# PREPARATION AND PROPERTIES OF THE MICRO-POWDER PHASE AND A NEW PHASE OF AMMONIUM TETRAMOLYBDATES①

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**ABSTRACT** The micro-powder phase and a new phase of ammonium tetramolybdate were prepared using polyphase ammonium molybdate as the starting material. Their chemical properties were studied by XRD, TG, DSC and chemical quantitative analyses. It was discovered that the composition of the new phase is $(NH_4)_2Mo_4O_{13}$ and it transforms to the micro-powder phase when heated below 280 ℃.

**Key words** new phase of ammonium tetramolybdate micro-powder phase of ammonium tetramolybdate phase transformation molybdenum

## 1 INTRODUCTION

Four phases of ammonium tetramolybdate have been reported which are α-$(NH_4)_2Mo_4O_{13}$, β-$(NH_4)_2Mo_4O_{13}$[1], and the micro-powder $(NH_4)_2Mo_4O_{13}$[2] and $4MoO_3 \cdot 2NH_3 \cdot H_2O$ (see ASTM card 21-570). High-purity $MoO_3$ and high-quality metal molybdenum powder can be produced using the micro-powder ammonium tetramolybdate as the starting material. The micro-powder ammonium tetramolybdate is white powder with natural fine physical shape. Its DTA and TGA performance have been studied by Wang *et al*[3]. In order to measure the thermochemical properties further, single phase of micro-powder ammonium tetramolybdate was prepared using polyphase ammonium molybdate of analytical purity as the initial material. As the solution chemistry of ammonium molybdate is very complicated, the phase composition of the substance crystallized from the solution alters if the precipitation condition during the preparation process changes slightly. In this paper, the micro-powder phase and a new phase of ammonium tetramolybdate were prepared and some of their chemical properties, especially those of thermochemistry were reported.

## 2 PREPARATION

The starting material was a polyphase ammonium molybdate of analytical purity. XRD analysis showed that it consisted of such ammonium molybdates as $7MoO_3 \cdot 6NH_3 \cdot 7H_2O$ (see ASTM card 21-571) and $(NH_4)_2Mo_3O_{10} \cdot 2H_2O$ (see ASTM card 35-879).

$HNO_3$ was added slowly to the solution of ammonium molybdate of 250~270 $g \cdot L^{-1}$ $MoO_3$ at 25~75 ℃ until the pH of the solution reached 1.5~2.5. White precipitate appeared, which was then separated quickly from the acidic solution through filtration. The precipitate was dried below 280 ℃ to get the micro-powder ammonium tetramolybdate which is symbolized as MPP-ATM for simplification.

With the same experimental procedure

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white precipitate was obtained which was treated further with distilled water at 25~ 75 ℃. Another white precipitate was prepared which was dried below 280 ℃ to get the new phase of ammonium molybdate symbolized as NP-ATM for simplification.

## 3 CHEMICAL PROPERTIES OF MPP-ATM AND NP-ATM

### 3.1 Measurement method

X-ray diffraction (XRD) measurement was performed on a 3014 X-ray diffractometer (Rigaku, Japan). Cu-$K_\alpha$ radiation was used and the scanning rate of the diffraction angle 2 θ was 5°/min. Thermal gravimetric (TG) and differential scan calorimetric (DSC) analyses were performed on a differential calorimeter (Du Pont, USA) at a scanning rate of 5 ℃/min. The amount of sample for TG and DSC measurements was 20~ 30 mg. Spectrographic detection was carried out on a native WSP-1 grating spectrography. The content of molybdenum in ammonium molybdate was analyzed with the chemical quantitative method of lead acetate.

### 3.2 Properties of MPP-ATM

The XRD result of MPP-ATM sample is shown in Table 1 where its d and $I/I^0$ are compared with those of literature[2]. Table 1 indicates that our sample has the same XRD pattern as that of the reference MPP-ATM.

The chemical quantitative analysis result of molybdenum in MPP-ATM was 60. 83% (in weight) which was higher than that of the literature[2] (60. 60% ~ 60. 70%). Therefore, MPP-ATM prepared in our experiment contained less impurity and was more pure. As the theoretical content of molybdenum in $(NH_4)_2Mo_4O_{13}$ is 61. 13%, the purity of MPP-ATM is estimated to be 99. 5%. The result of the spectrographic analysis on the MPP-ATM sample was as follows(in weight): W 0. 02%, Fe 0. 003%, Mg 0. 003%, Mn 0. 001%, Si 0. 001%, Cu 0. 0001%, Bi< 0. 001%, Sn < 0. 001%, Sb< 0. 001%, Ti< 0. 001%.

