TG–DTA–MS studies on the thermal decomposition behaviour of homogeneously precipitated $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$

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Abstract

Studies on the thermal decomposition behaviour of homogeneously precipitated $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ using a TG–DTA–MS coupling technique are reported for the first time. The positive ion mass spectra of evaporated gases during the process of thermal decomposition O^+ (m/z 16); H_2O^+ (m/z 18); SO^+ (m/z 48); SO_2^+ (m/z 64) versus temperature are also given.

INTRODUCTION

In order to prepare the zirconium oxide ceramics with high strength and toughness, greater demands concerning the raw materials for oxide preparation have been made [1, 2]; this means the superfine powder of high purity should be of homogeneous composition distribution, have minimum impurities and its particles appear spherical in shape or be of the equal axis type [3, 4]. If the precipitation method is used to prepare zirconium oxide powder, the quality of the powder is variable due to the uncontrolled nature of the precipitation process. In order to keep the precipitate in solution in a balanced state and to effectively control the process of precipitation, the homogeneous precipitation method can be used to control the concentration and pH of the precipitant in solution. The amount of precipitant should be increased slowly, so that the precipitate in the solution can be accrued homogeneously and particles of regular shape can be obtained [5, 6].

By means of the homogeneous precipitation method, in which the values of $[SO_4^{2-}]/[ZrO_2]$ and $[urea]/[ZrO_2]$ are controlled and a suitable cooling speed is used $Zr(SO_4)(OH)_6 \cdot 6H_2O$ particles of spherical shape are obtained [6]. In order to completely understand the homogeneous

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precipitation process and the composition of the precipitate, to select conditions for thermal decomposition and the sintering temperature, studies on the thermal decomposition behaviour of the homogeneously precipitated material are necessary. The traditional TG–DTA method can be used to study the increase or decrease of mass of $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ and its endothermal and exothermal effects, but the types of gases evaporating during the thermal decomposition process cannot be detected by this method.

Fortunately, the TG–DTA–MS coupling technique which has been developed in recent years is able to remedy the shortcomings of TG–DTA. By TG–DTA–MS, not only can the types of evaporated gases be detected, but the positive ion mass spectra versus temperature can also be plotted [7, 8]. In this work, the TG–DTA–MS coupling technique has been used successfully for the first time to study the process of the thermal decomposition of the precipitate $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$. As well as the TG–DTA curves, the positive ion mass spectra of the evaporated gases (O^+ (m/z 16); H_2O^+ (m/z 18); SO^+ (m/z 48); SO_2^+ (m/z 64) versus temperature are also given.

EXPERIMENTAL

Sample preparation

By means of precipitation, filtering and washing (to remove Cl^-), pure $Zr(OH)_4$ is obtained from $ZrOCl_2 \cdot 8H_2O$ solution. A certain amount of H_2SO_4 (AR) is then added to the precipitate giving zirconium sulphate. Urea is then added, to keep the [Urea]/(ZrO_2] ratio in the mixed solution at a constant value and the amount of ZrO_2 is kept at 0.0543 M. The mixed solution is heated to 85°C with constant stirring in a water bath. After some time, the precipitate begins to appear, and the temperature is maintained for 15–120 min; the mixture is allowed to cool in air and centrifuged. The precipited particles are washed with distilled water to remove unnecessary ions.

TG–DTA–MS measurements

An STA-429 simultaneous thermal analyzer (Netzsch Co., Germany) was used with a QMG-511 quadrupole mass spectrometer (Balzers Co., Switzerland). The mass of sample is 79 mg and the reference compound for DTA is Al_2O_3 (100 mg). The full scale of TG is 25 mg. The full scale of DTA is 0.2 mV. The response time of the instrument $X_n = 8$. The magnifying number $T_p = 7$. The region of temperature increase is 20–1270°C and the rate of temperature increase is 20°C min^{-1}. The experiments were carried out in argon atmosphere. Parameters for MS are as follows: (1) The proposed mass numbers of each tested ion are O^+ (m/z 16),

channel 1; H_2O^+ (m/z 18), channel 2; SO^+ (m/z 48), channel 3; SO_2^+ (m/z 64), channel 4; channels 11 and 12 represent the partial pressure curve (P) of the vacuum and the temperature curve (T) in the system, respectively. (2) The mass scanning speed is 1 a.m.u. s^{-1}. (3) The time for mass filtering is 0.03 s. (4) The receiving device is a Faraday cup. (5) The system is under vacuum, 2.0×10^{-5} Torr.

