



Simultaneous characterizing study of the metallic iron—organic coordination compounds by TG–DSC–MS coupling techniques

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Abstract

In this work, thermogravimetry–differential scanning calorimetry–mass spectrometry (TG–DSC–MS) coupling techniques were used to make a simultaneous characterizing study for the metallic iron–organic coordination compounds formed by iron ions and organic solvent glycol during the sol–gel process of preparing the iron oxide nanometer films. The positive ion mass spectra $[\text{Fe}(\text{OCH}_2\text{CH}_3)_3]^+$ (mass to charge (m/z) = 191) and $[\text{Fe}(\text{OCH}_2\text{CH}_2\text{OH})_3]^+$ (m/z = 239) of the organic iron coordination compounds were obtained by experimental methods for the first time. Through the comparison analysis with the results of the TG–DSC–MS for the glycol, it can be found that the thermal decomposition temperature for the metallic iron–organic coordination compounds formed with glycol is higher than that of pure glycol. The results in this research work show that the simultaneous TG–DSC–MS coupling techniques can be applied to characterize some of the metallic–organic coordination compounds appeared in the gas state at lower temperature.

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1. Introduction

The iron oxide system nanometer films have been applied to produce different microwave and optical devices and magnetic apparatus in recent years. Up to now, many physical and chemical methods such as liquid phase epitaxy, sputtering and plasma splay etc can be used to prepare the magnetic Fe_3O_4 and other iron oxide nanometer films [1].

Takahashi et al. [2] successfully prepared magnetite films using sol–gel method to which many researchers paid great attentions. In the process of preparing the magnetite films, it was the first step to synthesize

non-crystal gel including large amount of organic groups. After thermal treatment, a certain amount of crystal phases were separated out from the amorphous structure. The large amount of pores in materials formed due to evolution of the organic groups and the contrast surface area of materials were increased greatly. Therefore, the catalysis performances and gas sensitivity are optimized. However, the studies on the mechanism and process of preparing magnetite (Fe_3O_4) films by sol–gel are seldom to see in literature. Costa et al. [3] obtained several mixtures of hematite (Fe_2O_3) and magnetite (Fe_3O_4) by means of using the sol–gel reaction between Fe(III) ions of $\text{Fe}(\text{NO}_3)_3$ and glycol and the thermal treatment for the reaction products. The sol–gel reaction products were characterized by mössbauer spectrometry

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and X-ray diffraction (XRD) and transform electron microscopy (TEM). The research results show the existence of large amount of ion, but its origin is not clear. Amelao et al. [4] synthesized α -Fe₂O₃ nanometer structure films by dipping silica slides into the alcoholic solution of Fe(OCH₂CH₃)₃. Then the films were studied by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) methods. The results show the coating films at temperature ≤ 300 °C are amorphous and at 400 and 500 °C, nanometer hematite particles which possess the same stoichiometry and iron coordination as that of the crystallized phase were dispersed in an amorphous matrix. The results in [3] show none convincing experimental data to confirm the forming of metallic iron organic coordination compounds during the process of preparing magnetite films by sol–gel method.

According to the reference [5], the super fine powders of γ -Fe₂O₃ and γ -Fe₂O₃ added with Y₂O₃ of average diameter 10 nm were obtained by sol–gel reaction between Fe(NO₃)₃·9H₂O and glycol. In this work, we used TG–DSC–MS coupling technique to characterize and study the treatment process of preparing the Fe₃O₄ magnetic films obtained by sol–gel method. The positive ion mass spectra [Fe(OCH₂CH₃)₃]⁺ ($m/z = 191$) and [Fe(OCH₂CH₂OH)₃]⁺ ($m/z = 239$) are obtained by experimental methods for first time in this research. The comparative measurements for the two samples of adding Fe(NO₃)₃·9H₂O and alcohol and adding Fe(NO₃)₃·9H₂O and alcohol and glycol are also made by TG–DSC–MS. The other positive ion mass spectra for the decomposed products and the segments obtained in the experiments are discussed preliminarily.

