

# Reaction mechanism of carbon gasification in CO<sub>2</sub> under non-isothermal conditions

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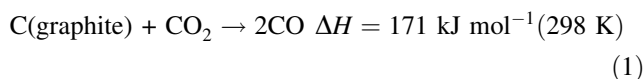
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**Abstract** Experiments of carbon (graphite) gasification in CO<sub>2</sub> have been carried out by thermal analysis techniques (TG-DTG-DSC) under non-isothermal conditions. The results indicate that the entire carbon gasification process can be divided into an exothermic slow gasification stage during the initial period and an endothermic fast gasification later. The analyses of energy conservation and non-isothermal kinetics arrive at the following conclusions; (1) The exotherm of the initial stage is caused by the combined effect of the exothermic chemisorption and the endothermic chemical reaction. The gasification reaction may be expressed by the series of chemisorption and chemical reaction and the overall process is controlled by interface reaction via chemisorption. (2) The endothermic effect of fast gasification stage is almost equal to the reaction heat of carbon gasification, which implies that the chemisorption step disappears. The gasification process can be expressed by a simple interface reaction.

**Keywords** Carbon gasification · Non-isothermal · Reaction mechanism · CO<sub>2</sub>

## Introduction

The gasification of carbon in CO<sub>2</sub>



is one of the main reactions when solid carbon is used as fuel and reducing agent.

As early as in 1955, Von Fredersdorff [1] proposed that the gasification rate can be described by a Langmuir–Hinshelwood absorption rate equation. Afterward, Ergun [2] proposed a two-step mechanism for carbon gasification: first, CO<sub>2</sub> is chemically adsorbed on the active reaction sites C<sub>f</sub> on the carbon surface. The complex C<sub>f</sub>(O) is formed, while CO<sub>2</sub> is reduced to CO. Then, C<sub>f</sub>(O) is broken into CO. This is the slowest step of the reaction. Chen et al. [3] also proposed a reaction mechanism for carbon gasification. They considered that, in addition to C<sub>f</sub>, CO<sub>2</sub> is also adsorbed on C<sub>f</sub>(O), which forms a new type of complex C(O)C<sub>f</sub>(O). Because the C(O)C<sub>f</sub>(O) structure is less stable than the C<sub>f</sub>(O) structure, the C(O)C<sub>f</sub>(O) can break down at lower temperatures, whereas the C<sub>f</sub>(O) breaks down at higher temperatures.

Thermogravimetry has been widely used to study the kinetics of gas–solid reactions and has also been applied in kinetic studies of carbon gasification [4–7]. Because thermogravimetry kinetics is applied the solid structure model to predict the reaction mechanism, thermogravimetry becomes even more essential while studying the effect of the pore structure of coke on the gasification kinetics [8–10]. Since thermogravimetric analyzer (TGA) measures the dependencies of the conversion and the reaction rates of the solid samples on time or temperature, and moreover, since adsorption and reaction are always interwoven closely

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with each other in the carbon gasification process, the effect of chemisorption kinetics cannot be considered to be unimportant and thus cannot be neglected. Lizzio et al. [11] considered that adsorption and desorption coexist in the carbon gasification process. The conversion rate measured by thermogravimetry is the combined result of adsorption and desorption and not that of chemical reaction. The conversion curves should thus be corrected by chemisorption. Feng and Bhatia [12] discussed the effects of carbon gasification and chemisorption on the sample mass loss using the pseudo-steady assumption. They concluded that, when the active surface area of carbon is less than  $312 \text{ m}^2 \text{ g}^{-1}$ , or at low temperature and low  $\text{CO}_2$  partial pressure with active surface area larger than  $312 \text{ m}^2 \text{ g}^{-1}$ , the effect of chemisorption on the sample mass loss is negligible.

The entire carbon gasification process includes adsorption and interface reaction. Thermal effect of either step is different. Adsorption is exothermic, whereas carbon gasification is endothermic with carbon loss. Therefore, the principal aim of applying thermogravimetry kinetics to the carbon gasification processes is to determine the existence conditions of adsorption step and its effect on the entire reaction process.

