KINETICS OF THERMAL DECOMPOSITION OF AMMONIUM THIOTUNGSTATE OF GRANULARITY 62 ~ 72 μm IN N_2 ①

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ABSTRACT The thermal decomposition mechanism of ammonium thiotungstate of granularity 62~ 74 μm in N_2 was investigated by means of DTA and XRD methods. The thermal decomposition reaction occurs in three steps: $(NH_4)_2WS_4H_2O \rightarrow (NH_4)_2WS_4 + H_2O \rightarrow 2NH_3 + H_2 + 2S + WS_2 \rightarrow 2NH_3 + H_2S + S + WS_2$. The thermal decomposition activation energy and orders of $(NH_4)_2WS_4H_2O$ in granularity of 62~ 74 μm in three steps were calculated according to Kissinger, Freeman-Carrol, Coasts-Redfern methods from the DTA curves. The value of activation energy and the orders of reactions is 551.87 kJ/mol and 1.4 in the first step, 125.65 kJ/mol and 0.52 in the second step as well as 277.69 kJ/mol and 0.8 in the third step respectively. The reaction rate in every step has also been given.

Key words $(NH_4)_2WS_4 \cdot H_2O$ thermal decomposition kinetics N_2 DTA XRD

1 INTRODUCTION

Ammonium thiotungstate is used as a raw material for preparing WS_2[1,2] by thermal decomposition method, its size has noticeable effect on the kinetics of the reaction. In this thesis, the kinetics of thermal decomposition of ammonium thiotungstate of 62~ 74 μm in granularity has been investigated by means of DTA and XRD methods, thus it would be useful to determine the technique parameters in preparing WS_2.

2 EXPERIMENTAL

The TAS-100 type DTA analysis instrument made in Japan was used for the experiment. The full scale of amplifier is ±250 μV. The samples used in the present experiments were confirmed to be pure ammonium thiotungstate by XRD and chemistry analysis, its granularity is 62~ 74 μm. A sample of 10.0 ± 0.1 mg was placed in a platinum boat, over which a flow capacity of 25~ 30 ml/min of N_2 was passed. The heating rate was 10 ℃/min.

The ammonium thiotungstate was decomposed in a constant thermal state for 20 min at 190, 290 and 410 ℃, which are selected from the end of the peak on the DTA curves respectively; then XRD analysis was carried out.

SiC bar furnace was used to heat the sample and JWK703 type controlling temperature instrument was used to control the temperature of the furnace. The heat couple for controlling temperature is made of PtRh-Pt, the heat couple for detecting temperature is made of NiCr-Ni-Si.

3 RESULTS

Fig. 1 illustrated that there are three peaks appeared during the thermal decomposition of ammonium thiotungstate. The first and the second peak are endothermic peaks, the third peak is exothermic peak. The three peaks were processed according to Freeman-Carrol (FC) and Coasts-Redfern(CR) method, and the activation energy and the order of each peak were

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Fig. 1 DTA curve of $(NH_4)_2WS_4 \cdot H_2O$

calculated.

The general equation of FC method could be expressed as[3]

$$\frac{\Delta \ln(\mathrm{d}a/\mathrm{d}T)}{\Delta \ln(1-a)} = -\frac{E}{R}\left[\frac{\Delta(1/T)}{\Delta \ln(1-a)}\right] + n \quad (1)$$

where a is the variation rate of reaction, E is the apparent activation energy of reaction, n is the reaction order, T is the absolute temperature, R is the gas constant. The plot of $\Delta \ln(\mathrm{d}a/\mathrm{d}T)/\Delta \ln(1-a)$ *vs* $\Delta(1/T)/\Delta \ln(1-a)$ equation is a straight line, the activation energy could be obtained from the slope $-E/R$ of the plot; the intercept is reaction order n, a can be obtained by integrating the area blow DTA curves.

CR method can be expressed as[4]

$$\ln\left[\frac{1-(1-a)^{1-n}}{T^2(1-n)}\right] = \ln\frac{AR}{\Phi E}\left[1-\frac{2RT}{E}\right] - \frac{E}{RT} \quad (2)$$

where A is frequency factor, Φ is the heating rate. The relation between $\ln[1-(1-a)^{1-n}/T^2(1-n)]$ and $1/T$ is linear. The activation energy E could be calculated from the slope $-E/R$. The E obtained by CR method is very accurate as long as n is supposed correctly.

In order to get the accurate kinetics parameters, we determine the activation energy E and order n roughly by FC method first, and verify the order n by Kissinger method(KG), then calculate the activation E accurately by CR method according to the verified order n. From $\mathrm{d}a/\mathrm{d}T = (A/\Phi)\exp(-E/RT)$, A can be calculated. Then according to the equation $k = A\exp(-E/RT)$, reaction rate constant k can be gained eventually. The reaction rate can be expressed as $\mathrm{d}a/\mathrm{d}t = k(1-a)^n$, here t is time. The results are shown in Table 1, which shows that the activation energy values and orders of the three peaks calculated by KG, FC and CR methods are close to each other.

