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Note

Study on the thermal decomposition of a commercial polyphase ammonium tetramolybdate

Z.L. Yin [a,*], X.H. Li [a], Q.S. Zhao [a], S.Y. Chen [a], G.R. Liu [b], S.Q. Wang [b]

[a] *Central-South University of Technology, Changsha 410083, People's Republic of China*
[b] *Baoji Nonferrous Metal Works, Baoji 721014, People's Republic of China*

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Abstract

High-temperature XRD was employed to study the thermal decomposition of a commercial polyphase ammonium tetramolybdate which is composed of $(NH_4)_2Mo_4O_{13}$, β-$(NH_4)_2Mo_4O_{13}$ and a small amount of $(NH_4)_2Mo_4O_{13} \cdot 2H_2O$. It was determined that the thermal decomposition reactions of the three phases of ammonium tetramolybdate begin below 300°C following the steps: $(NH_4)_2Mo_4O_{13}$, β-$(NH_4)_2Mo_4O_{13}$ and $(NH_4)_2Mo_4O_{13} \cdot 2H_2O \rightarrow (NH_4)_2Mo_{14}O_{43} \rightarrow (NH_4)_2Mo_{22}O_{67} \rightarrow MoO_3$.

The ammonium tetramolybdate mixture decomposes to MoO_3 when calcined in the open air. When calcined in a closed system, the decomposition product MoO_3 is partly reduced to MoO_2.

Keywords: Ammonium tetramolybdate; Calcination; Decomposition; Molybdate; XRD

1. Introduction

The starting material for the production of metallic molybdenum is usually ammonium molybdate which is converted to MoO_3 when calcined. The subsequent reduction of MoO_3 in two steps gives molybdenum as the final product.

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[*] Corresponding author.

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The polyphase ammonium tetramolybdate studied is used commercially as the starting material for the production of molybdenum. It is a mixture consisting of $(NH_4)_2Mo_4O_{13}$, β-$(NH_4)_2Mo_4O_{13}$ and a small amount of $(NH_4)_2Mo_4O_{13} \cdot 2H_2O$ [1]. Because the different phase components possess different physical and chemical properties, during the course of calcination the resultant calcination product MoO_3 will be affected greatly by the composition of the starting ammonium tetramolybdate. For this reason, high-temperature XRD was employed to study the thermal decomposition of the mixture in the open air and in a closed system in order to supply a theoretical basis for the selection of suitable calcination conditions in the practical production process.

2. XRD measurements

The ammonium tetramolybdate mixture was ground and then mixed with absolute alcohol into a paste which was mounted in the sample set of a 3014 X-ray diffractometer, before being heated at a heating rate of 10°C $\min^{-1}$ in the open air or in a closed system which was maintained at 1 atm. The sample was kept at room temperature (13°C), and 100, 200, 300, 350, 375, 400, 425 and 450°C for 2 min before XRD measurements were performed. Cu Kα radiation was used and the sweep rate of the diffraction angle 2θ was 4 deg $\min^{-1}$. The XRD patterns obtained are shown in Figs. 1 and 2 which indicate the phase developments of the ammonium tetramolybdate mixture in the open air and in a closed system. The new phases formed and the original phases remaining in tiny amounts are marked on the figures, see the captions.

3. The thermal decomposition of the ammonium tetramolybdate mixture

The thermal decompositions of monophase $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ have been studied. When heated, $(NH_4)_2Mo_4O_{13}$ decomposes at 360°C to form MoO_3 [2]

$$(NH_4)_2Mo_4O_{13} \xrightarrow{\approx 360^\circ C} MoO_3 + NH_3(g) + H_2O(g) \tag{1}$$

The thermal decomposition of β-$(NH_4)_2Mo_4O_{13}$ begins at approx. 316°C–348°C [3]

$$\beta\text{-}(NH_4)_2Mo_4O_{13} \xrightarrow{\approx 316^\circ C-348^\circ C} MoO_3 + NH_3(g) + H_2O(g) \tag{2}$$

$(NH_4)_2Mo_4O_{13} \cdot 2H_2O$ is essentially identical with the octamolybdate, $(NH_4)_4Mo_8O_{26} \cdot 4H_2O$, which dehydrates without structural change at 287°C before decomposition to MoO_3 [4].

Two intermediary phases, namely $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$, were also identified during the thermal decomposition of monophase $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ [5].