In this article, experiments of carbon gasification in  $\text{CO}_2$  have been carried out by thermal analysis techniques (Thermogravimetry-Derivative thermogravimetry-Differential scanning calorimetry, TG-DTG-DSC) under non-isothermal conditions. Based on the energy conservation analysis of thermal effects and the kinetic analysis of adsorption and reaction rates, the mechanism of the carbon gasification is proposed and the region where chemisorption exists is determined, thereby providing a basis for the non-isothermal kinetics of carbon gasification.

## Experimental

### Experimental methods

Thermogravimetric curves are obtained using a Labsys TGA (Setaram Co., France). The sample is of graphite powder (purity 99.99%) with a mean particle size of  $37.5 \mu\text{m}$ . Samples ( $8 \pm 0.5 \text{ mg}$ ) are placed in a platinum crucible (diameter 3 mm). The temperature is recorded from 383 to 1523 K, with constant heating rates of 5, 10, 20, and 30  $\text{K min}^{-1}$ , respectively, under (99.99%) carbon dioxide flowing at a rate of  $40 \text{ mL min}^{-1}$ .

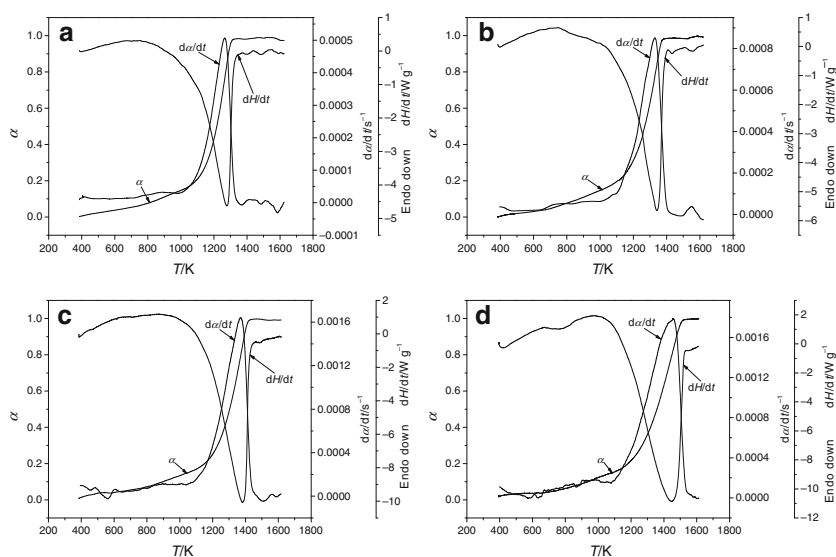
In order to dry the samples, they are placed in an electric stove and heated at 383 K for 8 h.  $\text{CO}_2$  passes through deoxidizing and dehydrating agents, and then enters into the TGA. Before the experiments,  $\text{CO}_2$  was introduced into the analyzer for 4 h to drive off the air inside the analyzer. Omnistar quadrupole mass spectrometer is used to analyze the exit gas composition.

### Experimental results

TG-DTG-DSC curves of carbon gasification are shown in Fig. 1. As shown in Fig. 1, the entire carbon gasification process can be divided into a slow gasification stage during the initial period, and a fast gasification stage later. The slow gasification stage is exothermic, and the fast gasification stage is endothermic.

As shown by the dependence of  $d\alpha/dt$  on  $\alpha$  in Fig. 2, at different heating rates, the value of  $\alpha$  is 0.18–0.19 when the process is changing from slow gasification to fast gasification. This indicates that the change of gasification rate is determined by the characteristic of carbon gasification

**Fig. 1** TG-DTG-DSC curves of carbon gasification reaction. **a** 5  $\text{K min}^{-1}$ , **b** 10  $\text{K min}^{-1}$ , **c** 20  $\text{K min}^{-1}$ , **d** 30  $\text{K min}^{-1}$



