

## **THERMAL DECOMPOSITIONS OF PURE AND MIXED MANGANESE CARBONATE AND AMMONIUM MOLYBDATE TETRAHYDRATE**

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### **Abstract**

The thermal decompositions of pure and mixed manganese carbonate and ammonium molybdate tetrahydrate in molar ratios of 3:1, 1:1 and 1:3 were studied by DTA and TG techniques. The prepared mixed solid samples were calcined in air at 500, 750 or 1000°C and then investigated by means of an XRD technique. The results revealed that manganese carbonate decomposed in the range 300–1000°C, with intermediate formation of MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>. Ammonium molybdate tetrahydrate first lost its water of crystallization on heating, and then decomposed, yielding water and ammonia. At ≥340°C, MoO<sub>3</sub> was the final product, which melts at 790°C. The thermal treatment of the mixed solids at 500, 750 or 1000°C led to solid-solid interactions between the produced oxides, with the formation of manganese molybdate. At 1000°C, Mn<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> were detected, due to the mutual stabilization effect of these oxides at this temperature.

**Keywords:** solid–solid interactions, thermal decomposition, transition metal oxides

### **Introduction**

A great deal of fundamental research has been performed on mixed transition metal oxides in the field of heterogeneous catalysis [1–5]. The combination of two transition metal oxides may result in modifications in their thermal behaviour, geometric structures and electronic properties that lead to changes in their catalytic functions [6]. The present work reports a study of the thermal decompositions of pure and mixed manganese carbonate and ammonium molybdate tetrahydrate by means of DTA, TG and XRD techniques and a follow-up of the mutual interaction of manganese and molybdenum oxides.

### **Experimental**

#### *Materials*

The materials used in this investigation were pure manganese carbonate (MnCO<sub>3</sub>) and ammonium molybdate tetrahydrate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O]. Three mixtures, with molar ratios of 3:1, 1:1 and 1:3 with respect to MnO<sub>2</sub>:MoO<sub>3</sub>, were prepared by mixing

the two components, followed by homogenization and grinding of the salts. The prepared samples were calcined for 4 h at 500, 750 or 1000°C.

### *Techniques*

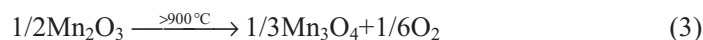
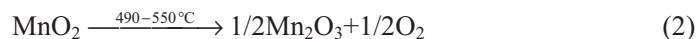
DTA and TG analysis of the various solids were carried out with a Shimadzu DT-40 thermal analyzer. The samples were studied in air atmosphere at a flow rate of 30 mL min<sup>-1</sup>.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as reference. The DTA range was +200  $\mu$ V; the chart speed was 5 mm min<sup>-1</sup>. The rate of heating was kept at 15°C min<sup>-1</sup>. The thermoanalytical curves were recorded up to a temperature of either 500 or 1000°C.

X-ray investigation of the thermal products of the different mixed solids was performed with a Philips X-ray diffractometer (Goniometer PW 1050/50), with cobalt radiation as the X-ray source. The diffraction angle,  $2\theta$ , was scanned at a rate of 2° min<sup>-1</sup> at 2·10<sup>-3</sup> cps. The results obtained for all samples calcined at the different temperatures (500, 750 or 1000°C) were compared with the data from the ASTM diffraction file.

