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Arrhenius parameters determination in non-isothermal conditions for the uncatalyzed gasification of carbon by carbon dioxide

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ABSTRACT

Non-isothermal thermogravimetric data were used to evaluate the Arrhenius parameters (activation energy, *E*, and pre-exponential factor, *A*) for the uncatalyzed gasification by carbon dioxide of two carbons, select as steam activated carbon (BPL) and SP-1 spectroscopically pure graphite. The paper reports on the application of the model-free isoconversional method (KAS/Vyazovkin linear method) for evaluating the activation energy of the gasification process. Activation energies have been calculated by this method were in good agreement with literature data for similar carbons. On the other hand, by means of the kinetic compensation relation between *E* and ln *A*, which was established by the model-dependent Coats–Redfern method, the value of the pre-exponential factor was estimated from the known value of the model-independent activation energy.

1. Introduction

The gasification reaction of carbon by carbon dioxide gas is also known as the Boudouard reaction. This reaction is an important industrial process and plays important roles in numerous industrial operations, such as generation of water and producer gases and smelting of ores. The kinetics of the carbon gasification reaction, therefore, has been studied by numerous authors [1–13]. Most of these authors usually applied the model-fitting methods to kinetic analysis of isothermal and non-isothermal data. However, the model-fitting methods tend to produce highly uncertain values of Arrhenius parameters. Possible reasons are that Arrhenius parameters are highly model-dependent and that the reaction model may not have been determined correctly[14]. Therefore, in this paper, the model-free isoconversional method which can avoid making any assumptions about the reaction model was used in order to evaluate the Arrhenius parameters of the gasification of carbon by carbon dioxide gas.

2. Theory

The kinetic studies of thermally induced reactions in solids, such as the gasification of carbons, are traditionally performed by thermal analysis methods which measure a change in an extensive property, generally, mass (thermogravimetry, TG). The kinetics of thermal transformations studied by TG under non-isothermal conditions can be generally described by the following equation:

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

where $f(\alpha)$ is the reaction model, α is the extent of conversion, $k(T)$ is the rate constant (A and E are the pre-exponential factor and the activation energy, respectively), T is the temperature, t is the time, β is the heating rate, and R is the gas constant. The temperature dependence of the rate constant is generally assumed to follow an Arrhenius type dependence. The formal expression of $f(\alpha)$ depends on the conversion mechanism, and it represents the limiting step of the kinetic model.

Eq. (1), as well as numerous approximations of its integral form (Eq. (2)), underlies most of the methods of kinetic processing.

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT = \frac{AE}{\beta R}\int_x^\infty \frac{\exp(-x)}{x^2}dx = \frac{AE}{\beta R}p(x) \tag{2}$$

where $x = E/RT$ and $p(x)$ is the temperature integral, which cannot be exactly calculated. When operating under non-isothermal conditions, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and the determination of $f(\alpha)$, A and E (the so-called kinetic triplet) is an interlinked problem. A deviation in the determination of any of the three will cause a deviation in the other parameters of the

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triplet. Thus, it is highly recommended to start the analysis of non-isothermal experiments by determining one element of the triplet with high accuracy, such as the activation energy.

The methods of kinetics processing can be divided into two main categories [15]: those which employ data obtained under only one heating rate, and those based on performing a series of measurements under different heating rates (isoconversional methods). The attraction of isoconversional methods derives mainly from its ability to give activation energy values without the necessity of presuming the analytical form of the reaction model $f(\alpha)$. The basic assumption of model-free isoconversional methods is that the reaction rate at a constant conversion is only a function of temperature, and that the reaction model is not dependent on temperature or heating rate. These methods yield the dependence of the effective activation energy on the transformation degree. The existence of such dependence points to a complex character of the process (for a simple process the activation energy is constant at any transformation degree). The main disadvantage of isoconversional methods is that they do not suggest direct evaluation of the pre-exponential factor or reaction model.

The so-called integral isoconversional methods differ according to the approximation used to calculate the temperature integral. Among the integral isoconversional methods, Flynn–Wall–Ozawa (FWO) method [16–18] and Kissinger–Akahira–Sunose (KAS) method [19–21] have been popularly used to derive activation energies. However, considering the findings of Starink [22] and Liu [23] on the accuracy of these two methods, particularly that the Flynn–Wall–Ozawa method overestimates the activation energy, and is in fact quite inaccurate compared to the Kissinger–Akahira–Sunose method. For this reason, the KAS method is used in this study to calculate the activation energies for the process of carbon gasification. The integral isoconversional method suggested by Kissinger–Akahira–Sunose is based on the Murray and White approximation [24] of the temperature integral $p(x)$, which leads to:

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT} \tag{3}$$

Thus, for α = constant, the plot $\ln(\beta/T^2)$ *vs.* $1/T$, obtained from the curves recorded at several constant heating rates, should be a straight line whose slope can be used to evaluate the activation energy. Since the Kissinger–Akahira–Sunose (KAS) method is essentially identical to the linear method described by Vyazovkin [25], the KAS method is also termed the KAS/Vyazovkin linear method [23].

