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Kinetics of the thermal decomposition of intercalation compounds during exfoliation

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Abstract: The phase transformations and thermal decomposition of the following graphite intercalation compounds (GICs), HNO_3-CH_3COOH-GIC, H_2SO_4-GIC and H_2SO_4-CH_3COOH-GIC, were measured by an FTIR-associated TG apparatus. Using Kissinger and Ozawa principles, the kinetic parameters of some typical exfoliation reactions were evaluated and the thermal decomposition mechanism of the exfoliation process was determined. When the heating rate was in the range of 20–80 ℃/min, the activation energies of the exfoliation reactions were all less than 120 kJ/mol.

Keywords: Exfoliation; Thermal analysis; Kinetics; Intercalation

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1 Introduction

Expanded graphite is produced from graphite intercalation compounds that are subjected to a thermal shock[1]. As the intercalated species is rapidly volatilized, a significant expansion of the material along the crystallographic c-axis occurs[2,3]. When expanded graphite is used as fire extinguishers, electromagnetic shielding materials, and sealed gaskets, expanded volume and rate will directly influence its performance in these applications[4-7]. Whether exfoliation might occur, depends on the raw materials, heating rate, particle size, and intercalated species[8-10]. Studies indicated that intercalated graphite could not expand with frame heating or electric cooker heating when its size was smaller than 88 μm[11,12]. With laser heating method with a heating rate as high as 10^4℃/s, the exfoliation of intercalated graphite is remarkable. Study on kinetics and phase transformation in the expanding process is very important for obtaining information on structural control and properties of expanded graphite. However, because volume expansions are usually higher than 200 g/mL and sample pool is very limited, it is difficult to carry out thermal analysis of expanded graphite using DSC and TG. Up to date, only few reports have been published on thermal analysis of expanded graphite.

In this article, fundamentals of chemical dynamics about exfoliation of graphite intercalation compounds are discussed. The phase transformation and thermal decomposition were measured in situ with a FTIR-associated TG apparatus. Moreover, according to Kissinger and Ozawa principles, activation energy and exponent factor of exfoliation reaction were obtained from data tested under different heating rates.

2 Experimetal

2.1 Apparatus and testing conditions

Thermogravimetric apparatus (Pyris-TGA, Perkin-Elmer Corp.) with a sensitivity of 10^{-8} g was employed to measure the change in thermo-flux by no more than microwatt in one minute.

Fourier transform infrared spectrometer (FTIR, Spectrum GX, Perkin-Elmer Corp.) with resolution of 0.1 cm^{-1} and signal-to-noise ratio over 9 000∶1 was employed to analyze the infrared spectra of the decomposed products collected, from which the decomposed products and their concentrations were obtained and decomposition mechanism was deduced.

In this study, phase transformation and thermal decomposition of three expandable graphite intercalation compounds (H_2SO_4-GIC, HNO_3-CH_3COOH-GIC, and H_2SO_4-CH_3COOH-GIC[13-15]) were in situ measured by the FTIR-associated TG apparatus. The mass of each sample was lower than 7 mg under nitrogen atmosphere. Experimental temperature was changed from 25 ℃ to 600 ℃ with different heating rates of 20, 40, 60, and 80 ℃/min.

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2.2 Analysis theory

The exfoliation process is denoted as the formula:

$$A(s) \xrightarrow{\text{heated}} B(s) + C(g).$$

The kinetics equation of reactions can be calculated with differential and integral forms. Kissinger arithmetic belongs to differential method [16]. According to Arrhenius law, reaction rate can be written as:

$$\frac{d\alpha}{dt} = A\exp(-E/RT)f(\alpha), \quad (1)$$

where, α – reacted proportion after time, t;

A – apparent exponential factor;

E – apparent activation energy, kJ/mol;

R – gas constant, $R = 8.314$ J/mol · K;

$f(\alpha)$ – differential form of dynamics mechanism function.

Suppose experimental temperature is raised steadily, substituting $f(\alpha) = (1-\alpha)^n$ into equation (1) and by differential operation on either sides, equation (2) is obtained:

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt}\left[\frac{E\left(\frac{dT}{dt}\right)}{RT^2} - An(1-\alpha)^{n-1}\exp(-E/RT)\right]. \quad (2)$$

When temperature of reaction reach the highest temperature (T_P), $\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = 0$.