2. Experimental

2.1. Sample preparation

According to the certain molar proportion (the molar ratio of glycol/Fe(NO₃)₃·9H₂O was kept to be 15:1), the Fe(NO₃)₃·9H₂O (analytical purity) was dissolved in glycol and alcohol. The concentration of iron(III) nitrate dissolved in glycol and alcohol solution was 0.3M. Then the solution flows back at 70 °C for certain time. The obtained sol was distilled at 80 °C

to form gel. Then it was dried to obtain the sample F(A).

According to the same procedure mentioned above to prepare the sample F(B). The only difference between the preparation of F(A) and F(B) is that the glycol was not used as solvent for preparing F(B).

2.2. TG–DSC–MS measurement

The Netzsch STA 449C TG–DSC device coupled with Balzers Thermostar Quadrupole Mass Spectrometer was used in the experiments. The quartz capillary tube was used as the interface between thermal analyzer and the quadrupole. The mass of F(A) is 8 mg. The mass of F(B) is 8.9 mg. Gas Ar of 5 ml/min was used for the protective gas of TG–DSC furnace. Gas He with a flow speed of 40 ml/min was used as the carrying gas. The vacuum for the system of quadrupole was 10^{−4} Pa. All of the procedures were controlled according to a proposing program.

The TG–DSC program was operated first. The temperature region was from room temperature to 1200 °C. The heating rate was 10 °C/min.

The MS program was operated secondly. The MID mode was used for the measurement. In each channels, the different m/z mass numbers were proposed one by one (the zero channel was proposed for symbolizing temperature; the other m/z propositions in other channels can be seen from Table 1). The mass filtering

Table 1
Mass numbers propositions^a

m/z	Expected positive ion mass spectra
2	H ₂ ⁺
12	C ⁺
14	N ⁺
18	[H ₂ O] ⁺
19	[H ₃ O] ⁺
26	[C ₂ H ₂] ⁺
28	CO ⁺ /N ₂ ⁺
30	NO ⁺
31	[CH ₃ O] ⁺
33	[CH ₃ OH ₂] ⁺
44	CO ₂ ⁺
46	NO ₂ ⁺ /[C ₂ H ₆ O] ⁺
62	C ₂ H ₆ O ₂ ⁺
191	[Fe(OCH ₂ CH ₃) ₃] ⁺
239	[Fe(OCH ₂ CH ₂ OH) ₃] ⁺

^a The intensities of the positive ion mass spectra mentioned above were proposed automatically.

time was 1 s. The mass scanning speed was 1 s. The channel-tron was used to record the positive ion mass spectra signals.

The calculations and data treatment were in progress after complete the proposed programs.

3. Results and discussion

3.1. TG–DSC–MS results for the sample F(A) (added with glycol)

The TG–DSC–MS results for the sample F(A) are shown in Figs. 1 and 2. The TG curves in Fig. 1 show mass losses: 26.1% (RT–300 °C); 28.96% (300–410 °C); 16.8% (410–570 °C). There are no mass loss appears over 600 °C basically. The DSC in Fig. 1 appear a small endothermic peaks at 169 and 343 °C, a big endothermic peak at 533 °C.

The parts of MS results for the sample F(A) are shown in Fig. 2. Corresponding to the DSC curves, the MS curves appear the positive ion mass spectra peaks of $m/z = 239$ and 191 at 343 °C. The ion current intensities are 5.8×10^{-13} A ($m/z = 239$) and 5.5×10^{-13} A ($m/z = 191$) separately. The two peaks are related to the vaporization of metallic iron organic coordination compound. The formed positive ion mass spectra should be $[\text{Fe}(\text{OCH}_2\text{CH}_2\text{OH})_3]^+$ ($m/z = 239$)

and $[\text{Fe}(\text{OCH}_2\text{CH}_3)_3]^+$ ($m/z = 191$), respectively. This result shows no difference with the view in literature [6] that some metallic organic compounds exist in the state of metallic vapor at lower temperature. The ion current intensities of $m/z = 239$ and 191 are so small due to the most of the metallic iron organic coordination compounds decomposed to CO, CO₂ and other fragments. Fe(OCH₂CH₂OH)₃ and Fe(OCH₂CH₃)₃ decomposed to CO, CO₂ or other organic fragments, as well as H₂O or H₂.