RESULTS AND DISCUSSION

The process of thermal decomposition and mechanism for $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$

The TG–DTA curves and mass spectra of $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ are shown in Figs. 1 and 2, respectively.

There are three steps in the TG curve. The first step is from 67–403°C; its mass loss is 31.1% of the total. There is an endothermic peak at 228°C in the DTA curve. Channel 2 symbolizes the mass spectrum for H_2O^+ (m/z 18), and its peak appears at 163°C. Channel 1 symbolizes the mass spectrum for O^+ (m/z 16), and the first oxygen peak appears at 210°C. The results show that in the first stage of the thermal process for $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$, not only was a lot of water removed, but also that partial loss of oxygen occurred. The following reaction can be postulated:

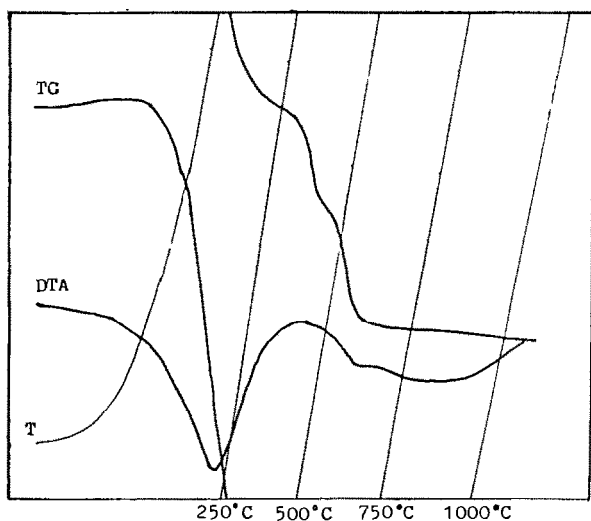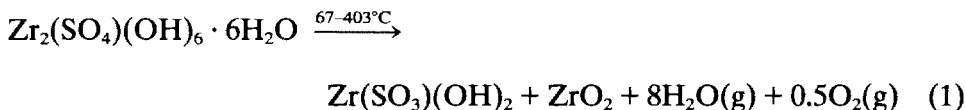$$Zr_2(SO_4)(OH)_6 \cdot 6H_2O \xrightarrow{67-403°C}$$

$$Zr(SO_3)(OH)_2 + ZrO_2 + 8H_2O(g) + 0.5O_2(g) \quad (1)$$

Fig. 1. TG and DTA curves for $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$.
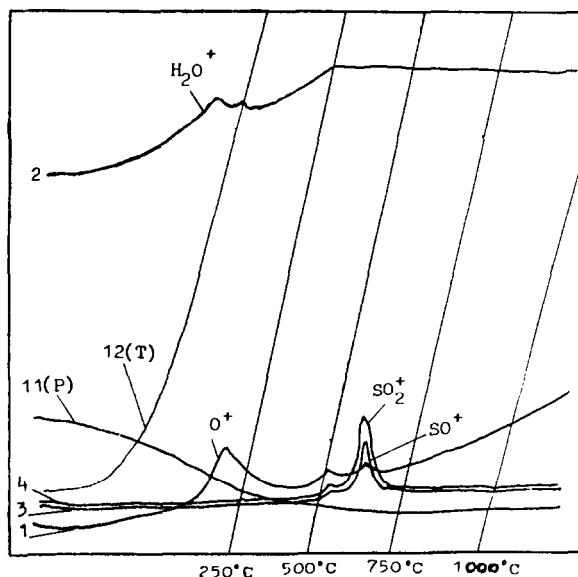
Fig. 2. Mass spectra for $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ obtained using the TG–DTA–MS technique.

The second step occurs from 403°C to 570°C, its mass loss is 6.3% of the total and there is an exothermic peak in the DTA curve at 510°C. In channel 2 of the mass spectrum, the H_2O^+ (m/z 18) curve moves up continually, and exceeds the full scale. In channel 1 (550°C), the second O^+ (m/z 16) peak appears and its height is about half of the first peak. In channel 3 (565°C), the first SO^+ (m/z 48) peak appears and in the fourth channel (565°C) the first SO_2^+ (m/z 64) peak also appears. These results show that in the second stage of thermal decomposition, $Zr_2(SO_3)(OH)_2$ continued to lose water, oxygen, and there was partial evaporation of SO and SO_2. The second stage of thermal decomposition could be