Suppose $n(1-\alpha)^{n-1}e^{-E/RT_P}$ is independent of linear heating rate β and it is approximately equal to 1 in Kissinger equation [17], equation (2) is rewritten as:

$$\frac{E\beta}{RT_P^2} = Ae^{-E/RT_P}. \quad (3)$$

Kissinger equation is obtained from logarithmic operation on either sides of equation (3):

$$\ln\left[\frac{\beta_i}{T_{pi}^2}\right] = \ln\frac{A_K R}{E_K} - \frac{E_K}{R}\frac{1}{T_{pi}},$$
$$i,k = 1,2,3,4 \text{ (or 5 and 6)}. \quad (4)$$

A line can be drawn when X-axis is $\frac{1}{T_{pi}}$ and Y-axis is $\ln\left[\frac{\beta_i}{T_{pi}^2}\right]$. The apparent activation energy E_k and exponent factor A_k can be obtained from slope and intercept of this line.

Ozawa adopted integral operation. $G(\alpha)$ is represented by dynamics mechanism function and it can be related to $f(\alpha)$ as:

$$f(\alpha) = \frac{1}{G'(\alpha)} = \frac{1}{d[G'(\alpha)]/d\alpha}. \quad (5)$$

Through approximate calculation, it is found that heating rate β, exponent factor A, and apparent activation energy E obeys the following equation:

$$\ln\beta = \lg\frac{AE}{RG(\alpha)} - 2.315 - 0.4567\frac{E}{RT}. \quad (6)$$

Because the quantity that reacted is close to equivalency at peak temperature regardless of different heating rates, accurate solution of apparent activation energy is determined by Ozawa' law, which is based on the linear relationship between $\lg\beta$ and T^{-1}.

3 Results and discussion

Expandable graphite is a nonstoichiometric compound and its chemical structure cannot be determined. From Fig. 1, TG curves of H_2SO_4-GICs are similar at different heating rates ranging from 40 to 80 ℃/min. When H_2SO_4-GICs were heated, their TG curves started to decline slowly, indicating a gradual weight loss. From DTG curve, thermal decomposition of H_2SO_4-GICs is divided into two steps. A small dehydration peak is located at temperature between 110 and 140 ℃ with a weight loss of 1.7 %–2.0 %. A significant weight loss began from around 250 ℃, where intercalated species decomposed to release radicals of SO_4^{2-} and H_2SO_4. The total weight loss is 21 %–8 % below 500 ℃.

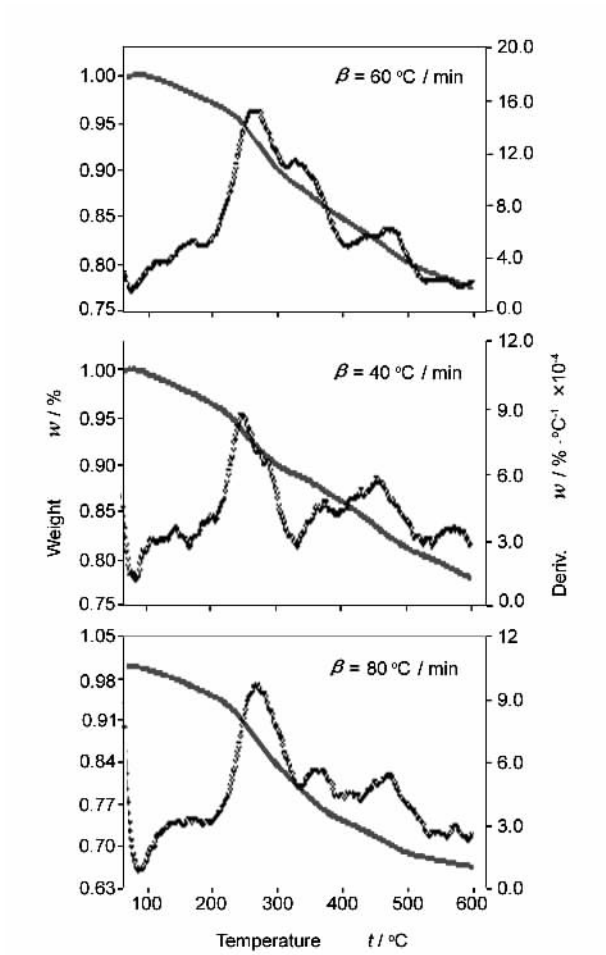

Fig. 1 TG and DTG curves of H_2SO_4-GIC

To discuss exfoliation process of ternary graphite intercalation compounds, HNO_3-CH_3COOH-GIC is regarded as research object to analyze thermal decomposition of two guest species. Fig. 2 shows TG and DTG curves of HNO_3-CH_3COOH-GIC with a heating rate of 60 ℃/min. The weight loss of HNO_3-CH_3COOH-GIC mainly occurs between 220 and 350 ℃, and the second decomposition peak is more evident.