The other eight positive ion mass spectra for the sample F(A) are listed in Table 2.

3.2. TG–DSC–MS results for the sample (B) (without glycol)

The TG–DSC results for the sample F(B) are shown in Fig. 3. The TG curve shows a big step. The DSC curve shows a small endothermic peak at 169 °C and two small exothermic peaks at 245 and 429 °C. Corresponding to the DSC small endothermic peak at 169 °C, the MS spectra for sample F(B) are shown in Figs. 4 and 5. In Fig. 4, the H₂O⁺ ($m/z=18$), NO⁺ ($m/z = 30$), CO⁺/N₂⁺ ($m/z = 28$), CO₂⁺ ($m/z = 44$) peaks appear at 169 and 232 °C. These peaks are probably related to the disorption of the H₂O and HNO₃ in Fe(NO₃)₃·6H₂O and the alcohol in sample F(B). In Fig. 5, N⁺ ($m/z = 14$),

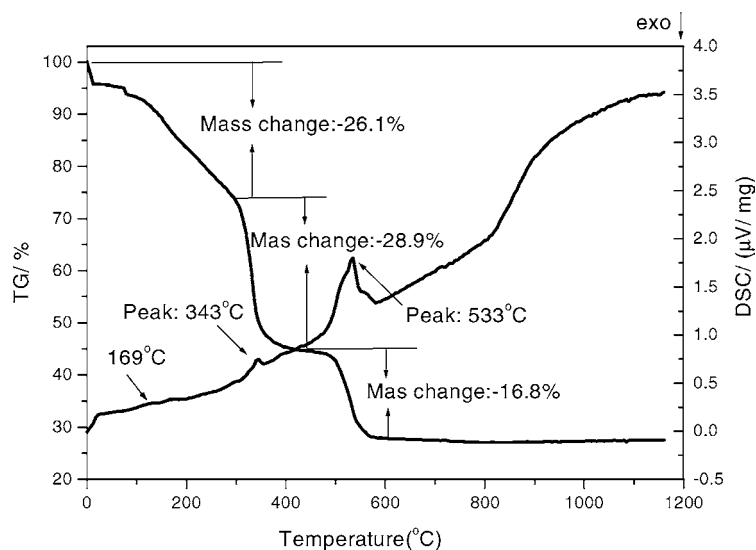


Fig. 1. The TG–DSC curves for sample F(A).

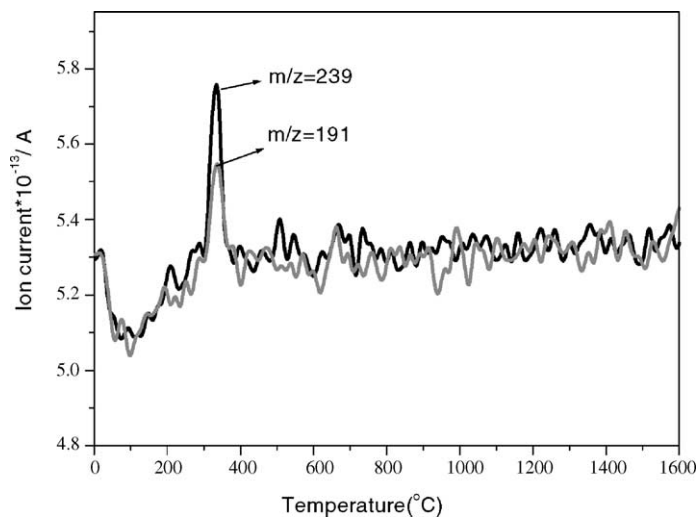


Fig. 2. The MS spectra for sample F(A): $[\text{Fe}(\text{OCH}_2\text{CH}_3)_3]^+$ ($m/z = 191$) and $[\text{Fe}(\text{O}-\text{CH}_2\text{CH}_2\text{OH})_3]^+$.