Among the methods that only consider a single thermoanalytical curve recorded at a single heating rate for determining E, and also A, the Coats–Redfern method [26,27] is probably the most employed in the literature. This method uses the equation:

$$\ln\frac{g_j(\alpha)}{T^2} = \ln\left[\frac{A_jR}{\beta E_j}\left(1-\frac{2RT}{E_j}\right)\right] - \frac{E_j}{RT} \cong \ln\frac{AR}{\beta E_j} - \frac{E_j}{RT} \tag{4}$$

The subscript j has been introduced to emphasize that substituting a particular reaction model in Eq. (4) results in evaluating the corresponding Arrhenius parameters. This method assumes that the Arrhenius parameters do not depend on α. By using this method, it is observed that the values of the activation energy and the pre-exponential factor, obtained for different analytical forms of $g(\alpha)$, are correlated through the following relation of compensation (Eq. (5))

$$\ln A_j = a + bE_j \tag{5}$$

where the subscript j refers to one of the possible models $g_j(\alpha)$ considered to describe the process. This means that the rate of the process investigated can be satisfactorily described by Eq. (4) with practically any model $f(\alpha)$ and fitting $k(T)$ which compensates the error of the reaction model-choice. Therefore, an implication of the $f(\alpha) - k(T)$ compensation results in a linear correlation. Vyazovkin and Lesnikovich [28] proposed a procedure to calculate the value of the pre-exponential factor based on the use of the compensation effect. Thus, once the correlation parameters a and b have been evaluated, the model-free activation energy calculated by isoconversional methods is substituted for E_j in Eq. (5), and, subsequently A is estimated.

3. Experimental

The two carbons employed in this study were steam activated carbon (BPL) from Huaiyushan Activated Carbon Tec & Sci (Zhuhai) Co., Ltd. (China) and SP-1 spectroscopically pure graphite from Qingdao Hensen Graphite Co., Ltd.(China). The elemental analysis of the samples revealed that the major component in both carbons was carbon (>98% mass%), and the ash content was negligible. The textural properties, as revealed by N_2 adsorption analysis, were markedly different for both carbons. BPL carbon showed a high surface area of 1000 $m^2\,g^{-1}$, while SP-1 graphite had a noticeable lower surface area of 1.8 $m^2\,g^{-1}$. BPL carbon and SP-1 graphite both had a mean particle size of 40 μm.

Thermogravimetric curves were obtained using a Setsys Evolution thermogravimetric analyzer TGA (Setaram Co., France). Samples (8 ± 0.5 mg) were placed in platinum crucibles (diameter 3 mm). The temperature was record from 383 to 1523 K, with constant heating rates of 5, 10, 15 and 20 K min^{-1}, respectively, under (99.9995 vol%) carbon dioxide flowing at a rate of 40 mL min^{-1}.

It was noted that carbon dioxide gas was also used as a purge gas to displace air in the carbon gasification zone, thus avoiding unwanted oxidation of the samples.

4. Results and discussion

The normalized mass loss or conversion α was typically calculated from the corresponding TG curves as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{6}$$

where m_t represents the mass of the sample at arbitrary time t (or temperature T), whereas m_0 and m_f are the mass of the sample at the beginning and at the end of the mass loss process, respectively.

The thermogravimetric data collected during non-isothermal gasification of the carbon samples at several constant heating rates are shown in Fig. 1. It was found that BPL carbon was converted at temperatures noticeably lower than SP-1 graphite. The reaction occurred in a temperature range between 600–1100 and 950–1470 K, respectively. When increasing the constant heating rate the TG curves were shifted to higher temperature regions without any appreciable distortion in the typical sigmoidal shape.

It is widely accepted that the gasification of carbon by carbon dioxide occurs on surface carbon active sites that can detach an oxygen atom from a gaseous CO_2 molecule [29,30]. These active sites are primarily associated with edge or defects on the surface. The amount of these available carbon active sites is known to be strongly dependent on parameters such as the surface area [31]. Hence, carbons having a high surface area are more reactive. The higher reactivity (lower gasification temperatures) of BPL carbon was therefore associated with its larger quantity of active sites located at edge or defect sites on its surface.