$$2Zr(SO_3)(OH)_2 \xrightarrow{403–565°C} O_2(g) + 2H_2O(g) + Zr(SO_3)_2 \qquad (2)$$
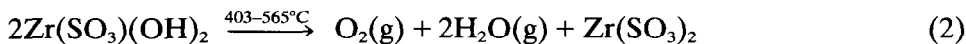
The small part of $Zr(SO_3)_2$ gave SO, SO_2 and O_2, by the following reactions:

$$Zr(SO_3)_2 \xrightarrow{565–570°C} ZrO_2 + 2SO_2(g) \qquad (3)$$

$$2SO_2 \xrightarrow{565–570°C} 2SO(g) + O_2(g) \qquad (4)$$

The third step of the TG curve occurs between 570 and 838°C, the mass loss is about 8.9% of the total. There is an endothermic peak in the DTA curve (663°C). In channel 1 of the mass spectrum (660°C), the third O^+ (m/z 16) peak appears, the height of which is less than the first peak. In channel 3

(660°C), the second SO^+ (m/z 48) peak with greater intensity appears. In channel 4 (660°C), the second SO_2^+ (m/z 64) peak with greater intensity also appears. These results show that in the third stage of thermal decomposition, a large part of $Zr(SO_3)_2$ begins to decompose further

$$Zr(SO_3)_2 \xrightarrow{570-838°C} ZrO_2 + 2SO_2(g) \tag{5}$$

$$2SO_2 \xrightarrow{570-838°C} 2SO(g) + O_2(g) \tag{6}$$

All the results of TG–DTA–MS show that the sintering temperature for precipited $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ should not be less than 800–850°C.

The TG–MS coupling technique

In order to certify the reliability of the TG–DTA–MA method for studing the thermal decomposition of $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ we used the TG–MS coupling technique to measure the same sample again. The SO^+ (m/z 48) is proposed for channel 7 and SO_2^+ (m/z 64) is proposed for channel 10. The TG curve and SO_2^+ and SO^+ mass spectra of $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ are shown in Figs. 3 and 4, respectively. Again there are three steps in the TG curve. The first step is from 68 to 402°C; the mass loss is about 30.4% of the total. The second step is from 402 to 568°C; the mass loss is about 7.3% of the total. The third step is from 568 to 840°C; the mass loss is about 8% of the total. Those results show that both TG
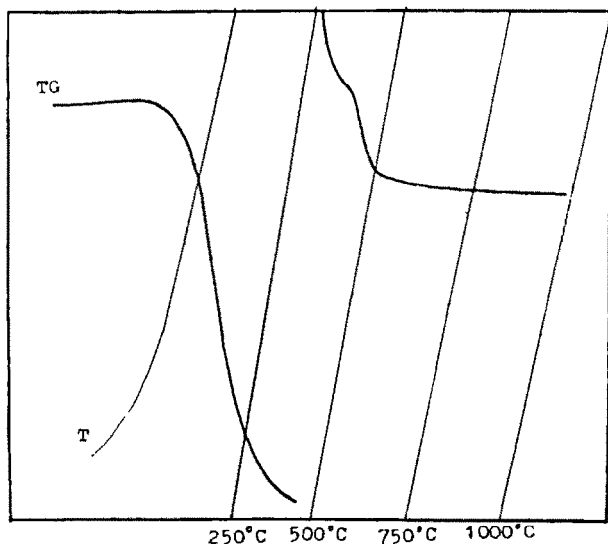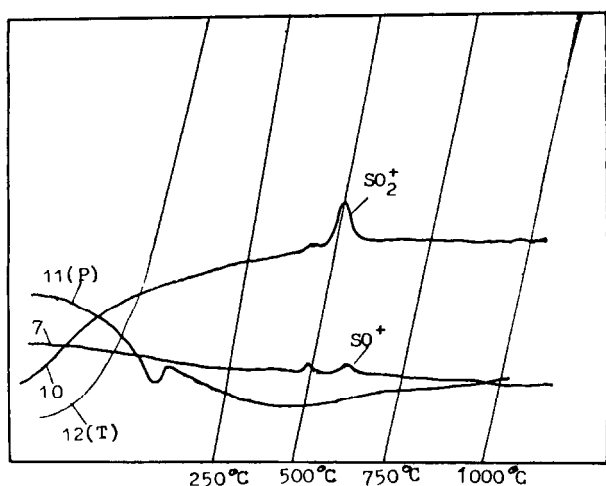

Fig. 3. TG curve for $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ from TG–MS.