Table 2

The other eight positive ion mass spectra for the sample F(A) obtained by TG–DSC–MS

Positive ion	H_2^+	C^+	H_2O^+	H_3O^+	C_2H_2^+	CO^+	CH_3O^+	CH_3OH_2^+
m/z	2	12	18	19	26	28	31	33
Intensity (A)	10^{-9}	10^{-10}	10^{-8}	10^{-11}	10^{-10}	10^{-9}	10^{-10}	10^{-12}
Amplifying rate ^a	$4 \times c$		$2.1 \times a$	$6 \times a$	$0.7 \times a$	$4.2 \times b$	$1.3 \times a$	$6 \times a$
	$2.5 \times d$	$2.8 \times c$			$1.3 \times c$	$2.3 \times e$	$0.7 \times c$	$3.5 \times b$
	$0.5 \times e$	$2.3 \times e$						$2 \times c$

^a The alphabetical letters imply as follows: a, 169; b, 273; c, 343; d, 379; and e, 533 °C.

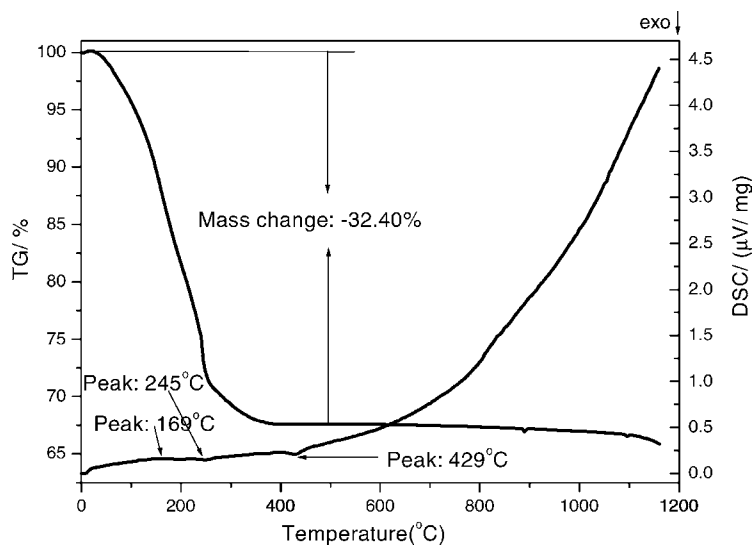


Fig. 3. The TG–DSC curves for sample F(B).

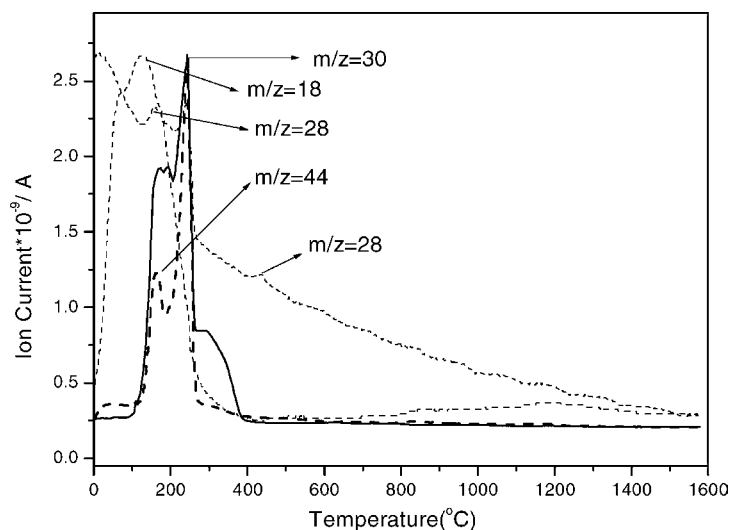


Fig. 4. The MS spectra for sample F(B): H_2O^+ ($m/z = 18$), NO^+ ($m/z = 30$), CO^+ ($m/z = 28$) and CO_2^+ ($m/z = 44$).