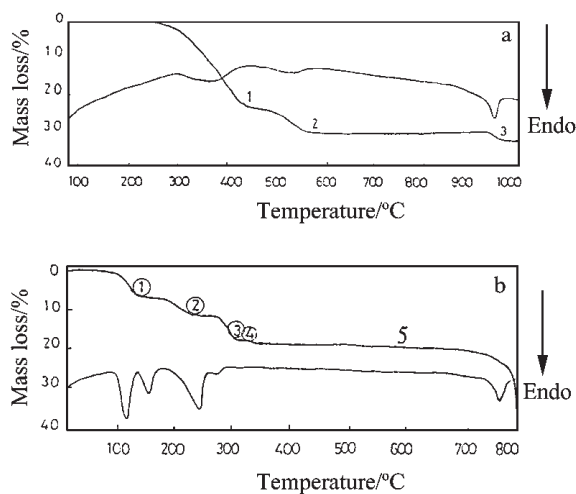
## Results and discussion

### *Thermal decomposition of manganese carbonate*

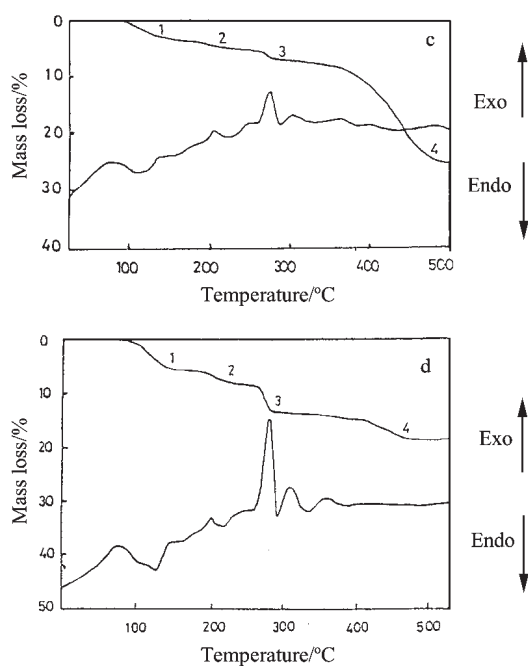
Figure 1a presents DTA and TG results on manganese carbonate. The DTA peaks located at 330, 535 and 950°C correspond closely to the mass changes observed in the TG curve. The first mass loss starts at about 300°C, and achieves a constant level of 24.30% at about 400°C, due to the decomposition of manganese carbonate to manganese dioxide. The second mass loss starts at about 440°C, and reaches a constant level of 31.22% at about 550°C, due to the reduction of manganese dioxide to manganese sesquioxide. These peaks correspond to the above two decomposition processes of manganese carbonate to manganese dioxide [7] and the transformation of manganese dioxide to manganese sesquioxide [8–10], respectively. The third step, which starts at >900°C and is accompanied by a mass loss of 33.57%, is due to the formation of Mn<sub>3</sub>O<sub>4</sub> [11, 12]. The DTA curve displays a strong and sharp endothermic peak with minimum at about 950°C, corresponding to the last process. The probable mechanism of manganese carbonate decomposition is described by the following equations:



The data on the thermal analysis of manganese carbonate at different temperatures, and the corresponding formulae, are listed in Table 1.



**Fig. 1a-b** Thermal analysis (DTA and TG) of pure manganese carbonate (a) and ammonium molybdate tetrahydrate (b)



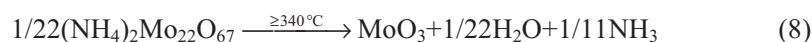
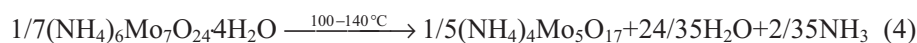
**Fig. 1c-d** Thermal analysis (DTA and TG) of mixed solids with molar formula  $3\text{MnCO}_3 \cdot 1/7(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (c) and  $1\text{MnCO}_3 \cdot 3/7(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (d)

**Table 1** Percentage mass losses and corresponding formulae of the products in the thermal decomposition of  $\text{MnCO}_3$ 

| Thermal step | Temperature range/ $^{\circ}\text{C}$ | Mass loss/% |             | Suggested formulae of product |
|--------------|---------------------------------------|-------------|-------------|-------------------------------|
|              |                                       | calculated  | theoretical |                               |
| 1            | 300–440                               | 24.30       | 24.34       | $\text{MnO}_2$                |
| 2            | 490–550                               | 6.92        | 6.96        | $1/2\text{Mn}_2\text{O}_3$    |
| 3            | >900                                  | 2.35        | 2.32        | $1/3\text{Mn}_3\text{O}_4$    |

*Thermal decomposition of ammonium molybdate tetrahydrate*

Figure 1b illustrates the thermal decomposition of ammonium molybdate tetrahydrate. The DTA curve exhibits five endothermic peaks, with minima at 115, 160, 235, 280 and  $790^{\circ}\text{C}$ , corresponding to the following reactions [13–14]:



From the above equations, it can be seen that the decomposition of ammonium molybdate proceeds in all stages with the evolution of water and ammonia. Water of crystallization is evolved in the first stage, while  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are obtained in the other steps, leading finally to the formation of  $\text{MoO}_3$ . The last endothermic peak, at about  $790^{\circ}\text{C}$ , corresponds to the melting point of  $\text{MoO}_3$  [14], after which a sharp increase in mass loss is observed. This may be attributed to the sublimation  $\text{MoO}_3$  [15]. The data on the thermal analysis of ammonium molybdate in different decomposition stages, together with the suggested formulae, are listed in Table 2.

