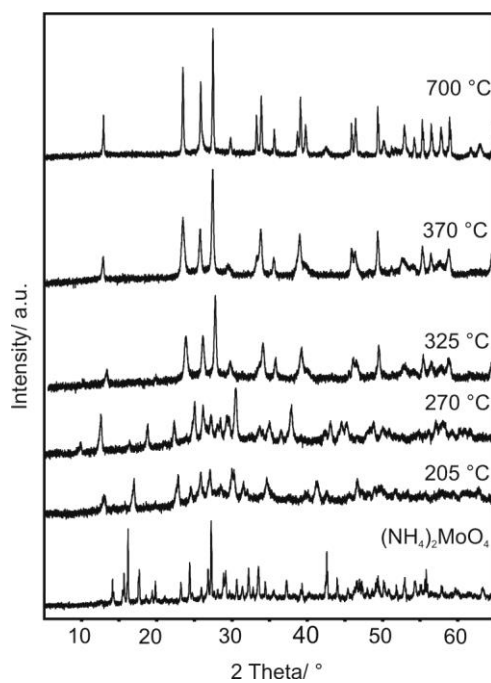


Figure 13. XRD patterns of **2** and its decomposition products in air

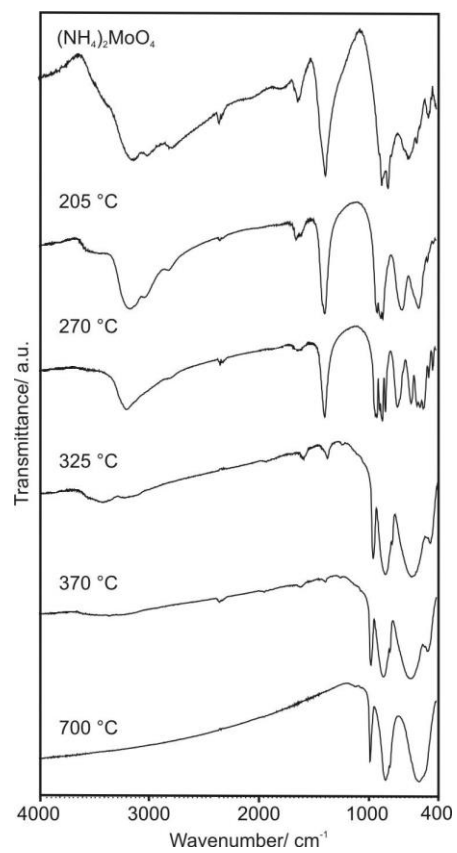


Figure 14. FTIR spectra of **2** and its decomposition products in air