C^+ ($m/z = 12$) and NO_2^+ ($m/z = 46$) peaks appear at 169 and 232 °C separately. These peaks are probably related to the decomposition of $\text{Fe}(\text{NO}_3)_3$ with an exothermic effect. The N^+ ($m/z = 14$) belongs to the fragments of N_2^+ or NO^+ or NO_2^+ . The CH_3O^+ ($m/z = 31$) peaks (at 169 and 232 °C) in Fig. 6 probably formed by the fragments of $\text{CH}_3\text{CH}_2\text{OH}$ [7].

3.3. The TG–DSC–MS results for pure glycol

The TG–DSC cures for pure glycol are shown in Fig. 7. The TG curve shows a big mass loss step. The DSC curve shows a big endothermic peak at 146.9 °C and a small accompanying “shoulder” endothermic peak at 165.2 °C. Corresponding to the DSC peaks at 146.9 and 165.2 °C, the main obtained

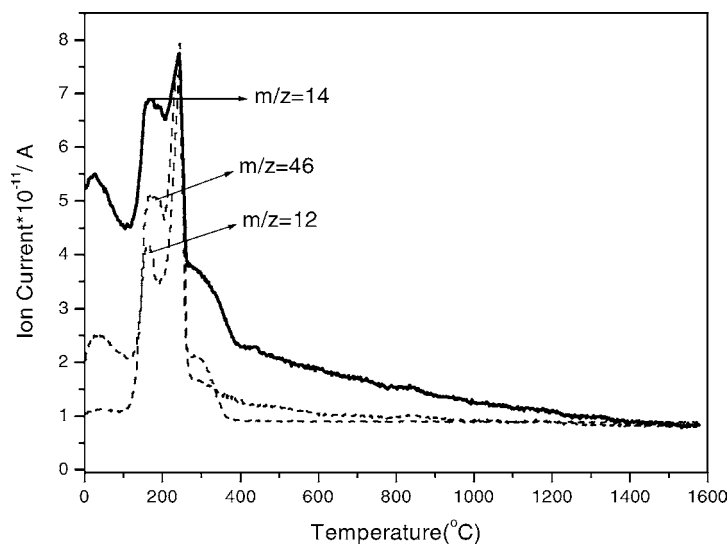


Fig. 5. The MS spectra for sample F(B): N^+ ($m/z = 14$), C^+ ($m/z = 12$) and NO_2^+ ($m/z = 46$).

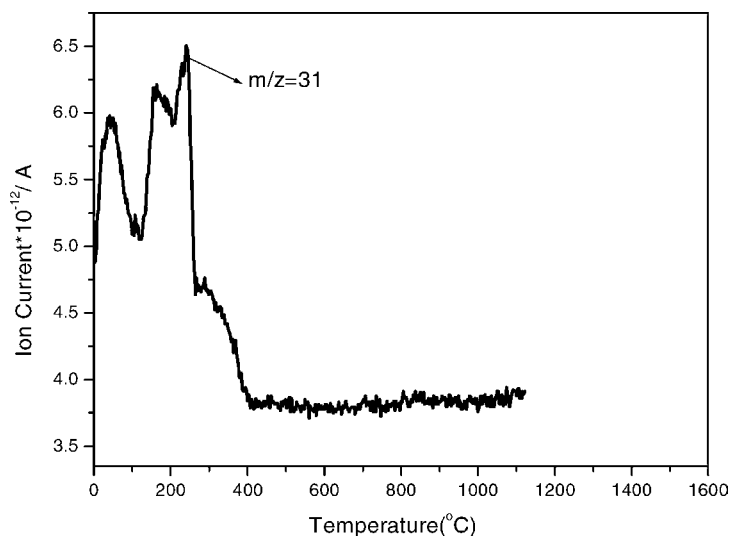


Fig. 6. The MS spectra for sample F(B): CH_3O^+ ($m/z = 31$).

MS spectra for pure glycol are shown in Fig. 8. These peaks are OH^+ ($m/z = 17$), H_3O^+ ($m/z = 19$), $\text{C}_2\text{H}_5\text{OH}^+$ ($m/z = 46$) and $\text{C}_2\text{H}_6\text{O}_2^+$ ($m/z = 62$).