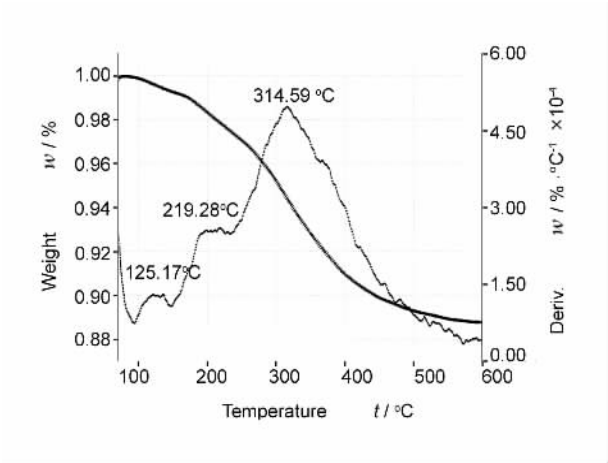

Fig. 2　TG curve of HNO_3-CH_3COOH-GIC with a heating rate of 60 ℃/min

On the basis of the reaction equations listed in references[6-8], HNO_3-GIC, H_2SO_4-CH_3COOH-GIC, and HNO_3-CH_3COOH-GIC can be expressed as: $[\ graphite^+ \cdot HNO_3 \cdot NO_3^-\ ]_n$, $[\ graphite^+ \cdot SO_4^{2-} \cdot CH_3COOH\ ]_n$, and $[\ graphite^+ \cdot NO_3^- \cdot CH_3COOH\ ]_n$. In this study, nitric acid radical ion and acetic acid molecule in HNO_3-CH_3COOH-GIC are also contained in HNO_3-GIC and H_2SO_4-CH_3COOH-GIC. So, thermal analysis of H_2SO_4-CH_3COOH-GIC and HNO_3-GIC were tested by the same heating rate as shown in Fig. 3.

Compared with the decomposition of H_2SO_4-GIC as demonstrated in Fig. 1, the first decomposition peak of H_2SO_4-CH_3COOH-GIC as observed in Fig. 3(a) corresponds to dehydration, and two smaller peaks are identified to correspond to the decomposition of SO_4^{2-} around 210 ℃. The highest weight loss is observed between 300 ℃ and 320 ℃, which is not found in TG curve of H_2SO_4-GIC. As seen from material components to ternary expandable graphite that are synthesized, the content of CH_3COOH is more than that of HNO_3 or H_2SO_4. It could be deduced that proportion of acetic acid molecule that is intercalated into graphite is more than the intercalation of other functional groups. Hereby, the maximal weight loss should have occurred due to the release of acetic acid, which is seen in TG curves of HNO_3-CH_3COOH-GIC and H_2SO_4-CH_3COOH-GIC. As observed in Fig. 3(b), the first weight loss is attributed to the dehydration, and the subsequent to the release of NO_3^-, HNO_3. On the basis of the above-mentioned information, it could be predicted that weight loss at 200 ℃ corresponds to the loss of nitric acid radical ion, and the strongest peak at 350 ℃ corresponds to the decomposition of HNO_3. These results are also verified by infrared spectrograms of gas products.