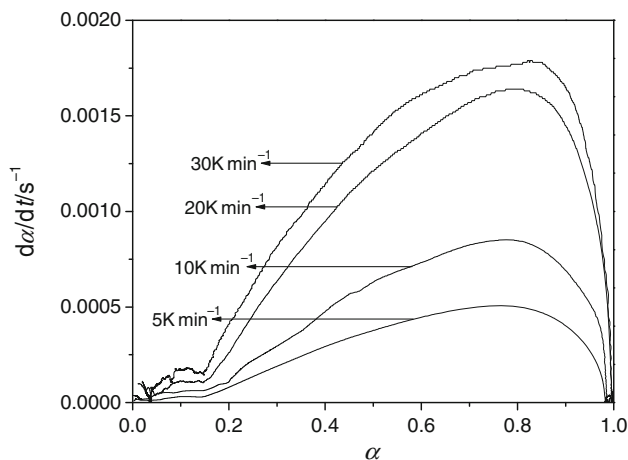


Fig. 2  $d\alpha/dt$  vs.  $\alpha$

reaction and is independent of the experimental conditions (heating rates).

### Elementary steps and rate of the gasification process

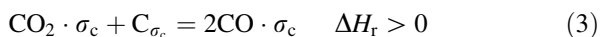
#### Elementary steps

There may be two reaction mechanisms for carbon gasification by carbon dioxide, one being the interface reaction via surface adsorption [1–3] during the reaction process, and the other being a sole interface reaction [12] with the effect of adsorption being negligible under certain operating conditions. The interface reaction via surface adsorption comprises the following elementary steps:

1. CO<sub>2</sub> is available for chemisorption on the active sites of the carbon particle surface. The reaction equation is
 
$$CO_2 + \sigma_c = CO_2 \cdot \sigma_c \quad \Delta H_a < 0 \tag{2}$$

where  $\sigma_c$  is the active site of CO<sub>2</sub> adsorbed by the carbon particle surface and  $\Delta H_a$  is the adsorption heat.

2. CO<sub>2</sub> adsorbed and C undergo an endothermic chemical reaction,



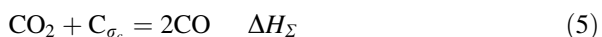
where  $\Delta H_r$  is the heat of carbon gasification reaction.

3. The reaction product CO adsorbs heat and desorbs from active sites,



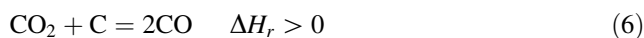
where  $\Delta H_d$  is the heat of desorption.

Combining the above three steps, carbon gasification reaction can be written as follows:



where  $\Delta H_{\Sigma}$  is the total heat of carbon gasification.

The interface reaction can be achieved in one step through the collision of CO<sub>2</sub> with C. The reaction equation is



According to energy conservation, the total heat of the interface reaction via adsorption is

$$\frac{dH_{\Sigma}}{dt} = \frac{dH_a}{dt} + \frac{dH_r}{dt} + \frac{dH_d}{dt} \tag{7}$$

The algebraic sum of the adsorption and desorption heat is defined as an effective heat of adsorption, that is

$$\frac{dH_{ae}}{dt} = \frac{dH_a}{dt} + \frac{dH_d}{dt} \tag{8}$$

Equation 7 can then be written as

$$\frac{dH_{\Sigma}}{dt} = \frac{dH_{ae}}{dt} + \frac{dH_r}{dt} \tag{9}$$

The standard mol enthalpy of carbon gasification reaction is about 171 kJ mol<sup>-1</sup>. According to  $-dH_{\Sigma}/dt > 0$ ,  $\Delta H_{\Sigma} > -166.55$  kJ mol<sup>-1</sup>. In general, the heat of physical adsorption is less than -40 kJ mol<sup>-1</sup>, and the heat of chemical adsorption is from -80 to -400 kJ mol<sup>-1</sup> [13]. Therefore, the heat of slow carbon gasification stage indicates that the carbon gasification reaction takes place via chemisorption.