3.4. The comparative analysis for the TG–DSC–MS results of F(A) and F(B) and pure glycol

Compared with the TG–DSC–MS results of F(A) and F(B), we can see the following differences:

- (1) The TG curve for F(A) shows obvious two big mass loss steps. However, the TG curve for F(B) shows one big large mass loss step.
- (2) The DSC curve for F(A) shows endothermic peaks at 169, 343 and 533 °C separately. However, the DSC curve for F(B) shows one small endothermic peak at 169 °C and two exothermic peaks at 245 and 429 °C. Not only the quality of the thermal effect is different, but also the temperature

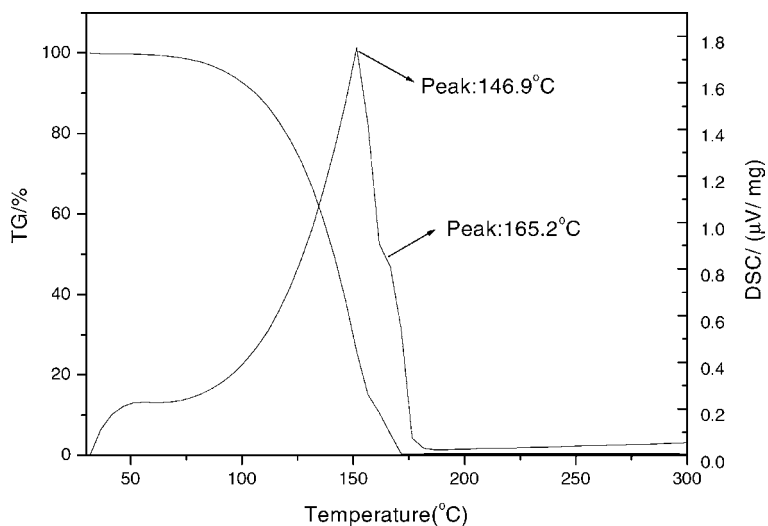


Fig. 7. The TG–DSC curves for pure glycol.

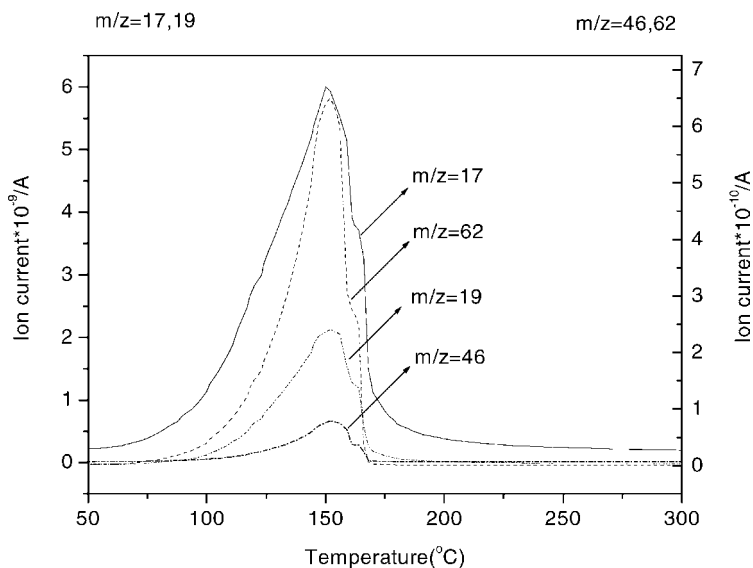


Fig. 8. The MS spectra for pure glycol.

of the peaks corresponding to the thermal effects for F(A) is about 60–70 °C higher than that of F(B).