**Table 1 XRD results of MPP-ATM**

| The author's | | From Ref. [2] | |
|---|---|---|---|
| $d$/ Å | $I/I^0$ | $d$/ Å | $I/I^0$ |
| 8. 522 | 7 | 9. 13 | 15 |
| 8. 117 | 27 | 8. 50 | 13 |
| 7. 375 | 15 | 8. 14 | 48 |
| 7. 255 | 23 | 7. 37 | 37 |
| 6. 981 | 10 | 7. 24 | 43 |
| 6. 211 | 100 | 6. 96 | 25 |
| 5. 458 | 3 | 6. 20 | 100 |
| 4. 695 | 4 | 5. 47 | 7 |
| 3. 723 | 2 | 4. 79 | 6 |
| 3. 619 | 30 | 4. 69 | 6 |
| 3. 480 | 10 | 3. 71 | 6 |
| 3. 356 | 8 | 3. 61 | 42 |
| 3. 269 | 12 | 3. 47 | 17 |
| 3. 211 | 5 | 3. 35 | 13 |
| 3. 081 | 15 | 3. 26 | 23 |
| | | 3. 20 | 11 |
| 3. 012 | 7 | 3. 08 | 17 |
| 2. 923 | 3 | 3. 01 | 14 |
| 2. 717 | 5 | 2. 95 | 8 |
| 2. 411 | 4 | 2. 71 | 7 |
| 2. 319 | 5 | 2. 41 | 6 |
| 2. 149 | 9 | 2. 31 | 6 |
| | | 2. 15 | 13 |

The DSC curve of MPP-ATM in Fig. 1 shows that there is a small endothermic peak before 100 ℃. As MPP-ATM powder is extremely fine, it absorbs the water in the atmosphere very easily. The small peak is, therefore, inferred to the desorption of the absorbed water. Itis known that the evaporation heat of water is2 270. 87 J/g[4]. From Fig. 1, the endotherm of water evaporation is 11. 4 J/g. Thus, the amount of the absorbed water in MPP-ATM sample can be evaluated to be 11. 4/2 270. 87, that is about 0. 5%.

From Fig. 1, it can also be seen that there is a large endothermic peak from 337 ℃ which can be identified as the thermal decomposition of MPP-ATM to ammonium dodecamolybdate and the subsequent decomposition of the ammonium dodecamolybdate to $MoO_3$[2]. There still exists a small exothermic peak prior to the large en-

dothermic peak in Fig. 1. It may be caused by the transformation of MPP-ATM to a more stable phase of ammonium tetramolybdate. Further study is necessary about this phase transformation.

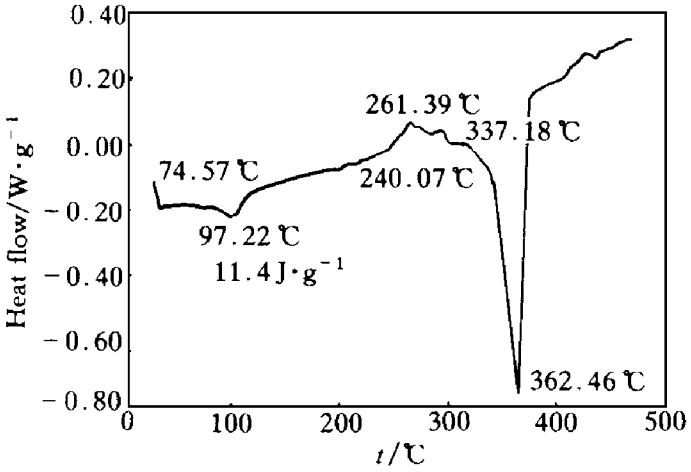


**Fig. 1 DSC curve of MPP-ATM**

### 3.3 Properties of NP-ATM

The XRD pattern of NP-ATM is shown in Fig. 2, with $d$ and $I/I^0$ as follows:

| $d$/ Å | $I/I^0$ |
|---|---|
| 9.550 | 5 |
| 9.369 | 2 |
| 7.563 | 100 |
| 6.559 | 2 |
| 6.185 | 2 |
| 3.789 | 4 |
| 3.739 | 3 |
| 3.339 | 3 |
| 3.232 | 2 |
| 3.189 | 3 |
| 3.151 | 3 |
| 2.155 | 2 |

This ammonium molybdate has not been reported before. The strength of the diffraction peak is very weak with the exception of that at $d$= 7.563 Å. It reveals that NP-ATM crystallizes along certain direction very well. Experiment also showed that it turns to MPP-ATM thoroughly when heated below 280 ℃.

The TG and DSC curves of NP-ATM are illustrated in Fig. 3. From the TG result, it can be seen that there exists some adsorption water in the NP-ATM sample and the weight loss before 100 ℃ due to the desorption of water is 3.05%. There is a strong endothermic peak at about 130 ℃ on the DSC curve, while there is no weight loss on the corresponding TG curve. Therefore, a phase transformation reaction occurs in NP-ATM at this temperature. XRD measurement indicates that the micro-powder ammonium tetramolybdate forms as the transformation product. As a result of that, it can be deduced that the chemical formula of NP-ATM is the same as that of the micro-powder ammonium tetramolybdate, that is $(NH_4)_2Mo_4O_{13}$. By comparing the DSC curves in Fig. 1 and Fig. 3, it is observed that the thermochemical properties of the phase transformation product of NP-ATM is the same as that of MPP-ATM, which proves the above conclusion again. And there is also an exothermic peak in the DSC curve of NP-ATM prior to the thermal decomposition of MPP-ATM into ammonium dodecamolybdate and then $MoO_3$.