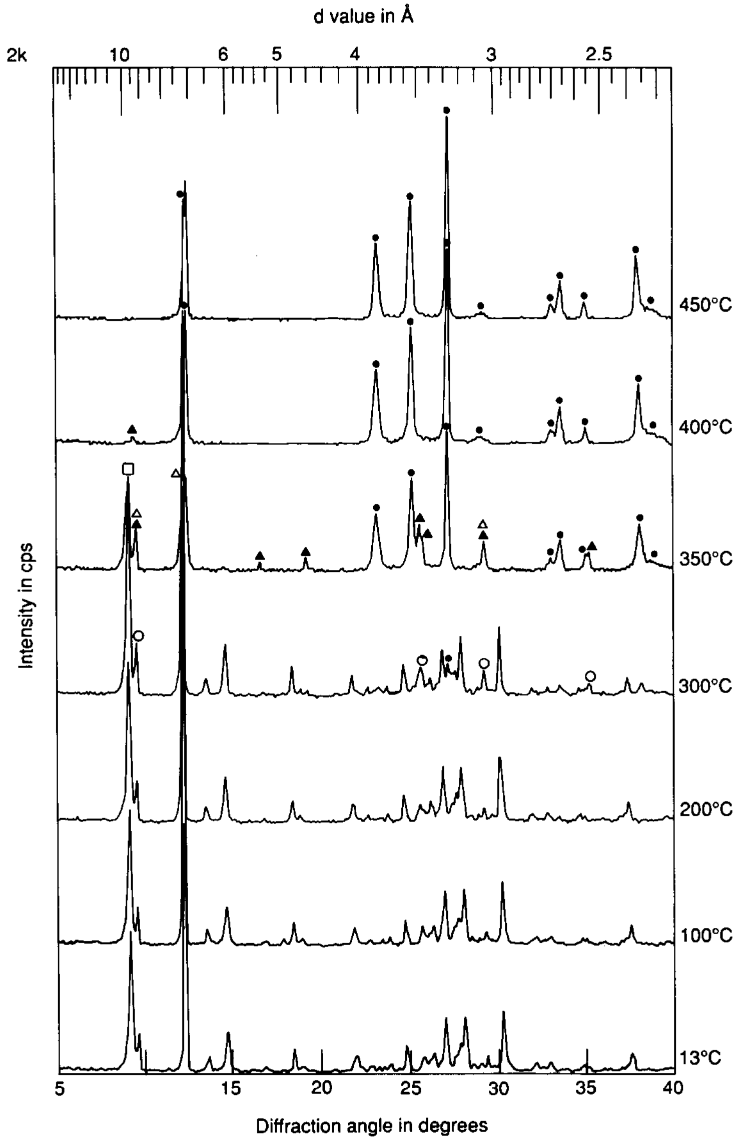

Fig. 1. The XRD patterns of the ammonium tetramolybdate mixture in the open air at different temperatures. △, $(NH_4)_2Mo_4O_{13}$; □, β-$(NH_4)_2Mo_4O_{13}$; ○, $(NH_4)_2Mo_{14}O_{43}$; ▲, $(NH_4)_2Mo_{22}O_{67}$; ●, MoO_3.

It can be seen from Fig. 1 that there is no chemical change or thermal decomposition when ammonium tetramolybdate mixture is heated at 200°C in the open air. When the temperature reaches 300°C, the new phases $(NH_4)_2Mo_{14}O_{43}$ and MoO_3 form in small amounts. From the XRD patterns in Fig. 1, the phases in the mixture at different temperatures can be identified, and are listed in Table 1.

