Thermal decomposition of magnesium acetate in nitrogen

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Abstract—In this paper, the thermal decomposition process of magnesium acetate, Mg(CH₃COO)₂·4H₂O, in nitrogen atmosphere was studied by thermal analysis methods, and the solid products after thermal decomposition were analyzed by XRD, FE-SEM and EDS. The results show that the thermal decomposition process of magnesium acetate went through four steps: the first step was the dehydration of magnesium acetate to produce anhydrous magnesium acetate; the second step was the conversion of anhydrous magnesium acetate to magnesium oxalate; the third step was magnesium oxalate to magnesium carbonate, and the final step was magnesium carbonate to magnesium oxide.

1. Introduction
Magnesium acetate is an important metal magnesium organic compound, which can be used as an intermediate, catalyst and analytical reagent in organic synthesis [1-4], and a precursor when preparing nanometer magnesium oxide [5]. The study of the thermal decomposition of magnesium acetate is of major interest because it can be used to explore the phase transformation in the decomposition process, as well as to prepare magnesium oxide [6-8].

At present, there are few reports on the decomposition of magnesium acetate. Makhluf study group used magnesium acetate and water as precursor to prepare nanometer magnesium oxide by microwave-assisted method [9]. Isa, et al. analyzed the mass loss and the corresponding DSC curve of magnesium acetate during thermal decomposition process and they found that the water loss stage of magnesium acetate was divided into three parts [10]. Sun, et al. established a kinetic model for the second stage of magnesium acetate decomposition by using the multiple scanning rate method, and made conjectures about the specific in the second stage [11]. However, the analysis of the decomposition steps of magnesium acetate and the decomposition products of each step in the previous studies are still controversial, so it is necessary to further study the thermal decomposition process of magnesium acetate. In this study, the decomposition of magnesium acetate in nitrogen atmosphere was investigated. The decomposition products of each step of magnesium acetate were determined, and the composition process of magnesium acetate was determined.
2. Experimental

The raw material used in this study was 99% magnesium acetate powder (Tianjin Damao Chemical Reagent Factory), and its chemical formula is Mg(CH$_3$COO)$_2$·4H$_2$O. The thermal decomposition experiment of Mg(CH$_3$COO)$_2$·4H$_2$O was carried out on a synchronous thermal analyzer (NETZSCH STA 449 F3). The sample of about 10~13 mg magnesium acetate powder, ground to 100 mesh before the experiment, was placed in the standard Al$_2$O$_3$ crucible and heated to 600 °C at rates of 1, 3, 5, 8 and 10 °C/min. The measurement was conducted with N2 as protective gas and purge gas, and its flow rate was 50 ml/min.

In order to further confirm the thermal decomposition mechanism of magnesium acetate, the thermal decomposition experiments were also carried out on a tube resistance furnace (SK-G05123K) with a quartz tube in a N2 atmosphere. Approximately 1.0 g Mg (CH$_3$COO)$_2$·4H$_2$O sample, placed in alumina crucibles, was transferred into the quartz tube of the tube resistance furnace. N2 was then fed into the quartz tube at a flow rate of 50 ml/min and the sample was heated to 300 °C, 310 °C, 315 °C, 320 °C, 325 °C, 330 °C, 340 °C and 350 °C for 30 minutes, respectively.

The decomposition products were analyzed by X-ray diffractometer (XRD), Infrared spectrometer (IR), field emission scanning electron microscope (FE-SEM) and energy dispersive spectrum (EDS).

3. Results and discussion

3.1. TG analysis

Figure 1 depicts the TG and DTG curves of Mg (CH$_3$COO)$_2$·4H$_2$O in N2 atmosphere at the flow rate of 50 ml/min at different heating rate. The DTG curve derived from the TG curve was used to improve the resolution of the TG curve, which makes the decomposition step easy to identify [12-14]. It can be seen from Figure 1 that during temperature-programmed process, there are two obvious platforms on all TG curves, and the shapes of the curves were similar at different heating rates and the weight loss percentages were also very close. Since each platform on the TG curve corresponds to a decomposition reaction step, Mg (CH$_3$COO)$_2$·4H$_2$O had two clear decomposition reaction processes from room temperature to 600 °C and the heating rate had little effect on the decomposition process. However, on DTG curve, there were two downward peaks at the position corresponding to the second platform of TG curve, which indicates there were two decomposition reactions between 300 and 400 °C.