4 DISCUSSION

4.1 *The Mechanism of Thermal Decomposition of Ammonium Thiotungstate in Nitrogen Gas*

Fig. 2(a) is the XRD pattern of the sample maintained at 190 ℃ for 20 min, it shows that the sample is a highly pure ammonium thiotungstate, its first endothermic peak appeared in DTA curves at 146~ 190 ℃ is attributed to the endotherm during dehydrating crystal water. Because the number of crystal water calculated by weight loss method is 1.0 so that the molecular formula of ammonium thiotungstate should be $(NH_4)_2WS_4 \cdot H_2O$. Fig. 2(b) shows that the

Table 1 The activation energy E, reaction order n and linear coefficient r of each peak according to KG, FC, CR methods

parameter	the 1st peak of			the 2nd peak of			the 3rd peak of		
	KG	FC	CR	KG	FC	CR	KG	FC	CR
E		560.32	551.87		119.82	125.65		283.64	277.69
n	1.39	1.42	1.40	0.52	0.53	0.52	0.9	0.70	0.80
r		−0.974	−0.990		−0.990	−0.999		−0.934	−0.990

sample was decomposed into WS_2 completely, its reaction equation should be as following:

$$(NH_4)_2WS_4(s) = 2NH_3(g) + H_2(g) + 2S(s) + WS_2(s) \quad (3)$$

The peaks of WS_2 in XRD pattern are wide and smooth, it means the crystal of WS_2 arranged irregularly. Fig. 2(c) is the XRD pattern of the sample maintained at 410 ℃ for 20 min, it shows that the product of the sample is still WS_2. The narrow and steep peaks indicate that the arrangement of WS_2 crystal is more regular than that of Figs. 3(a) and 3(b). The transformation of phases didn't occur at 290 ℃ to 410 ℃. The exothermic peak in DTA curves which is narrow and steep indicates that the rate of reaction is rapid and the reaction can finish in short times, the exothermic peak is caused by reaction (2), that is,

$$H_{2(g)} + S_{(s)} = H_2S_{(g)} \quad (4)$$

where H_2S was synthesized with H_2 and S which decomposed according to reaction (1). This can be testified by the result of DTA analysis of S shown in Fig. 3. The DTA curve of S shows that the peak is very similar to the exothermic peak of $(NH_4)_2WS_4 \cdot H_2O$ not only in shape but also in range of the temperature at which the peak appeared, thus the exothermic peak of $(NH_4)_2WS_4 \cdot H_2O$ is proved to be caused by reaction (2). So the thermal decomposition process of $(NH_4)_2WS_4$ can be expressed as three steps (stages), that is $(NH_4)_2WS_4H_2O \rightarrow (NH_4)_2WS_4 + H_2O \rightarrow 2NH_3 + H_2 + 2S + WS_2 \rightarrow 2NH_3 + H_2S + S + WS_2$

4.2 *Determination of Kinetics Parameters of Thermal Decomposition of* $(NH_4)_2WS_4 \cdot H_2O$

As shown in Table 1, The values of E, n and r of the first peak calculated by FC method are 560.32 kJ/mol, 1.42 and 0.974, respectively. On the other hand, n obtained by KG method is 1.39, which illustrates $n = 1.42$ is accurate. Considering the average value of n gained by KG, FC and CR methods is 1.40, let $n = 1.40$, then the accurate E can be calculated eventually by CR method, and its corresponding r is − 0.990. The frequency factor A can also

Fig. 2 XRD patterns of Phase development of $(NH_4)_2WS_4 \cdot H_2O$ when heated in N_2

(a) —190 ℃; (b) —290 ℃; (c) —410 ℃

Fig. 3 DTA curve of S

be obtained on the basis of n and E, and then the reaction rate constant k can be determined as 0.15. So the reaction rate equation of the first peak can be expressed finally as:

$$\frac{da}{dt} = 0.15(1-a)^{1.4} \quad (5)$$

The same is true for the second peak, the ultimate accurate values of it's E, n, r, k are 125.65 kJ/mol, 0.52, -0.999, 0.34 respectively; the reaction rate equation can be expressed as

$$\frac{da}{dt} = 0.34(1-a)^{0.52} \quad (6)$$

The same is true for the third peak, the ultimate accurate values of it's E, n, r, k are 277.69 kJ/mol, 0.8, -0.990, 0.61 respectively; the reaction rate equation can be expressed as

$$\frac{da}{dt} = 0.61(1-a)^{0.8} \quad (7)$$

DTA curves show that the initial temperature of the three peaks are 146, 190 and 360 ℃ respectively; the ultimate temperature are 170, 290 and 382 ℃ respectively.

WS_2 has been produced when the second peak ended. So, if we want to prepare WS_2 by thermal decomposition of $(NH_4)_2WS_4 \cdot H_2O$, the controlling temperature should be at about 300 ℃; if better crystal of WS_2 is needed, the temperature should be elevated properly.

5 CONCLUSIONS

(1) The apparent activation energy of the three peaks in process of thermal decomposition of $(NH_4)_2WS_4H_2O$ are 551.87, 125.65, 277.69 kJ/mol respectively; the corresponding orders are 1.4, 0.52 and 0.8 respectively; the reaction rate equations are $da/dt = 0.15(1-a)^{1.4}$, $dz/dt = 0.34(1-a)^{0.52}$ and $da/dt = 0.61(1-a)^{0.8}$ respectively.

(2) The initial and ultimate temperatures of the thermal decomposition of $(NH_4)_2WS_4 \cdot H_2O$ in N_2 are about 146 ℃ and 390 ℃ respectively.

(3) The thermal decomposition of $(NH_4)_2WS_4 \cdot H_2O$ occurs in three stages: $(NH_4)_2WS_4 \cdot H_2O \rightarrow (NH_4)_2WS_4 + H_2O \rightarrow NH_3 + H_2 + 2S + WS_2 \rightarrow 2NH_3 + H_2S + S + WS_2$

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