Fuel 103 (2013) 29–36

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Isothermal differential characteristics of gas–solid reaction in micro-fluidized bed reactor

Jian Yu, Xi Zeng, Juwei Zhang, Mei Zhong, Guangyi Zhang, Yin Wang *, Guangwen Xu *

State Key Laboratory of Multi-phase Complex System, Institute of Process Engineering, Chinese Academy of Science, Beijing 100190, China

ARTICLE INFO

Article history:
Received 2 January 2011
Received in revised form 27 August 2011
Accepted 10 September 2011
Available online 24 November 2011

Keywords:
Micro-fluidized bed
Gas–solid reaction
Isothermal differential characteristics
Reaction kinetics
Graphite combustion

ABSTRACT

The isothermal differential characteristics of the gas–solid reaction occurring in a micro-fluidized bed reactor were studied using the indigenously developed Micro-Fluidized Bed Reaction Analyzer (MFBRA). The combustion of graphite powder in micrometers was taken as the model reaction because of its negligible internal diffusion and chemical-reaction simplicity. With minimized inhibitions from both the internal and external diffusions, the reaction in MFBRA at a preset temperature was analyzed by using the isothermal kinetic approach, resulting in an activation energy of 165 kJ/mol and a pre-exponential factor of 10^6 1/s. The reaction was further found to be subject to the nucleation and growth model expressed by $G(\alpha) = -\ln(1-\alpha)$. Measuring this reaction in TG via the programmed heating method resulted in the similar activation energy and the same reaction function model (by extrapolating to zero conversion). Comparing with the non-isothermal approach for TG that involves complicated mathematical calculations, the isothermal differential approach for MFBRA allowed the separation of the temperature effect (i.e., the reaction rate constant) and kinetic function model, thus providing a simple and reliable determination of the gas–solid reaction kinetics.

1. Introduction

Gas–solid reactions exist widely in the fundamental research and technology development in the fields of, for example, chemistry, chemical engineering, energy, metallurgy, environment and material. The measurement of their characteristics and kinetics are the basis for the related scientific research and technology development. Various self-made gas–solid reaction testing apparatus and many customized instruments (methods) including thermal gravimetric, microscopic, diffractive, spectroscopic, electrical and magnetic analyzers have been used to measure or analyze gas–solid reactions [1,2]. Of them, the thermal gravimetric analyzer (TG) stands out as the representative gas–solid reaction testing instrument for its spot sample need, short testing time, accurate temperature control and easy utilization and quantification. The measurement via TG is based on monitoring the mass variation of a spot sample in different atmospheres during a specified heating program. The non-isothermal kinetic approach is accordingly used to calculate the kinetic parameters of the tested reaction. The thermogravimetric method is capable of distinguishing the different stages of mass variation of a sample in a heating process to reveal the different reactions or physical changes involved in the heating process to calculate their respective kinetic parameters. For the samples like coal and biomass which have complex composition and are strongly endothermic or exothermic during heating, the TG analysis can hardly distinguish the mass variation of continuous reactions, while the inevitable gas diffusion inhibition in TG makes the overall kinetics hardly reflect the process intrinsic characteristics. Furthermore, the highly endothermic or exothermic reactions like the combustion of coal or other high-energy materials would cause the reaction temperature to deviate greatly from the preset value. In fact, via the non-isothermal kinetic method of TG it is impossible to separate the actions of reaction temperature and reaction time, which not only complicates the kinetic calculation process but leads also to big uncertainty in quantification.

Using various self-made reactors, many researchers have therefore tried the isothermal approach to study the gas–solid reaction characteristics [3–6]. However, in most cases the isothermal reaction conditions cannot be fully guaranteed, such as the reactor with fast-lifting furnace, not mention the difficulty for real-time monitor of the reaction variation in this kind of reactors [7,8]. The thermogravimetric analysis could also realize isothermal process for thermally stable materials by using the gas switching operation method. For example, Miura and Silveston [9] obtained an consistent kinetics for char gasification with CO_2 in TG under gas switching and programmed heating method under low reaction rate, suggesting that TG could be suitable for the measurement

---

* Corresponding authors. Tel./fax: +86 10 62550075 (G. Xu).
E-mail addresses: Wangyin@home.ipe.ac.cn (Y. Wang), gwxu@home.ipe.ac.cn (G. Xu).

0016-2361/$ - see front matter Crown Copyright © 2011 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2011.09.060

of the reactions with slow rate and for stable materials. However, this capability of TG is conditional, and the required conditions are that the reactant must be stable in heating and the heating rate would be slow enough to make the gas mixing and diffusion effects negligible. The measurement via TG is at all restricted by the diffusion of the reactant gas from the cell circumstance to the reactant sample, and for the gas switching case it is further limited by the inert gas purity in heating and the replace of the inert gas circumstance by the reactant gas after switching. Consequently, there is actually no popularly recognized isothermal differential reaction analyzer for measuring arbitrary gas–solid reactions.

