Kinetic analysis of the non-isothermal decomposition of carbon monofluoride

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ABSTRACT

The kinetic mechanism of carbon monofluoride ($(CF)_n$) decomposition and the products generated in this reaction were studied. Given the non-isothermal differential scanning calorimetry and thermogravimetric analysis curves, nucleation mechanisms for $(CF)_n$ decomposition were proposed using model-free method. According to the extent of conversion of the reaction, the kinetic process could be described by the two-dimensional Avrami–Erofeev equation $f(\alpha) = 2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$, one-dimensional Avrami–Erofeev equation $f(\alpha) = 1-\alpha$ and two-parameter Šesták–Berggren equation $f(\alpha) = \alpha^m(1-\alpha)^n$ ($m = -0.294$, $n = 1.428$), respectively. Due to the heterogeneity of the thermal decomposition process of $(CF)_n$, the apparent activation energy of the thermal decomposition varied with the extent of conversion. In addition, the final decomposition products of $(CF)_n$ were confirmed to be gaseous CF_4 and C_2F_6, and amorphous carbon via Raman spectroscopy and gas chromatography, and the volume ratio of CF_4/C_2F_6 was found to be approximately 12.

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1. Introduction

Fluorinated carbon materials are an area of intense research because of their important practical applications as lubricants, water repellants, and battery electrode. Typically, graphite fluoride ($(CF_x)_n$, $0.5 \leq x < 1.2$) is synthesized by direct reaction of fluorine gas with graphite at 573–873 K [1–4] or via electrolysis in fluoride melts using a carbonaceous anode [5–9]. Graphite fluoride includes dicarbon monofluoride and carbon monofluoride, of which the layer structures are very different. Dicarbon monofluoride ($(C_2F)_n$ ($(CF_x)_n$ with $0.5 \leq x < 0.6$) is a double-decker monolayer, of which every pair of adjacent carbon sheets are bound together by C—C bonds, while carbon monofluoride ($(CF)_n$ ($(CF_x)_n$ with $0.6 < x < 1.2$) has a structure composed of chair-type cyclohexane rings axially bound to fluorine atoms [10–12]. The diffraction lines of XRD pattern are 9.02, 4.46, 2.16, and 1.27 Å for $(C_2F)_n$ and 5.85, 2.90, 2.22, and 1.29 Å for $(CF)_n$ [10–12]. Obviously, the graphite fluoride should not be expected for a homogeneous substance but a class of similar compounds owing

to it uncertain values of x and n, even if it can be expressed by a constant stoichiometric F/C ratio.

On the thermal decomposition of $(CF)_n$, some reported investigations had been done in detailed by means of isothermal-gravimetric or gravimetric analysis under 573–943 K [13–17]. The samples used in those investigations had a wide range of the stoichiometric F/C ratio from 0.61 to 1.12. In those investigations, CF_4 and C_2F_6 were found to be the most prominent gas-phase products of the decomposition, but some other perfluorocarbons, such as CF_2, C_2F_4 and C_3F_8, were also reported by different authors [13–16]. Thus, the thermal decomposition reaction of $(CF)_n$ could be described by a comprehensive equation [16]:

$$(CF)_n \rightarrow \text{amorphous carbon} + C_2F_6 + CF_4 + \text{other perfluorocarbons}$$

(1)
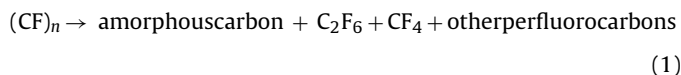
Moreover, Ruff et al. found that decomposition of $(CF)_n$ started very slowly around 573 K and was most violent at 773–873 K [13]. The average F/C ratio of the gases was 2.81 for a gradual decomposition, while that was 3.7 for an explosive decomposition. Kamarchik and Margrave reported the apparent average F/C ratio for all the gas-phase species was about 2.0, as led the authors to suggest the decomposition was occurring at the edges of $(CF)_n$

crystallites and propose a two-dimensional growth mechanism for the product–reactant interface [15]. Watanabe et al. suggested that the thermal decomposition was initiated at a point on a grain boundary or at CF_2 or CF_3 group on the surface of a particle and the nucleus of carbon spread along two-dimensional but anisotropic [16,17]. Meanwhile, they described the rate equation for the decomposition of $(CF)_n$ using the following two equations [17]:

$$\alpha = (kt)^n \tag{2}$$

or

$$-\ln(1-\alpha) = (kt)^n \tag{3}$$

where α is the decomposed fraction, k is the linear rate constant of nucleus growth, t is time, and n is the dimension of nucleus growth. And the suggested value of n was 1 or 2. Those mechanism equations were related with the extent of conversion of the decomposition [17].

The major goal of the present work was the investigation of kinetic properties of the $(CF)_n$ non-isothermal decomposition processes via differential scanning calorimetry and the products of $(CF)_n$ decomposition. Based on the obtained experimental data, the kinetic mechanism and other kinetic parameters could be established via model-free kinetics (MFK) method. The decomposed products were also identified by gas chromatography (GC) and Raman spectrometry (RS).