The application of the isoconversional methods requires the determination of the absolute temperature at which a fixed extent of gasification from the several TG curves recorded at different heating rates. The conversion range between 10% and 90% was investigated. The KAS/Vyazovkin linear method involves

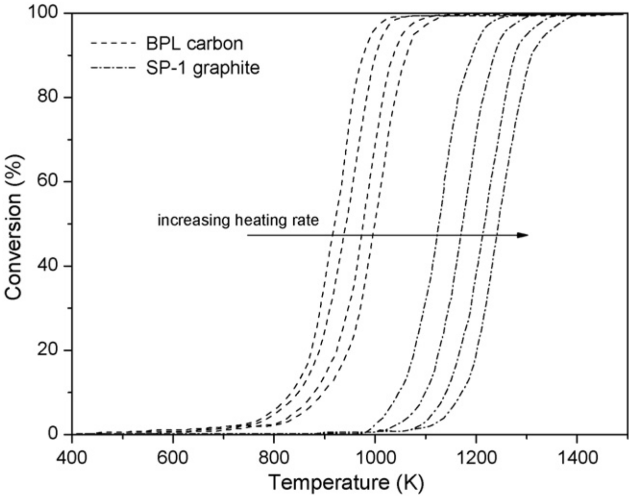

Fig. 1. Experimental mass kinetic curves obtained at different heating rates for BPL carbon and SP-1 graphite.

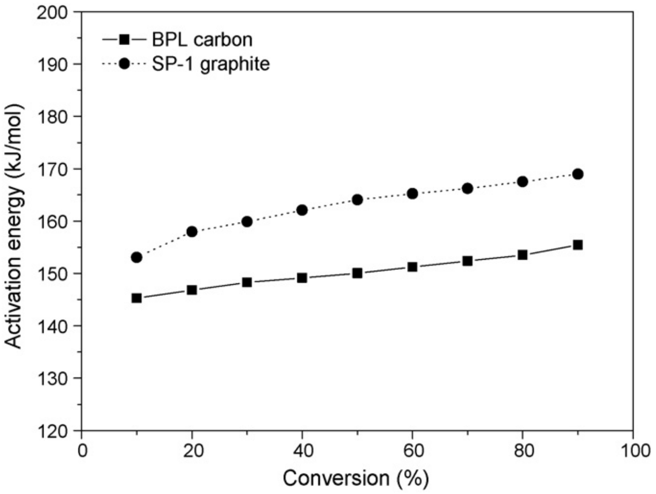

Fig. 2. Model-independent values of the activation energy as a function of the degree of conversion for the gasification of both carbons.

plotting $\ln(\beta/T^2)$ *vs.* $1/T$. The slope of such plots gives the activation energy for the selected conversion degrees. The calculated results from the application of this isoconversional method in the 10–90% conversion range are listed in Table 1. For BPL carbon, $E = 145–155\ \mathrm{kJ\,mol^{-1}}$, and for SP-1 graphite, $E = 153–169\ \mathrm{kJ\,mol^{-1}}$, are in accordance with data reported in literature for similar carbons [32,33].

Table 1
Activation energies of BPL carbon and SP-1 graphite calculated from the KAS/Vyazovkin linear method.

α (%)	BPL carbon		SP-1 graphite	
	E (kJ mol^{-1})	R^2	E (kJ mol^{-1})	R^2
10	145.29	0.9981	153.06	0.9973
20	146.81	0.9965	157.95	0.9982
30	148.30	0.9971	159.91	0.9958
40	149.15	0.9969	162.09	0.9964
50	150.06	0.9928	164.07	0.9920
60	151.22	0.9946	165.23	0.9936
70	152.39	0.9937	166.22	0.9949
80	153.51	0.9955	167.54	0.9912
90	155.43	0.9918	168.96	0.9925

The results of isoconversional calculations are presented in Fig. 2 in terms of the activation energy as a function of the extent of conversion. In the selected conversion range, the activation energies calculated from the KAS/Vyazovkin linear method increase with the level of conversion for both carbons. The dependence of activation energy on the level of conversion is probably due to the change in the gasification control mechanism. At low temperatures, layers of carbon atoms overlap each other, with only weak bonds between the layers. The unsaturated carbon atoms, and the unsaturated edge carbon atoms in particular, have high adsorptive capabilities. The adsorptions are mainly belong to chemisorption [34]. At high temperatures, the kinetic energy of CO_2 molecules increases. Meanwhile, for either carbon, the interatomic fore becomes weaken. In this case, the carbon atoms directly react with CO_2 molecules without the chemisorption [35]. According to the literature [36], the chemisorption needs less activation energy than the kinetics in the carbon gasification. With low levels of conversion, the carbon is gasified at low temperatures and, hence, the carbon gasification could be under the combined control of kinetics and chemisorption. That is, at low temperatures, the weight change profiles are not always governed only by the gasification kinetics because of the effect of chemisorption [36]. However, with high levels of conversion, the gasification temperatures are high and, hence, the chemisorption does not significantly influence thermogravimetric data, for gasification in CO_2. Reif [37] has also reported that the adsorption of carbon dioxide by carbon is negligible at higher temperatures. The gasification of either carbon is predominantly controlled by kinetics and the effect of chemisorption could be neglected.