The heat of chemical adsorption is much greater than that of desorption, which is equal to physical adsorption, Eq. 9 can then be written as

$$\frac{dH_{ae}}{dt} = \frac{dH_{\Sigma}}{dt} - \frac{dH_r}{dt} \tag{10}$$

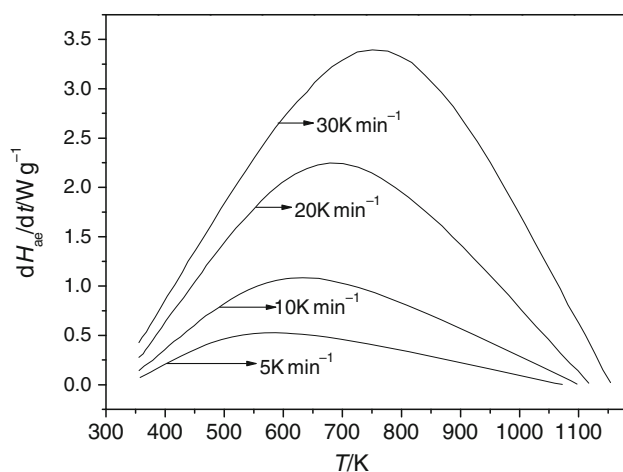
According to Eq. 10, the relationships between  $dH_{ae}/dt$  and temperature at different heating rates are shown in Fig. 3. As shown in Fig. 3,  $dH_{ae}/dt$  curves increased first and decreased subsequently. The curves are in parabolic shape. When entering the fast gasification stage ( $-dH_{ae}/dt \leq 0$ ), the heat of adsorption is equal to desorption and is less than the reaction heat. Because the heat of desorption is much lower than that of chemisorption, it can be concluded that chemisorption does not exist when entering the fast gasification stage.

If chemisorption does not exist in the fast gasification stage, then Eq. 9 can then be written as

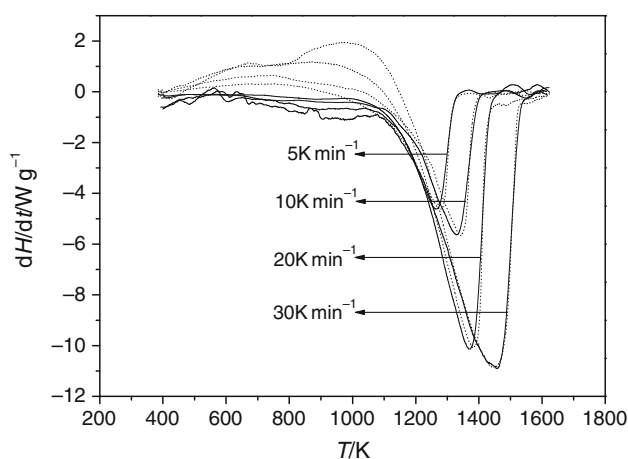
$$\frac{dH_{\Sigma}}{dt} = \frac{dH_r}{dt} \tag{11}$$

The relationships between heat flow and temperature are shown in Fig. 4. As shown in Fig. 4, in fast gasification stage, the  $dH_{\Sigma}/dt$  and  $dH_r/dt$  curves almost overlap correspondingly. This again proves that chemisorption does not occur when entering the fast gasification stage.

This shows that, under non-isothermal conditions, the reaction mechanisms for carbon gasification can be divided



**Fig. 3**  $dH_{ae}/dt$  vs.  $T$



**Fig. 4** Heat flow vs. temperature. ( $-dH_{\Sigma}/dt$ ,  $\dots dH_f/dt$ )

into interface reaction via adsorption in slow gasification stage, and interface reaction alone in fast gasification stage.

### Reaction rate

Under non-isothermal conditions, the entire carbon gasification process can be divided into an exothermic slow gasification stage during the initial period and an endothermic fast gasification stage later. In these two stages, carbon gasification reaction follows different mechanisms. Slow gasification follows a three-step mechanism with adsorption, reaction, and desorption in series, whereas fast gasification follows a one-step mechanism of a sole reaction. Because these two stages cannot be described by the same reaction mechanism, kinetics needs to be analyzed separately. The entire gasification conversion is  $[0, 1]$ . If the critical gasification conversion is  $\alpha_c$ , then the gasification interval in slow gasification stage is  $[0, \alpha_c]$ , and the gasification interval in fast gasification stage is  $[\alpha_c, 1]$ . The

gasification conversion and reaction rates in slow gasification stage are respectively as follows:

$$\alpha_s = \frac{\alpha}{\alpha_c} \quad (0 \leq \alpha \leq \alpha_c) \quad (12)$$

$$\frac{d\alpha_s}{dT} = \frac{1}{\alpha_c} \frac{d\alpha}{dT} \quad (0 \leq \alpha \leq \alpha_c) \quad (13)$$

where  $\alpha$  is the gasification conversion with reference to the entire gasification.