![Figure 1. TG curves at different heating rates and DTG curve at 1(°C/min)](image-url)
Figure 2. Relationship between initial temperature and the heating rate

Figure 2 shows the change of the initial temperature of the decomposition reaction with the heating rate. The data of the initial temperature was derived from the DTG or TG curve above [15]. As can be seen, the heating rate had an effect on the start temperature of each platform. With the increase of heating rate, the initial temperature of both platforms increased, indicating that the initial temperature of the decomposition reaction had an upward trend with the increase of heating rate. It is assumed that when the heating rate is small enough, the heat transfer will be more sufficient. At this time, the initial temperature of the two platforms can be obtained by extrapolation. The results are shown in Table 1.

Table 1. Starting temperatures of the two platforms when the heating rate was small enough

| Platform No. | Starting temperature(°C) | Molecular formula of final solid product |
|--------------|--------------------------|-----------------------------------------|
| 1            | 61.45                    | Mg(CH₃COO)₂                              |
| 2            | 308.5                    | MgO                                     |

3.2. DSC analysis

Figure 3 shows the TG-DSC curve of Mg(CH₃COO)₂·4H₂O from 20 °C to 600 °C at the heating rate of 10 °C/min in N₂ atmosphere. There is an upward endothermic peak before 200 °C, indicating that the water loss process of magnesium acetate [16]. It can be seen that before 250 °C, there was a downward exothermic peak, indicating that magnesium acetate started melting. It can be seen from DSC curve in Figure 3, between 300 °C and 400 °C, that there were at least two endothermic peaks, showing that the decomposition of Mg(CH₃COO)₂ into MgO was not done in one step.

Figure 3. TG-DSC curve of Mg(CH₃COO)₂·4H₂O at 10(°C/min) in N₂ atmosphere.

Figure 4 shows that in the temperature range of 285 °C-365 °C, there were two upward endothermic peaks on the DSC curve, which indicates Mg(CH₃COO)₂ decomposed in at least two steps in this temperature range. It can be assumed that a continuous multi-step reaction occurred in the decomposition process of Mg(CH₃COO)₂. That is to say, in the decomposition process, magnesium acetate first decomposed into magnesium oxalate, then immediately into magnesium carbonate, and finally was converted into magnesium oxide. DDSC curve showed that there was no overlapping peak in DSC curve of this temperature range.
3.3. XRD analysis

The X-ray diffraction patterns of Mg(CH₃COO)₂·4H₂O heated to different temperatures for 30 minutes were showed in Figure 5. As can be seen in Figure 5, the diffraction peaks at 310 °C were consistent with the PDF CARD 140826 of anhydrous magnesium acetate, which indicates that Mg(CH₃COO)₂·4H₂O had completely lost its crystal water at this temperature. The obvious sharp diffraction peak means that the crystallinity of Mg(CH₃COO)₂ was very good. At 325 °C, the peak intensity of magnesium acetate between 9° and 15° decreased, while the peaks of magnesium oxalate at 17.3°, 22.5° and 39.1° and the peaks of magnesium carbonate at 30.8° and 41.8° appeared. This indicates that magnesium acetate decomposed a little, and magnesium oxalate and magnesium carbonate were formed at the same time. At 330 °C, the peak intensity of magnesium acetate between 9° and 15° decreased and that of magnesium oxalate and magnesium carbonate increased. At 340 °C, the peak intensity of magnesium acetate between 9° and 15° continued to decrease, while that of magnesium oxalate and magnesium carbonate increased. At 345 °C, there was still a small amount of magnesium acetate in the product, but most of it was magnesium oxide. These results indicate that during the decomposition of Mg(CH₃COO)₂·4H₂O, magnesium acetate, magnesium oxalate and magnesium carbonate coexisted, but as the temperature increased, they were all transformed into magnesium oxide.
Figure 6 shows the XRD pattern of the decomposition residue of Mg(CH$_3$COO)$_2$·4H$_2$O at 600 °C. The pattern agrees with the PDF cards 450946 of MgO, indicating that the residue was high-purity MgO powder.