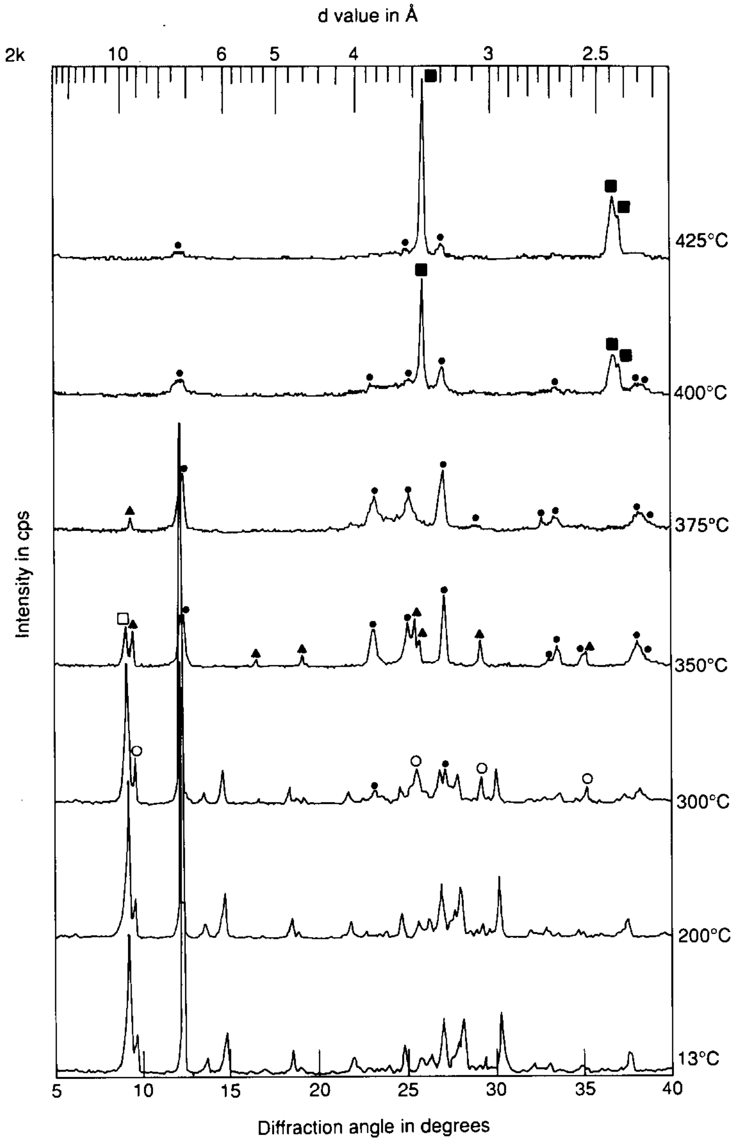

Fig. 2. The XRD patterns of the ammonium tetramolybdate mixture in a closed system at different temperatures. □, β-$(NH_4)_2Mo_4O_{13}$; ○, $(NH_4)_2Mo_{14}O_{43}$; ▲, $(NH_4)_2Mo_{22}O_{67}$; ●, MoO_3; ■, MoO_2.

Their amounts can be judged according to the intensity of the main diffraction peaks.

Table 1 shows that the thermal decomposition of the ammonium tetramolybdate mixture begins below 300°C with $(NH_4)_2Mo_{14}O_{43}$ as one intermediary phase and MoO_3 the final decomposition product. When the temperature reaches 350°C,

Table 1
Phase development of the ammonium tetramolybdate mixture when calcined in open air

Phase	13°C	100°C	200°C	300°C	350°C	400°C	450°C
$(NH_4)_2Mo_4O_{13} \cdot 2H_2O$	S	S	S	S			
$(NH_4)_2Mo_4O_{13}$	L	L	L	L	Tr		
β-$(NH_4)_2Mo_4O_{13}$	L	L	L	L	Tr		
$(NH_4)_2Mo_{14}O_{43}$				S			
$(NH_4)_2Mo_{22}O_{67}$					L	Tr	
MoO_3				S	L	L	L

Key: L, large amounts; S, small amounts; Tr, trace.

$(NH_4)_2Mo_{14}O_{43}$ disappears and another intermediary phase, $(NH_4)_2Mo_{22}O_{67}$, appears. Therefore, the mixture decomposes in the steps

$$(NH_4)_2Mo_4O_{13},\ \beta\text{-}(NH_4)_2Mo_4O_{13} \text{ and } (NH_4)_2Mo_4O_{13} \cdot 2H_2O \rightarrow (NH_4)_2Mo_{14}O_{43} + NH_3(g) + H_2O(g) \quad (3)$$

$$(NH_4)_2Mo_{14}O_{43} \rightarrow (NH_4)_2Mo_{22}O_{67} + NH_3(g) + H_2O(g) \quad (4)$$

$$(NH_4)_2Mo_{22}O_{67} \rightarrow MoO_3 + NH_3(g) + H_2O(g) \quad (5)$$

The intermediary products $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$ formed during the thermal decomposition of the ammonium tetramolybdate mixture are the same as those formed during the thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ [4].