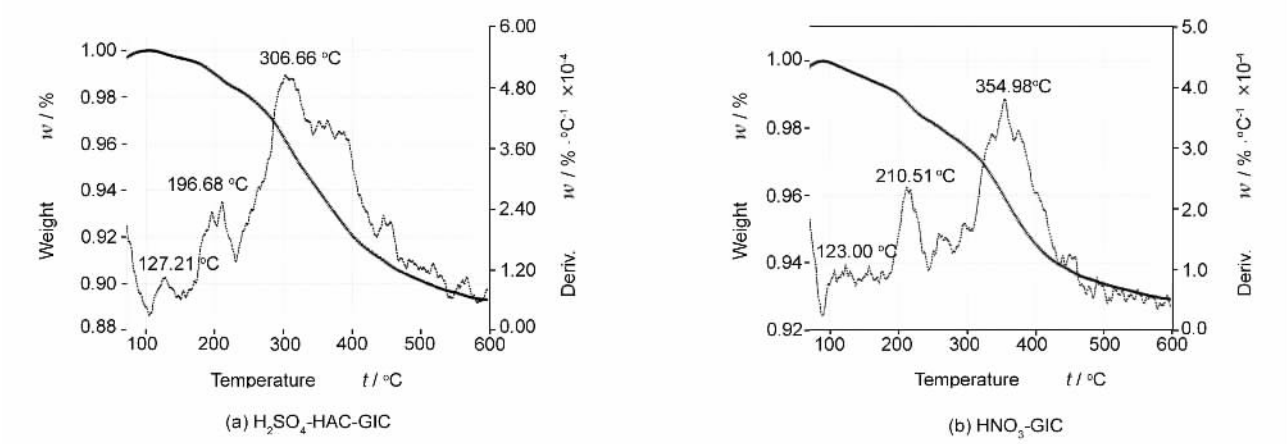

Fig. 3　TG curve s of HNO_3-GIC and H_2SO_4-CH_3COOH-GIC with a heating rate of 60 ℃/min

Fig. 4 shows FTIR spectra of decomposition of HNO_3-CH_3COOH-GIC heated to different temperatures. For HNO_3-CH_3COOH-GIC, there are two remarkable absorption peaks at 1 430 and 840 cm^{-1} when expandable GIC is heated to 220 ℃, which are characteristic peaks of nitric acid radical[18]. It demonstrates that the nitric acid radical ion escapes from graphite layers at ca. 220 ℃. The O—H band of carboxyl stretching vibration, C═O band stretching vibration, and O—H band bending vibration are often used to identify carboxyl acid using infrared spectroscopy. A sharp peak corresponding to decomposition

spectra arises at 1 710 cm^{-1} when the temperature of thermal analysis reaches 320 ℃. Furthermore, vibration frequencies of C—H band, including asymmetrical and symmetrical bending, are located around 1 470 and 1 380 cm^{-1}, of which the latter is used to identify methyl structure. When $—CH_3$ is linked to other atoms, the peak will shift due to the change of bending constant. The stronger the electronegativity of the adjoining group is, the higher is the shift of wavenumber of the peak located at 1 380 cm^{-1}[19]. As observed in Fig. 4, there is an absorption peak of the decomposition spectrum at 1 410 ℃. This results from the interaction of methyl and carboxyl groups. So, it is concluded that acetic acid molecule escapes from graphite layers when expandable graphite is heated to 320 ℃, which is consistent with results from thermal analysis.

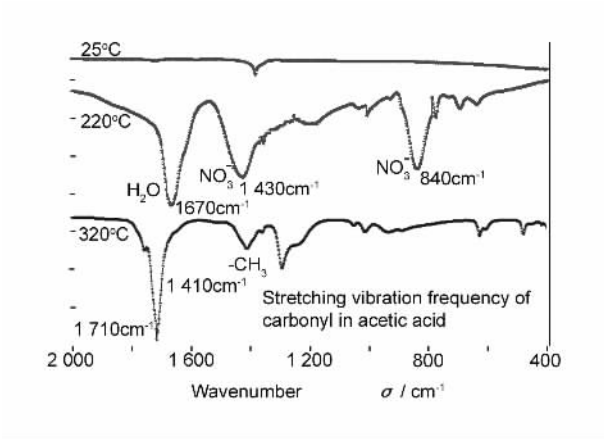

Fig. 4 FTIR spectra of decomposition of HNO_3-CH_3COOH-GIC heated to different temperatures

According to TG curves of H_2SO_4-GIC (Fig. 1) and HNO_3 - CH_3COOH - GIC (Fig. 5) at different heating rates, the decomposition process and dynamical parameters are calculated according to Kissinger and Ozawa principles, as summarized in Tables 1 and 2.