3.4. SEM/EDS analysis

Figure 7 shows the SEM images and corresponding EDS results of the decomposition products of Mg(CH$_3$COO)$_2$·4H$_2$O at different temperatures. It can be seen from Figure 7(a) that before Mg(CH$_3$COO)$_2$·4H$_2$O decomposition, it has larger volume with a more regular bulk and spherical particle crystal. Moreover, according to EDS, the regular bulk crystal contained a large number of Mg and O elements. The mass fraction ratio of C, O and Mg was about 3.1:4.7:2.1. As shown in Figure 7(b), at 250 °C, all spherical crystals have been broken down into small particles. The bulk crystals were broken into irregular flakes, which look like irregular bulk powder. The main components were C, O and Mg. The mass fraction ratio of C, O and Mg was about 5.43:9.94:4.63, which were close to the molar mass fraction ratio of magnesium acetate. From Figure 7(c), it can be seen that at 300°C, large bulk crystals began to decompose from the edges, smaller bulk powders appeared, and the particle distribution was relatively uniform. As indicated by EDS, the content of C decreased continuously, indicating that the properties of the compound changed at this temperature. At 350 °C, as shown in Figure 7(d), the small particles were glued together, and the massive surface had obvious flake or flocculent irregular magnesium oxide formation. The main elements on the solid surface are Mg and O with a mass fraction ratio of about 5.6:3.2, which is close to the molar mass fraction ratio of MgO.
Figure 7. SEM images and corresponding EDS results of the decomposition product of Mg(CH$_3$COO)$_2$·4H$_2$O: (a) before decomposition, (b) at 250 °C, (c) at 300 °C, (d) at 350 °C.

3.5. Kinetic analysis

Table 2. Residual mass and product formula of Mg(CH$_3$COO)$_2$·4H$_2$O decomposition.

| Platforms | Temperature (°C) | Residual mass percentage(%) | Molecular formula of product |
|-----------|------------------|-----------------------------|------------------------------|
|           |                  | Calculated                  | Experimental                 |
| 1         | 61.45-146.6      | 66.43                       | 60.16 Mg(CH$_3$COO)$_2$       |
| 2         | 308.5-395.4      | 52.05                       | 20.87 MgC$_2$O$_4$           |
|           |                  | 39.41                       | MgCO$_3$                     |
|           |                  | 18.84                       | MgO                          |

According to the above results, the residual mass after each decomposition reaction can be calculated based on the molar mass loss of 1mol (214.46g) Mg(CH$_3$COO)$_2$·4H$_2$O (The mass of Mg(CH$_3$COO)$_2$·4H$_2$O before water loss is assumed to be unit 1) [17], and the molecular formula of the decomposition reaction product of Mg(CH$_3$COO)$_2$·4H$_2$O at each step were obtained by molar mass loss calculation. The results were listed in Table 2.

Based on the DSC-TG curves and the results of Table 2, it can infer that the reactions of the decomposition of magnesium acetate may be as follows [18]:

1. Mg(CH$_3$COOH)$_2$·4H$_2$O $\rightarrow$ (0.66)Mg(CH$_3$COO)$_2$·4H$_2$O + (0.34)CH$_3$COOH
2. (0.66)Mg(CH$_3$COO)$_2$ $\rightarrow$ MgC$_2$O$_4$ + CH$_3$COOH + 0.5CH$_3$OH
3. (0.52)MgC$_2$O$_4$ $\rightarrow$ MgCO$_3$ + CO
4. (0.39)MgCO$_3$ $\rightarrow$ (0.18)MgO + CO$_2$

4. Conclusion
The thermal decomposition process of Mg(CH₃COO)₂·4H₂O in nitrogen atmosphere was studied. The TG curves show that the first step of the decomposition was the water loss process. DSC curves and phase analysis indicate that the second step of decomposing anhydrous magnesium acetate into MgO involved more than one reaction. This step includes three processes: anhydrous magnesium acetate was converted to magnesium oxalate, then to magnesium carbonate, and finally to magnesium oxide. The specific heat capacity and enthalpy change during the decomposition process were calculated by DSC. By exploring the decomposition process of magnesium acetate into magnesium oxide at high temperature, powder magnesium oxide with higher purity can be prepared.