1.1. Model-free kinetics (MFK) method

The cornerstone of the model-free approach to kinetic analysis is the use of the isoconversional principle. It states that at a constant extent of conversion the reaction rate is only a function of the temperature [18].

The kinetic model equation combined with the Arrhenius equation is almost universally described as:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \tag{4}$$

where $\alpha = \Delta H(t)/\Delta H$ is the extent of conversion, $\Delta H(t)$ the partial heat of reaction at any time t, ΔH the total heat of reaction, $f(\alpha)$ the function of kinetic mechanism, T (K) the absolute temperature, A (s^{-1}) the pre-exponential factor, E_α (kJ mol^{-1}) the apparent activation energy and R (kJ mol^{-1} K^{-1}) the universal gas constant. For dynamic data obtained at a constant heating rate, $\beta = dT/dt$, this new term is inserted in Eq. (4) which can be simplified as:

$$\beta \frac{d\alpha}{dT} = A \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \tag{5}$$

The integral isoconversional methods are based on the integration of Eq. (5):

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_\alpha}{RT}\right) dT = \frac{AE_\alpha}{\beta R} p(x) \tag{6}$$

where $p(x)$ ($x = E_\alpha/RT$) is the so-called temperature or exponential integral, which cannot be exactly calculated [19,20].

Taking logarithms in Eq. (6), then a method developed by Flynn and Wall [21] and Ozawa [22] using Doyle's approximation [23] (FWO) is described as:

$$\ln \beta = \ln \frac{AE_\alpha}{Rg(\alpha)} - 5.331 - 1.052 \frac{E_\alpha}{RT} \tag{7}$$

For a constant conversion α, a plot of $\ln \beta$ versus $1/T$, from the data at the different heating rates, leads to a straight line whose slope provides E_α calculation.

In the Kissinger–Akahira–Sunose method (KAS) [24,25], the expression $p(x)$ is expressed using the Coats–Redfern
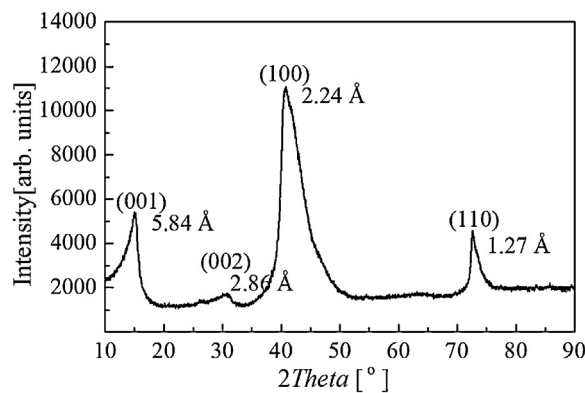

Fig. 1. The X-ray diffraction pattern of the carbon monofluoride ($(CF)_n$) sample.

approximation [26]. Then taking logarithms in Eq. (6), the KAS equation is obtained as:

$$\ln \frac{\beta}{T^2} = \ln \frac{AE_\alpha}{Rg(\alpha)} - \frac{E_\alpha}{RT} \tag{8}$$

A plot of $\ln(\beta/T^2)$ versus $1/T$ for a constant conversion gives the E_α at that conversion.

The differential isoconversional method suggested by Friedman (FR) [27] is based on Eq. (5) that leads to:

$$\ln \left[\beta_i \left(\frac{d\alpha}{dT}\right)_i\right] = \ln[Af(\alpha)] - \frac{E_\alpha}{RT_\alpha} \tag{9}$$

where T_α is the temperature at which the system approaches a conversion α, and β_i is the heating rate. Subscript i is the ordinal number of an experiment performed at a given heating rate. For a constant α, a plot of $\ln[\beta_i(d\alpha/dT)]$ versus $1/T_\alpha$ should be a straight line whose slope allows the calculation of the apparent activation energy E_α. The differential isoconversional method is potentially more accurate than the integral methods because it does not include any mathematical approximations [28–30], therefore, we more like to process the data using differential isoconversional method in the present work.

2. Experimental

2.1. The $(CF)_n$ sample

The graphite fluoride sample (purity >99.5%) was provided by the Research Center of Shanghai CarFluor Chemicals Co., Ltd. (Shanghai, China). The fluorine content of the graphite fluoride was 56 wt%, which suggested a stoichiometric F/C ratio of 0.8. The sample was gray color, and had an average particle size of 4–6 μm. We detected the sample using X-ray diffraction and found all the diffraction lines of the graphite fluoride sample were 5.84, 2.86, 2.24, and 1.27 Å (shown in Fig. 1). From the characterization approach, the X-ray diffraction (XRD) analysis of the investigated graphite fluoride sample confirmed that the carbon monofluoride ($(CF)_n$) is the full crystalline phase present.

2.2. Thermal measurements

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on NETZSCH simultaneous thermal analyzer (STA 449 C, Germany) under dynamic nitrogen atmosphere (purity 99.999%, 20 ml/min) with an initial sample mass of 4–6 mg. Heating rates of 10, 15, 20 and 25 K/min were applied. Considering the graphite fluoride had a widely decomposition temperature [1], the $(CF)_n$ samples were heated from room temperature to 1123 K. In the measurements, an alumina pan was used