Table 1 also illustrates that the small amount of $(NH_4)_2Mo_4O_{13} \cdot 2H_2O$ disappears first at 350°C, via dehydration and decomposition, while $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ disappear at 400°C. All the decomposition reactions are complete at 450°C, yielding the final product MoO_3.

In order to detect more accurately the temperatures at which the decomposition reactions begin or end, the reactions to equilibrium should be studied over a longer period of time and the XRD measurements should be performed at shorter temperature intervals.

Similarly, the phase compositions of the mixture in the closed system at different temperatures can be identified and are listed in Table 2 from the XRD patterns in Fig. 2. Table 2 shows that small amounts of $(NH_4)_2Mo_{14}O_{43}$ and MoO_3 appear at 300°C, which indicates that the thermal decomposition begins below 300°C. $(NH_4)_2Mo_4O_{13}$ and $(NH_4)_2Mo_4O_{13} \cdot 2H_2O$ disappear at 350°C while β-$(NH_4)_2Mo_4O_{13}$ disappears at 375°C when only a tiny amount of the intermediary phase $(NH_4)_2Mo_{22}O_{67}$ remains. Therefore, in a closed system the ammonium tetramolybdate mixture decomposes in the same way as in the open air, according to reactions (3), (4) and (5) with $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$ being the intermediary products.

The decomposition product NH_3, formed by reactions (3), (4) and (5) in the closed system exists in equilibrium at high temperatures

$$2NH_3 \leftrightharpoons 3H_2(g) + N_2(g) \quad (6)$$

Table 2
Phase development of the ammonium tetramolybdate mixture when calcined in closed system

Phase	13°C	200°C	300°C	350°C	375°C	400°C	425°C
$(NH_4)_2Mo_4O_{13} \cdot 2H_2O$	S	S	S				
$(NH_4)_2Mo_4O_{13}$	L	L	L				
β-$(NH_4)_2Mo_4O_{13}$	L	L	L	Tr			
$(NH_4)_2Mo_{14}O_{43}$			S				
$(NH_4)_2Mo_{22}O_{67}$				L	Tr		
MoO_3			S	L	L	S	Tr
MoO_2						L	L

Key: L, large amounts; S, small amounts; Tr, trace amounts.

The H_2 formed by reaction (6) can reduce MoO_3 to MoO_2

$$MoO_3 + H_2 \rightleftharpoons MoO_2 + H_2O(g) \tag{7}$$

Therefore, the reduction reaction of MoO_3 occurs

$$3MoO_3 + 2NH_3 \rightleftharpoons 3MoO_2 + 3H_2O(g) + N_2(g) \tag{8}$$

From the free enthalpies of MoO_3, NH_3, MoO_2, H_2O and N_2 [6], the equilibrium constant K of reaction (8) can be evaluated. For example, K at 400°C and 1 atm is estimated to be 4.69×10^{21}. Therefore, the reduction reaction (8) can take place thermodynamically at 400°C.

Table 2 illustrates that there is a large amount of MoO_2 on the surface of the sample at 400°C, which indicates that the reduction reaction (8) can occur at this temperature. Accordingly, if the NH_3 given off during the calcination of ammonium tetramolybdate is not pumped out from the practical production process, the decomposition product MoO_3 will be partly reduced to MoO_2.

4. Conclusions

The thermal decomposition of the polyphase ammonium tetramolybdate begins below 300°C with $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$ being the intermediary products. The dehydration and the thermal decomposition occur in the steps

$$(NH_4)_2Mo_4O_{13},\ \beta\text{-}(NH_4)_2Mo_4O_{13} \text{ and } (NH_4)_2Mo_4O_{13} \cdot 2H_2O \rightarrow (NH_4)_2Mo_{14}O_{43} + NH_3(g) + H_2O(g)$$

$$(NH_4)_2Mo_{14}O_{43} \rightarrow (NH_4)_2Mo_{22}O_{67} + NH_3(g) + H_2O(g)$$

$$(NH_4)_2Mo_{22}O_{67} \rightarrow MoO_3 + NH_3(g) + H_2O(g)$$

The ammonium tetramolybdate mixture will decompose into MoO_3 when calcined in the open air. When calcined in a closed system, the decomposition product MoO_3 will be partly reduced to MoO_2, because NH_3 produced during the calcination is a reductant at high temperatures.

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