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REFERENCES
[1] Shen G L, Zhang J, Ma X Y, et al. (2012) Study on synthesis technology of magnesium acetate. J. Chemical World, 12:57-61.
[2] Tyner T, Francis, James. (2017) Magnesium Acetate Tetrahydrate. ACS Reagent Chemicals: American Chemical Society.
[3] Rueda M, Sanz-Moral L M, et al. (2014) Martin A. Micronization of magnesium acetate by the supercritical antisolvent process as a precursor for the production of magnesium oxide and magnesium hydride. J. Crystal Growth & Design, 14(9):4768-4776.
[4] Fu X J, Chu M S, Gao L H. (2018) Stepwise recovery of magnesium from low-grade ludwigite ore based on innovative and clean technological route. J. Transactions of Nonferrous Metals Society of China, 28(11):2383-2394.
[5] Shi S C, Wang Q, Zhang Z K. (2020) Template-free synthesis of high-purity mesoporous MgO nano-particles as antimicrobial. J. Environmental Chemistry, 39(03):800-808.
[6] Zhou H X, Liu W J, Zhu F Y. (2014) Introduction of the nanometer magnesia preparation methods. J. Journal of Salt and Chemical Industry, 43(07):4-8.
[7] Gou S L. (2019) Preparation and characterization of antibacterial nano-magnesium oxide. Qinghai Institute of Salt Lake, Chinese Academy of Science, Qinhai.
[8] Xu S L. (2018) Accelerate the Development of Magnesium Compound Industry in China, Magnesium compound industry annual meeting and conference.
[9] Makhluf S, Dror R, Nitzan Y, et al. (2005) Microwave-assisted synthesis of nanocrystalline MgO and Its use as a bactericide. J. Advanced Functional Materials, 15(10):1708-1715.
[10] Isa K, Nagawa M. (1984) Thermal decomposition of magnesium acetate tetrahydrate under self-generated atmosphere. J. Thermochimica Acta, 75(1-2):197-206.
[11] Sun Q X, Song L, Yuan L J. (2009) Kinetics and mechanism of thermal decomposition of Mg(CH₃COO)₂·4H₂O. J. Journal of Hubei University(Natural Science), (3): 74-78.
[12] Li B, Gao J H, Xu Z H, et al. (2018) Application of thermal analysis in material analysis. J. Analytical Instrumentation, 217(02): 93-97.
[13] Huang Z H, Zhao H, Lv L Q, et al. (2010) Thermal analysis and its application. J. Hot Working Technology, 39(7): 26-29+33.
[14] Yang R, Chen L, Tang G P, et al. (2012) Application of thermo - analysis combination techniques in the thermal analysis of polymer. J. Polymer Notification, (12): 16-21.
[15] Hu X W, Li L, Gao B L. (2011) Thermal decomposition of ammonium hexafluoroaluminate and preparation of aluminum fluoride. J. Transactions of Nonferrous Metals Society of China, 21(9): 2087-2092.
[16] Zhang M F, Sun Q X, Zhang K L, et al. (2008) Study on Thermal Decomposition Mechanism and Kinetics of Mg(CH₃COO)₂·4H₂O. Proceedings of the Conference on Inorganic Chemistry and Chemical Industry in the Central and Western China in 2008.
[17] Merwe E M V D, Strydom C A. (2004) Quantitative thermo gravimetric analysis of binary mixtures. J. Journal of Thermal Analysis and Calorimetry, 76:149-456.

[18] Kahirou D, Zhan H J-H, Zhang D, et al. (2006) Kinetics of the thermal decomposition of magnesium salicylate powder in air. J. Chemical Research in Chinese Universities, 22(5): 617-620.

[19] Hu T Q, Fen Y, Pu Y Z, et al. (2015) Thermal decomposition kinetics of Fe₂(C₂O₄)₃·5H₂O prepared by solid-state reaction. J. Taiyuan University of Technology, 46(5): 520-525.