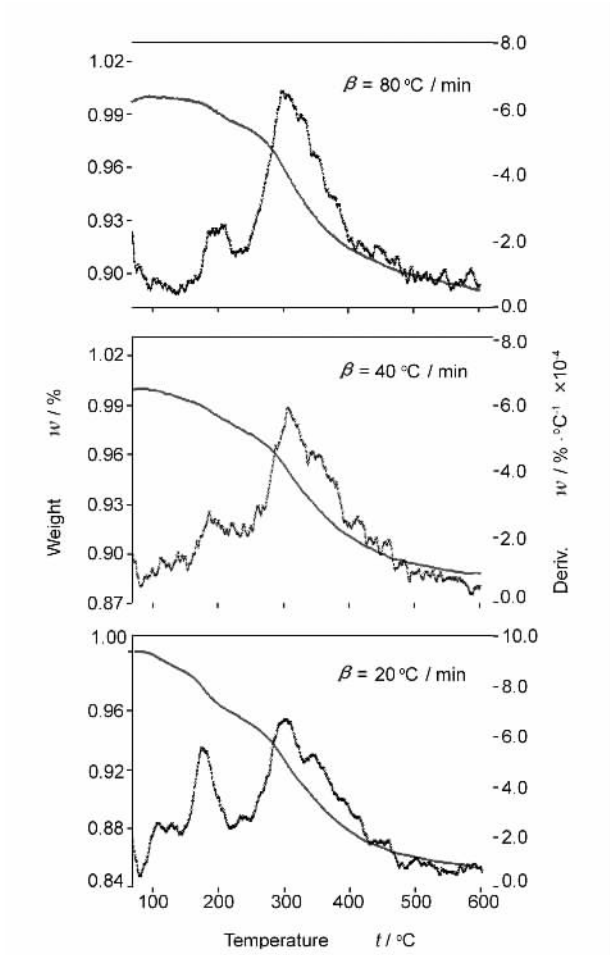

Fig. 5 TG curves of HNO_3-CH_3COOH-GIC at different heating rates

Table 1 Thermal decomposition of H_2SO_4-GIC and kinetics parameters

Peak	Peak temperature t/℃	Decomposition property and products	Kissinger law E/kJ · mol^{-1}	lg$A$	Ozawa law E/kJ · mol^{-1}
1st decomposition	247.4	Water and HSO_4^- escaping from graphite layers	90.29	7.49	94.22
2nd decomposition	333.2	Sulfuric acid molecule escaping from expandable graphite			
3rd decomposition	456.9	Decomposition of residual compounds			

Table 2 Thermal decomposition of HNO_3-CH_3COOH-GIC and kinetics parameters

Peak	Peak temperature t/℃	Decomposition property and products	Kissinger law E/kJ · mol^{-1}	lg$A$	Ozawa law E/kJ · mol^{-1}
1st decomposition	208.4	Water and nitric acid radical ion escaping from graphite layers	91.23	8.73	94.14
2nd decomposition	315.6	Acetic acid molecule escaping from expandable graphite	114.80	8.94	118.2

4 Conclusions

In summary, the phase change and decomposition process of HNO_3-CH_3COOH-GIC, H_2SO_4-CH_3COOH-GIC, HNO_3-GIC, and H_2SO_4-GIC were investigated by thermal analysis. By comparing TG curves of GICs, which contain similar groups, it was found that intercalated molecules, ions, and atoms escape from graphite layers. The absorbency spectra of decomposition products were in situ measured by the FTIR-associated TG apparatus. According to Kissinger and Ozawa principles, kinetics parameters of the exfoliation reactions are calculated. The main conclusions are as follows:

(1) NO_3^- and SO_4^{2-} escape from GIC at 200 ℃–210 ℃, $HSO4^-$ and H_2SO_4 escape at 240 ℃–250 ℃, and acetic acid molecule escapes from graphite layers at ca. 320 ℃

(2) On the basis of the thermal analysis theory, the activation energy of the exfoliation reactions are evaluated, and it was found that they are all lower than 120 kJ/mol.

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插层化合物在膨化过程中的热分解动力学

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摘 要： 采用红外傅立叶变换光谱仪与热重分析仪联动装置在线检测 HNO_3-CH_3COOH-GIC、H_2SO_4-GIC 及 H_2SO_4-CH_3COOH-GIC 等插层石墨的相变及热分解过程，同时通过快速扫描得到相应时间段内分解产物的红外光谱，并运用 Kissinger-Ozawa 原理计算了几种典型膨化反应的动力学参数。研究结果揭示了膨化过程的热分解机理，当升温速率在 20 ℃/min ~ 80 ℃/min 范围时，由实验数据计算出膨化反应表观活化能不大于 120 kJ/mol。

关键词： 膨化；热分解；动力学；插层

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