The Coats–Redfern analysis of the thermogravimetric data recorded at a single heating rate has been carried out by inserting various $g_j(\alpha)$ into Eq. (4) that results in a set of Arrhenius parameters determined from the plot $\ln[g_j(\alpha)/T^2]$ *vs.* $1/T$. It was found that each TG curve could be equally well described by several kinetic models resulting in correlation coefficients close to the unity. Hence, the Arrhenius parameters derived were highly variable, exhibiting a strong dependence on the reaction model chosen and a weak dependence on the heating rate. This extra flexibility in the fitting procedure allowed errors in the functional form of the reaction model to be concealed by making compensation errors in the Arrhenius parameters, sometimes by as much as one order of magnitude. Unfortunately, kinetic methods based on results obtained from single-rate run experiments did not permit an unambiguous determination of E. For a successful analysis at

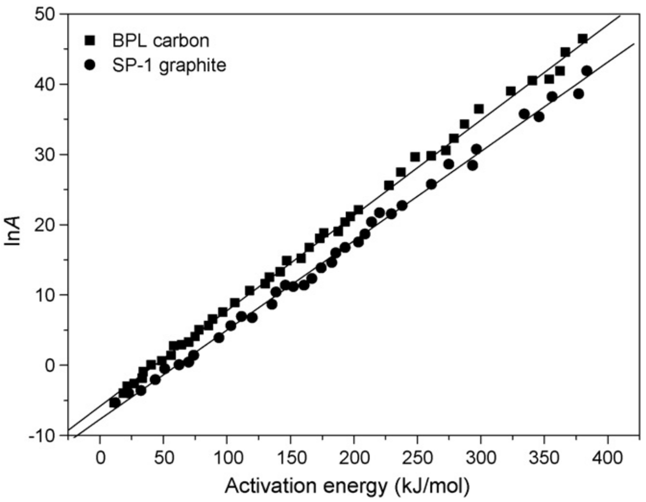

Fig. 3. $\ln A$ *vs.* E for the gasification of both carbons.

Table 2
Pre-exponential factors of BPL carbon and SP-1 graphite.

α (%)	BPL carbon A (min^{-1})	SP-1 graphite A (min^{-1})
10	7.06×10^5	2.51×10^5
20	8.69×10^5	4.59×10^5
30	1.07×10^6	5.84×10^5
40	1.20×10^6	7.63×10^5
50	1.36×10^6	9.73×10^5
60	1.59×10^6	1.12×10^6
70	1.87×10^6	1.27×10^6
80	2.18×10^6	1.49×10^6
90	2.83×10^6	1.78×10^6

least one kinetic parameter must be a priori known. Thus, once the correlation relation was established and a model-free activation energy value was available, the value of the pre-exponential factor could be unambiguously determined. The compensation relations corresponding to BPL carbon and SP-1 graphite are plotted in Fig. 3. The following equations were derived, respectively:

$$\ln A = 0.137\mathrm{E} - 6.438 \quad R^2 = 0.9981$$
$$\ln A = 0.123\mathrm{E} - 6.392 \quad R^2 = 0.9965$$

Hence, the values of pre-exponential factor that could be derived were summarized in Table 2.

5. Conclusions

The determination of the Arrhenius parameters (activation energy and pre-exponential factor) of the uncatalyzed gasification of two carbons, namely BPL carbon and SP-1 graphite, was analyzed by non-isothermal thermogravimetry. The activation energies of the gasification of both carbons by carbon dioxide were determined by model-free integral (KAS/Vyazovkin linear method) isoconversional method, which required thermoanalytical data obtained from a series of experiments at different heating rates. The calculated activation energies increased with increasing the carbon conversion level. The effect of chemisorption, which could be negligible at higher carbon conversion levels, is believed to be the main reason for the observation. The activation energies of CO_2 gasification of BPL carbon and SP-1 graphite were 145–155 and 153–169 kJ mol^{-1}, respectively. The compensation relation derived from the Coats–Redfern method was useful for the unambiguous determination of the pre-exponential factor once a model-free activation energy value was known.

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