**Table 2** Percentage mass losses and corresponding formulae of the products of thermal decomposition of ammonium molybdate

| Thermal step | Temperature range/ $^{\circ}\text{C}$ | Mass loss/% |             | Suggested formulae of product                       |
|--------------|---------------------------------------|-------------|-------------|---|
|              |                                       | calculated  | theoretical |   |
| 1            | 100–140                               | 6.70        | 6.89        | $1/5 [(\text{NH}_4)_4\text{Mo}_5\text{O}_{17}]$     |
| 2            | 175–235                               | 4.4         | 4.41        | $1/4 [(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}]$     |
| 3            | 275–298                               | 5.4         | 5.25        | $1/14 [(\text{NH}_4)_2\text{Mo}_{14}\text{O}_{43}]$ |
| 4            | 320–340                               | 0.7         | 0.76        | $1/22 [(\text{NH}_4)_2\text{Mo}_{22}\text{O}_{67}]$ |
| 5            | $\geq 340$                            | 1.3         | 1.33        | $\text{MoO}_3$                                      |

*Thermal decompositions of mixtures of MnCO<sub>3</sub> and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O*

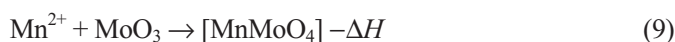
Figure 1c illustrates the DTA and TG curves of the mixed solids with a molar ratio 3Mn:1Mo. The DTA curve exhibits five small, broad endothermic peaks, at 112, 220, 320, 385 and 425°C.

The TG curve contains four steps for the thermal decomposition of this mixture. On the other hand, Fig. 1d presents DTA and TG curves of the mixed solids with a molar ratio 1Mn:3Mo. The DTA curve depicts four endothermic peaks, with minima at 110, 128, 212 and 325°C. The TG curve reveals four steps for the thermal decomposition of the mixture.

From Fig. 1c,d, it can be seen that ammonium molybdate tetrahydrate loses the water of crystallization in the first step [14]. The DTA curve shows endothermic peaks at 112°C for the 3Mn:1Mo mixture and at 110 and 128°C for the 1Mn:3Mo mixture. Other endothermic peaks are detected at 220, 320 and 385°C for the 3Mn:1Mo mixture, and at 212 and 325°C for the 1Mn:3Mo mixture. These peaks refer to the evolution of water and ammonia during the processes of decomposition of ammonium molybdate to MoO<sub>3</sub> [13]. The other endothermic peaks for both the 3Mn:1Mo and the 1Mn:3Mo mixtures refer to the decomposition of MnCO<sub>3</sub> to MnO<sub>2</sub>.

The thermal analysis of ammonium molybdate reveals the disappearance of the endothermic peak at about 290°C with respect to the 3Mn:1Mo and 1Mn:3Mo mixtures, and the appearance of a strong, sharp exothermic peak at 275°C for the 3Mn:1Mo mixture, and at 285°C for the 1Mn:3Mo mixture. This may point to the probability of solid–solid interactions between the decomposition products [8]. This appears to be supported by the XRD analysis of Mn:Mo mixtures preheated at 250°C, which demonstrates the formation of MnMoO<sub>4</sub> and/or the dissolution of one phase in another [8].

The height of the exothermic peak is related to the quantity of heat evolved from the reaction. For the 3Mn:1Mo mixture, the heat evolved is 1/3 of the quantity evolved from the 1Mn:3Mo mixture: ratio of heights=14/43≈1/3. The suggested exothermic reaction may be written as follows:



The TG curves in Fig. 1c,d illustrate the steps for the process of thermal decomposition of both the 3Mn:1Mo and the 1Mn:3Mo mixtures. These steps, the corresponding mass losses and the suggested formulae of the products are listed in Tables 3 and 4.