- (3) The 10 positive ion mass spectra measured for sample F(A) are: H_2^+ ($m/z = 2$); C^+ ($m/z = 12$); $[\text{H}_2\text{O}]^+$ ($m/z = 18$); $[\text{H}_3\text{O}]^+$ ($m/z = 19$); $[\text{C}_2\text{H}_2]^+$ ($m/z = 26$); CO^+ ($m/z = 28$); $[\text{CH}_3\text{O}]^+$ ($m/z = 31$); $[\text{CH}_3\text{OH}_2]^+$ ($m/z = 33$); $[\text{Fe}(\text{OCH}_2\text{CH}_2\text{OH})_3]^+$ ($m/z = 239$) and $[\text{Fe}(\text{OCH}_2\text{CH}_2\text{OH})_3]^+$ ($m/z = 191$). However, the positive ion mass spectra measured for sample F(B) are: C^+ ($m/z = 12$); N^+ ($m/z = 14$); $[\text{H}_2\text{O}]^+$ ($m/z = 18$); CO^+ ; N_2^+ ($m/z = 28$); NO^+ ($m/z = 30$); $[\text{CH}_3\text{O}]^+$ ($m/z = 31$); CO_2^+ ($m/z = 44$) and NO_2^+ ($m/z = 46$). Through the comparison, it is obvious that glycol plays key role for forming the metallic iron organic coordination compounds in the sample F(A). We found no N^+ ($m/z = 14$), NO^+ ($m/z = 30$) and NO_2^+ ($m/z = 46$) peaks in the MS spectra for the sample F(A). It shows the HNO_3 already completely evolved out in the process of preparing the films at the time of flowing back and distillation with $\text{Fe}(\text{NO}_3)_3$ using glycol.
- (4) We found the only organic group peak $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) for the sample F(B). It is probably

related to the fragments of alcohol molecule ions. Compared with the CH_3O^+ ($m/z = 31$) in the sample F(A), the corresponding decomposition temperature for the two samples is different. The first $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) peaks appear at 169 °C for the both samples. The second $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) peaks appear at 232 °C for the sample F(B) and at 343 °C for the sample F(A). Meanwhile, the ion current intensity of $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) peak for F(A) is higher than for F(B). The ion current intensity of $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) at 169 and 232 °C for F(B) are 6.1×10^{-12} A and 6.4×10^{-12} A respectively. But for F(A), the ion current intensity of $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) at 169 and 343 °C are 1.1×10^{-10} A and 8×10^{-11} A respectively. It shows the $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) produced from sample F(A) is formed probably from the fragments of alcohol and glycol. While the $[\text{CH}_3\text{O}]^+$ ($m/z = 31$) produced from sample F(B) is formed probably from only the fragments of alcohol.

- (5) It is obvious that the thermal decomposition temperature of the metallic iron organic coordination compounds $[\text{Fe}(\text{OCH}_2\text{CH}_3)_3]$ and $\text{Fe}(\text{OCH}_2\text{CH}_2\text{OH})_3$ is higher than that of pure glycol.

3.5. The characterization for the final product films under the different temperatures

The final products films by sol–gel method using sol of F(A) under the different temperatures were characterized by X-ray diffraction analysis. The results show that the final product films are α -Fe₂O₃, Fe₃O₄, the mixtures of the Fe₃O₄, FeO and Fe according to the different thermal treatment temperatures. The obtained results mentioned above are very useful for the preparation of the required nanometer magnetic films [8].

4. Conclusions

Through the TG–DSC–MS measurements and the comparative analysis, we can get the following conclusions:

- (1) The metallic iron organic coordination compounds Fe(OCH₂CH₃)₃ and Fe(OCH₂CH₂OH)₃ were formed in the process of preparing nanometer magnetite (Fe₃O₄) films for the sample F(A).
- (2) The thermal decomposition of the metallic iron coordination compounds Fe(OCH₂CH₃)₃ and Fe(OCH₂CH₂OH)₃ mainly completed in the two steps. The first step was taken place at 343 °C. The temperature for the second thermal decomposition was at 533 °C. The water and alcohol and glycol was desorbed at about 169 °C.
- (3) For the sample F(B), because without adding glycol, the Fe(OCH₂CH₂OH)₃ can not be produced from the reaction between Fe(NO₃)₃·6H₂O and alcohol.
- (4) Large amount of the positive ion mass spectra of the fragments appeared in the MS measurements. It shows the fragmentary process of metallic iron organic coordination could be very complicated. Besides the expected positive ion mass spectra, the further studies for the other fragments probably formed in the MS system and the thermal decomposition mechanism for the metallic iron organic coordination compounds are necessary.

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