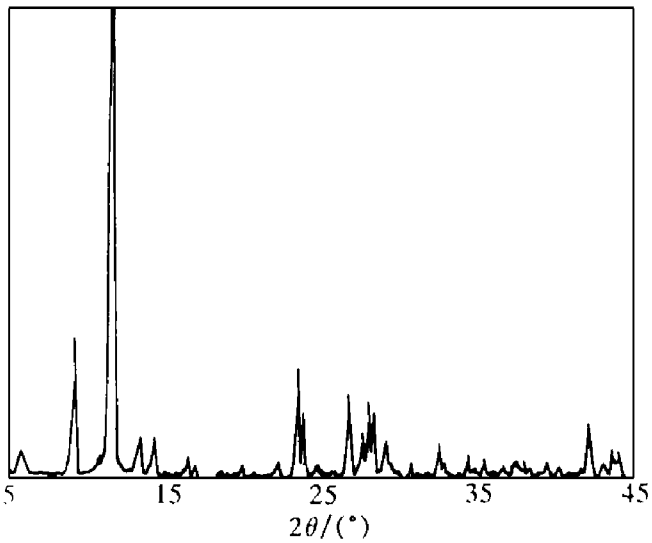


**Fig. 2 XRD patterns of NP-ATM**

The content of molybdenum in NP-ATM is 58.70% in the light of the chemical quantitative analysis. That is, there is 96.03% $(NH_4)_2Mo_4O_{13}$ in NP-ATM, which also illustrates that there exists some adsorption water in NP-ATM sample. If deducting the adsorption

water of 3.05%, the weight losses of II and III stages on the TG curve of Fig. 3 change to6.34% and 2.03% respectively. Therefore, the total weight loss is 8.37%. It is known that the theoretical weight loss resulting from the thermaldecomposition of $(NH_4)_2Mo_4O_{13}$ to $MoO_3$ is8.28%. The TG result also reveals that MPP-ATM decomposes into $MoO_3$ when heated.

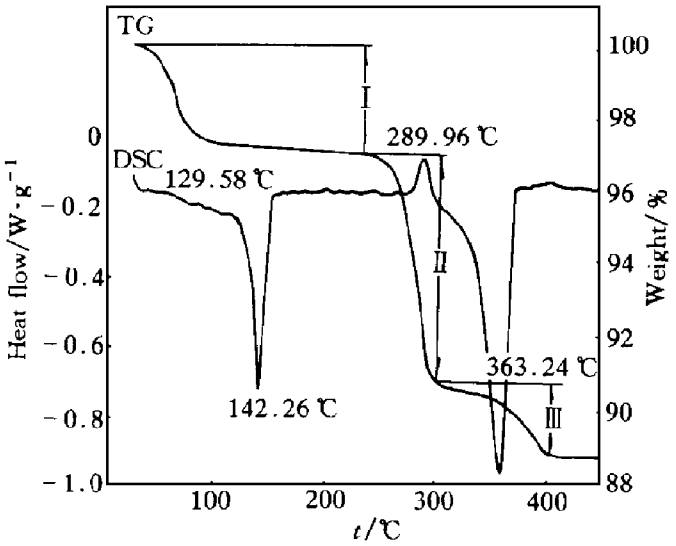


**Fig. 3 TG and DSC curves of NP-ATM**
I —3.05%; II —6.15%; III—1.97%

It was reported[2] that the intermediary phase during the micro-powder ammonium tetramolybdate decomposed thermally to $MoO_3$ is ammonium dodecamolybdate. If the composition of the intermediary phase is written as $12MoO_{13} \cdot n(NH_4)_2O$, whose $n$ can be judged to be 0.70 from the weight losses of II and IIIstages on the TG curve in Fig. 3. The properties of the intermediary phase, produced during the micro-powder ammonium tetramolybdate thermally decomposed to $MoO_3$ need to be further investigated.

## 4 CONCLUSIONS

(1) Single phase of the micro-powder ammonium tetramolybdate is prepared from polyphase ammonium molybdate. The powder is extremely fine and absorbs water from atmosphere easily. An exothermic phase transformation reaction occurs prior to the thermal decompositing of the micro-powder ammonium tetramdybdate to $MoO_3$.

(2) A new phase of ammonium molybdate with the composition $(NH_4)_2Mo_4O_{13}$ is prepared during the experiment. When heated, an endothermic phase transformation reaction occurs and it changes to the micro-powder ammonium tetramolybdate.

## REFERENCES

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