**Table 3** Percentage mass losses and corresponding formulae of decomposition products of the 3Mn:1Mo mixture

| Thermal step | Temperature range/°C | Mass loss/% |        | Suggested formulae of products  |
|--------------|----------------------|-------------|--------|---|
|              |                      | Calc.       | Theor. |   |
| 1            | 95–145               | 4.0         | 3.83   | 3MnCO <sub>3</sub> +1/4(NH <sub>4</sub> ) <sub>2</sub> Mo <sub>4</sub> O <sub>13</sub>        |
| 2            | 180–205              | 2.0         | 2.04   | 3MnCO <sub>3</sub> +1/22(NH <sub>4</sub> ) <sub>2</sub> Mo <sub>22</sub> O <sub>67</sub>      |
| 3            | 265–280              | 2.0         | 0.45   | 3MnCO <sub>3</sub> +MoO <sub>3</sub> or (MnMoO <sub>4</sub> +Mn <sub>2</sub> O <sub>3</sub> ) |
| 4            | 360–475              | 18.8        | 20.68  | 3/2Mn <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub>   |

**Table 4** Percentage mass losses and corresponding formulae of decomposition products of the 1Mn:3Mo mixture

| Thermal step | Temperature range/ $^{\circ}\text{C}$ | Mass loss/% |        | Suggested formulae of products                              |
|--------------|---------------------------------------|-------------|--------|---|
|              |                                       | calc.       | theor. |   |
| 1            | 90–145                                | 5.80        | 5.75   | $\text{MnCO}_3+3/5(\text{NH}_4)_4\text{Mo}_5\text{O}_{17}$  |
| 2            | 190–225                               | 3.40        | 3.53   | $\text{MnCO}_3+3/4(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$  |
| 3            | 260–280                               | 5.00        | 4.94   | $\text{MnCO}_3+3/22(\text{NH}_4)_2\text{Mo}_2\text{O}_{67}$ |
| 4            | 440–490                               | 5.30        | 5.43   | $\text{MnO}_2+3\text{MoO}_3$                                |

A comparison of the thermoanalytical curves of the individual and mixed solids  $\text{MnCO}_3$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (Figs 1a, d) reveals that:

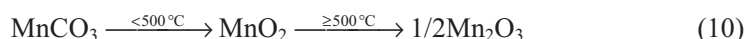
(1) The DTA curve for pure ammonium molybdate tetrahydrate demonstrates an endothermic peak at about  $290^{\circ}\text{C}$ . This peak is absent for both the 3Mn:1Mo and the 1Mn:3Mo mixtures. A strong, sharp exothermic peak is observed. This exothermic peak may be explained by solid-solid interactions and/or the dissolution of one phase in another.

(2) For the 3Mn:1Mo mixture, the presence of  $\text{MoO}_3$  with a large amount of manganese in the mixture affects the process of decomposition of  $\text{MnCO}_3$  to  $\text{Mn}_2\text{O}_3$ .

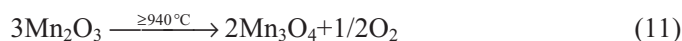
(3) For the 3Mn:1Mo mixture, there is a difference between the calculated and theoretical mass losses. This may be attributed to the partial decomposition of  $\text{MnCO}_3$  to  $\text{MnO}_2$ , most probably in response to the action of  $\text{MoO}_3$ .

#### *XRD characterization of pure manganese carbonate calcined at different temperatures*

X-ray diffraction patterns recorded for pure manganese carbonate heated at 500, 750 or  $1000^{\circ}\text{C}$  are illustrated in Fig. 2a. It can be observed that the heat treatment at  $500^{\circ}\text{C}$  produces a solid with a small degree of crystallinity, cubic  $\text{Mn}_2\text{O}_3$  [16] with  $d$ -spacings of 2.694, 2.339, 1.834 and  $1.658 \text{ \AA}$ . It has been reported [10, 16] that  $\text{MnO}_2$  is formed between 350 and  $500^{\circ}\text{C}$ , which is directly transformed into  $\text{Mn}_2\text{O}_3$  as follows:

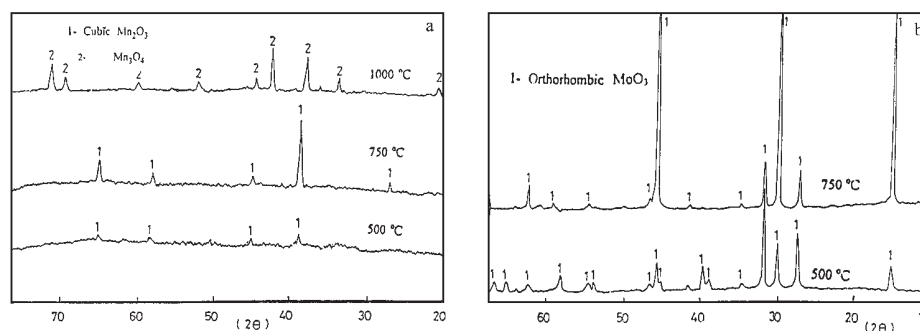


On increase of the treatment temperature up to  $750^{\circ}\text{C}$ , the crystallinity of the manganese sesquioxide phase increases, with  $d$ -spacings of 3.814, 2.705, 2.344, 2.06, 1.84 and  $1.66 \text{ \AA}$ . The X-ray analysis data on the samples heated at 500 or  $750^{\circ}\text{C}$  agree well with those of the ASTM cards. Further increase of the calcination temperature up to  $1000^{\circ}\text{C}$  leads to the formation of a new crystalline phase,  $\text{Mn}_3\text{O}_4$  [16, 17], as a result of the reduction of manganese sesquioxide according to the following equation:



*XRD characterization of pure ammonium molybdate tetrahydrate thermally treated at different temperatures*

Figure 2b presents the diffraction patterns of pure ammonium molybdate tetrahydrate thermally treated at 500 or 750°C. The XRD analysis data, as compared with the ASTM data [18] are included in Table 5. From this Table, it can be seen that the  $d$ -spacings of  $\text{MoO}_3$  calcined at 500 or 750°C agree well with the  $d$ -spacings on the ASTM cards, but there is a great difference in the degrees of intensity ( $I/I_0$ ) for  $\text{MoO}_3$  obtained at both 500 and 750°C and those indicated on the ASTM cards. This can be attributed to the presence of a preferred orientation process for lines with ( $hkl$ ) (020), (040), (021) and (060). It can further be seen that the solid preheated at 750°C exhibits some of the lines for the solid preheated at 500°C. The degree of crystallinity of  $\text{MoO}_3$  preheated at 750°C is greater than that obtained at 500°C, due to the preferred orientation process.



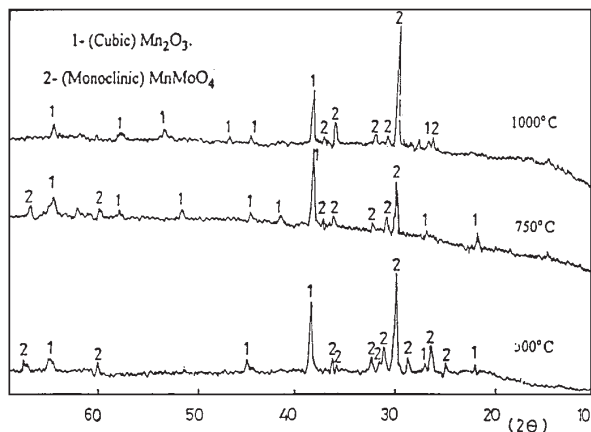
**Fig. 2** X-ray diffractograms of pure  $\text{MnCO}_3$  preheated in air at 500, 750 or 1000°C (a), pure  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and preheated in air at 500 or 1000°C (b)

**Table 5**  $d$ -spacings of  $\text{MoO}_3$  obtained at 500 or 750°C

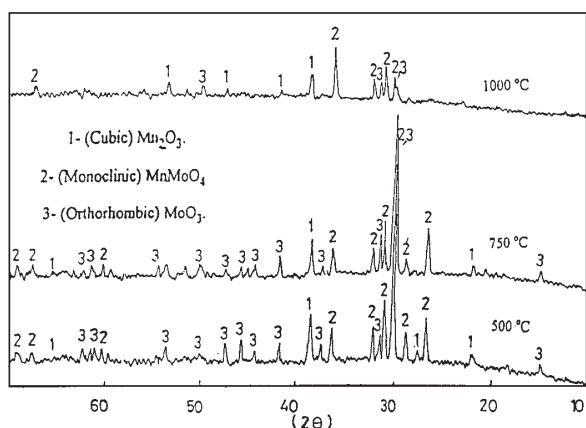
| $hkl$ | $d$ -ASTM | $(I/I_0)$<br>ASTM | $d$ -spacings<br>at 500°C | $(I/I_0)$<br>500°C | $d$ -spacings<br>at 750°C | $(I/I_0)$<br>750°C |
|-------|-----------|-------------------|---------------------------|--------------------|---------------------------|--------------------|
| 020   | 6.93      | 34                | 6.880                     | 25.4               | 6.79                      | 63.63              |
| 040   | 3.463     | 61                | 3.447                     | 46.72              | 3.438                     | 90.9               |
| 021   | 3.26      | 100               | 3.247                     | 100                | 3.247                     | 0.90               |
| 060   | 2.309     | 31                | 2.305                     | 28.68              | 2.299                     | 100                |