The Micro-Fluidized Bed Reaction Analyzer (MFBRA) developed in our previous work has been applied to studying the kinetics of gas–solid reactions for a series of materials [10–13]. The design idea of the MFBRA was: (1) strengthening heat and mass transfer and reaction differential features using micro-fluidized bed reactor, (2) on-line pulse feeding and rapid heating of powder reactant in milligrams and micrometers, (3) on-line monitoring of gas product with fast process mass spectrometer, and (4) calculating the reaction rate and kinetics and analyzing the reaction mechanism based on the measured time-series of product gas composition. Although the MFBRA possesses the features of instantaneous heating and rapid measurement, it is yet unclear whether this instrument can ensure the isothermal differential characteristics required for the kinetic analysis and quantification of the gas–solid reactions. This article is thus devoted to providing a justification for such a feature of the MFBRA by taking the combustion of fine graphite (in 15 μm) as a model reaction. Under the conditions with minimized effect of gas diffusions, the kinetic parameters of graphite powder combustion in TG and MFBRA are measured and compared according to the non-isothermal and isothermal differential kinetic approaches. The isothermal differential characteristics of the gas–solid reaction in the MFBRA are verified on the basis of the similarity between the resulting kinetic parameters and the reaction function models.

2. Kinetic approaches

The basic differential and integral equations based on thermal analysis data for calculating the gas–solid reaction kinetics are expressed by

$$\frac{d\alpha}{dt} = k(T) \times f(\alpha) = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

$$G(\alpha) = \int k(T)dt = \int A\exp\left(-\frac{E}{RT}\right)dt \tag{2}$$

and

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{3}$$

where α, A, E, R, T, $f(\alpha)$ and $G(\alpha)$ are the reaction conversion, pre-exponential factor, activation energy, gas constant, temperature in K, and model function equations in the differential and integral formats. Table 1 summarizes the major reaction model functions that have been widely referred to in the literatures regarding thermochemical reaction analyses [1].

2.1. Non-isothermal kinetic approach

Substituting the particularly defined parameters shown in Eq. (4) into the integral Eq. (2) transforms this equation into Eq. (5) [1]. The so-called FWO Eq. (7) is then obtained by using the integral approximate value of Eq. (6) to replace the same variable in Eq. (5). This FWO equation implies that the value of $\ln\beta$ is subject to a linear correlation with $1/T$ at a constant conversion, allowing the apparent activation energy E to be determined from the slope of the correlation line. This procedure determines the activation energies for different conversions. The apparent activation energy of the analyzed reaction is estimated through extrapolating the resulting energy values for different conversions to zero conversion or averaging the activation energies for different conversions.

$$T/t = \beta, \quad u = \frac{E}{RT}, \quad G(\alpha) = \int_0^\alpha [F(\alpha)]^{-1}d\alpha \tag{4}$$

$$G(\alpha) = \frac{A}{\beta}\int_0^T \exp\left(\frac{-E}{RT}\right)dT = \frac{AE}{\beta R}\int_\infty^u \frac{-e^u}{u^2}du = \frac{AE}{\beta R}P(u) \tag{5}$$

$$\ln P(u) = -2.315 - 0.4567\frac{E}{RT} \tag{6}$$

$$\ln\beta = \ln\frac{AE}{RG(\alpha)} - 2.315 - 0.4567\frac{E}{RT} \tag{7}$$

The above-mentioned FWO approach can avoid the selection of reaction mechanism and function model to enable the direct acquisition of the activation energy E, reducing thus the error for the kinetic data caused by improper selection of the reaction mechanism and function model. Hence, the FWO approach can be used to examine the accuracy of the various function models that are assumed to describe the proposed reaction mechanism. On the other hand, the Eq. (8) shown below represents the Frank–Kameneskii approximation method that can be adopted to select the reaction mechanism model. Combining Eqs. (5) and (8) then leads to the so-called Coats–Redfern equation:

$$\int_0^T \exp\left(-\frac{E}{RT}\right)dT = \frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right) \tag{8}$$

$$\ln\left(\frac{G(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{(RT)} \tag{9}$$

The mechanism function $G(\alpha)$ implicates the reaction mechanism. Substituting a model into Eq. (9) one can judge if the mechanism function model describes satisfactorily the reaction through examining the linearity and linear range of $\ln\{G(\alpha)/T^2\}$ versus $1/T$. For any specific function model that leads to linear correlation for the measured data (from programmed heating TG), the activation energy at the thermal equilibrium condition (i.e., $\beta = 0$) is determined by extrapolating the activation energies obtained at different heating rates to the zero heating rate. The essence of this extrapolation is that at the zero heating rate the gas diffusion effect would be completely avoided. Comparing the similarity of the activation energy at $\beta = 0$ with that calculated using the FWO equation one can judge the accuracy of the adopted mechanism function model and select the one leads to the closest approaching to the result given by the FWO equation. Obviously, this process of calculating the kinetic data and determining the mechanism function model is complicated and involves many approximation steps.

2.2. Isothermal kinetic method

Applying logarithm to the aforementioned Eq. (1) and expanding $k(T)$ lead to

$$\ln\frac{d\alpha}{dt} = \ln k(T) + \ln f(\alpha) \tag{10}$$

$$\ln(k(T)) = \ln(A) - \frac{E}{RT} \tag{11}$$

and