Fig. 4. SO^{2+} and SO^+ mass spectra obtained by TG–MS.

measurements are in agreement, as are corresponding rates of mass loss for each step. The difference of less than 1% shows that the measurements can be repeated. In the spectra, only SO_2^+ (m/z 64) of channel 10 and SO^+ (m/z 48) of channel 7 are listed for comparision and analysis. In channel 10 the first small SO_2^+ peak appears at 562°C and the second more intense SO_2^+ peak appears at 662°C. In channel 7, the first small SO^+ peak appears at 562°C and the second SO^+ peak appears at 662°C. These results are the same as those from TG–DTA–MS. We can find the difference of peak height from SO^+ and SO_2^+ mass spectra. This is because there are many factors which can affect the intensity of an ion mass spectrum. Therefore, further investigation to quantify the mass spectrum is needed.

Problems in MS experiments

(1) Splashing of the ultrafine powder sample. When the system is vacuumed, the powder sample is often splashed due to its small particle size. In order to avoid the splashing of the powder, we put a thin Al_2O_3 cover on the crucible, and allowed the gas to escape from the centre of the cover.

(2) Vacuum of the system. The vacuum of the system is 2.0×10^{-5} Torr before the temperature is increased. With increasing temperature and time for vacuuming, in the process of mass scanning, the vacuum degree will be increased gradually. The 11th channel P represents the partial pressure curve of the vacuum. We can see that with increase of temperature, the curve P becomes flat and the vacuum starts to stabilize. In Fig. 4, the peak of curve P may be caused by the partial pressure of the gas evaporated from the reaction.
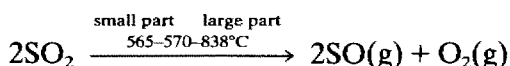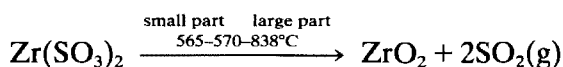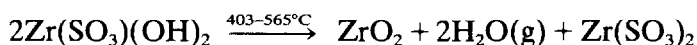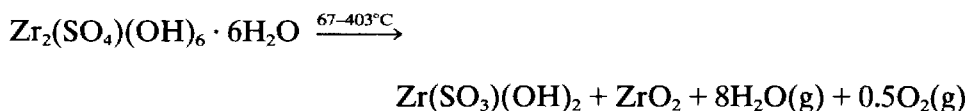
(3) The sensitivity of measurement. The sensitivity S of the instrument for measuring can be given in A Torr^{-1} from the formula

$$S = i^+/P \tag{7}$$

where i^+ is the intensity of ion current and P symbolizes the partial pressure of each gas. In the experiment the intensity of ion current for each gas should commence from the minimum scale, (which means from 10^{-11} A) and the magnifying factor is ×10, or ×1 (×100 is not usually used). If the recording is over the full scale, the proposed ion current intensity should be increased. For example, if the intensity of ion current is 10^{-9} A and the magnifying factor is ×10, the SO$^+$ (m/z 48) can be detected at 660°C as a weak peak, but it cannot be detected at 565°C. If the intensity of ion current is 10^{-11} A and the magnifying factor is ×1, the first peak of SO$^+$ (565°C) and the second stronger peak of SO$^+$ (660°C) can be detected in channel 7 at the same time. This shows that the ion current intensity can affect the sensitivity of measurement to a large degree.

CONCLUSION

The TG–DTA–MS study enables us to propose the following processes for the thermal decomposition of homogeneously precipitated $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$

$$Zr_2(SO_4)(OH)_6 \cdot 6H_2O \xrightarrow{67-403°C}$$

$$Zr(SO_3)(OH)_2 + ZrO_2 + 8H_2O(g) + 0.5O_2(g)$$

$$2Zr(SO_3)(OH)_2 \xrightarrow{403-565°C} ZrO_2 + 2H_2O(g) + Zr(SO_3)_2$$

$$Zr(SO_3)_2 \xrightarrow[565-570-838°C]{\text{small part \quad large part}} ZrO_2 + 2SO_2(g)$$

$$2SO_2 \xrightarrow[565-570-838°C]{\text{small part \quad large part}} 2SO(g) + O_2(g)$$

In order to prepare the ultrafine ZrO_2 powder, the sintering temperature for the homogeneously precipitated $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ should not be less than 800–850°C.

ACKNOWLEDGEMENTS

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