*XRD characterization of mixtures of  $\text{MnCO}_3$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  thermally treated at different temperatures*

Figures 3–5 depict the results of XRD analysis of the 3Mn:1Mo, 1Mn:1Mo and 1Mn:3Mo mixtures preheated at 500, 750 or 1000°C. The relationship between the degree of crystallinity (intensity of X-ray bands) and the composition of the mixture (Mn:Mo) is shown in Fig. 6. Inspection of these Figures indicates that the 3Mn:1Mo



**Fig. 3** X-ray diffractograms of mixed solids with molar formula  $3\text{MnCO}_3:1/7(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  preheated in air at 500, 750 or 1000°C



**Fig. 4** X-ray diffractograms of mixed solids with molar formula  $\text{MnCO}_3:1/7(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  preheated in air at 500, 750 or 1000°C

mixture preheated at 500°C is characterized by the well-crystalline phase of cubic  $\text{Mn}_2\text{O}_3$  (more crystalline than that detected for pure  $\text{MnCO}_3$  preheated at 500°C). This means that molybdenum oxide enhances crystallization of the phase  $\text{Mn}_2\text{O}_3$  at this temperature.

The 1Mn:1Mo mixture preheated at 500°C exhibits crystalline  $\text{MoO}_3$  and  $\text{Mn}_2\text{O}_3$ , the latter being in small quantity due to the lower amount of Mn present in the mixture. On the other hand, the 1Mn:3Mo mixture thermally treated at 500°C does not indicate the formation of  $\text{Mn}_2\text{O}_3$ , because of the small amount of Mn in the mixture, which favours the formation of another new phase:  $\text{MnMoO}_4$  (monoclinic).





1. In general, the intensities of the X-ray diffraction bands of the phase  $\text{MnMoO}_4$  formed in case of the sample preheated at  $750^\circ\text{C}$  are less than those detected at  $500^\circ\text{C}$ . This is because of the lower stability of the crystalline phase  $\text{MnMoO}_4$  [8].

2. The maximum degree of crystallinity of the phase  $\text{MnMoO}_4$  is found for the 1Mn:1Mo mixture preheated at  $750^\circ\text{C}$ . On increase of the amount of Mo in the mixture to 1Mn:3Mo, the intensities of the lines for  $\text{MnMoO}_4$  decrease in consequence of the formation of the well-crystalline phase  $\text{MoO}_3$ .

3. Further increase of the treatment temperature up to  $1000^\circ\text{C}$  for all Mn:Mo mixtures stabilizes the crystalline phase  $\text{MnMoO}_4$ . On the other hand the presence of molybdenum with manganese stabilizes the crystalline phase  $\text{Mn}_2\text{O}_3$  and delays the formation of the crystalline phase  $\text{Mn}_3\text{O}_4$ , as in case of  $\text{MnCO}_3$  thermally treated at  $1000^\circ\text{C}$ . In spite of the melting and evaporation of  $\text{MoO}_3$  at  $790^\circ\text{C}$ , as mentioned above, the presence of manganese in combination with molybdenum in the 1Mn:3Mo mixture stabilizes the crystalline phase  $\text{MoO}_3$  even at such high temperature.

From the above results, we can conclude that manganese carbonate decomposed to its oxides in the range  $300\text{--}1000^\circ\text{C}$ , while ammonium molybdate decomposed at about  $340^\circ\text{C}$  to  $\text{MoO}_3$ , which melts at  $790^\circ\text{C}$ . Moreover, a new compound, manganese molybdate, was formed as a result of solid-solid interactions between molybdenum and manganese oxides. The presence of manganese carbonate together with ammonium molybdate could affect the processes of thermal decomposition of their salts and the physical and chemical characterization of the thermal products.

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