The gasification conversion and reaction rates in fast gasification stage are respectively as follows:

$$\alpha_f = \frac{\alpha - \alpha_c}{1 - \alpha_c} \quad (\alpha_c \leq \alpha \leq 1) \quad (14)$$

$$\frac{d\alpha_f}{dT} = \frac{1}{1 - \alpha_c} \frac{d\alpha}{dT} \quad (\alpha_c \leq \alpha \leq 1) \quad (15)$$

Considering that the extent of adsorption is proportional to the effective heat of adsorption, the adsorption conversion  $\alpha_a$  can be derived from the following equation:

$$\alpha_a = \frac{H_a}{\Delta H_{ae}} \quad (16)$$

where  $\Delta H_{ae}$  is the effective total enthalpy of adsorption (total area under the DSC curve).

The adsorption rate is

$$\frac{d\alpha_a}{dT} = \frac{1}{\Delta H_{ae}} \frac{dH_{ae}}{dT} \quad (17)$$

Substituting the DTG data in slow gasification stage and the effective adsorption data (as shown in Fig. 3) into Eqs. 13 and 17, respectively, the gasification reaction and adsorption rates can be obtained as shown in Fig. 5.

Figure 5 shows that, when adsorption and carbon gasification occur simultaneously, with increasing temperature, the adsorption rate increases first and then decreases till it disappears. In the increasing stage of adsorption rate, the gasification reaction rate increases accordingly. In the decreasing stage of adsorption rate, the gasification reaction rate does not decrease but begins to increase when adsorption rate decreases to a certain extent.

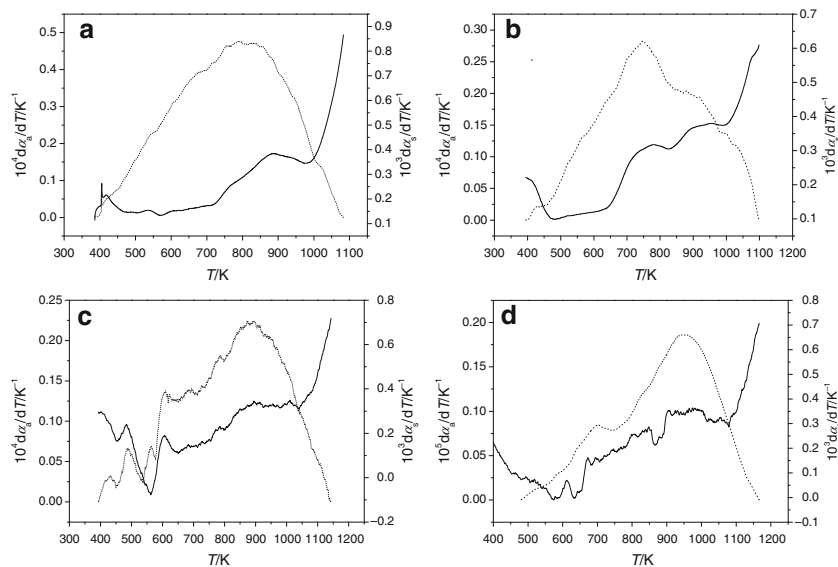
### Kinetic analysis

The rate equation of carbon gasification under non-isothermal conditions is commonly expressed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (18)$$

where  $\alpha$  is the extent of conversion,  $T$  is the temperature,  $A$  is the pre-exponential factor,  $\beta$  is the linear heating rate,  $E$  is the activation energy,  $R$  is the gas constant, and  $n$  is the reaction order.

**Fig. 5** Adsorption and gasification curves of carbon gasification reaction. **a** 5 K min<sup>-1</sup>, **b** 10 K min<sup>-1</sup>, **c** 20 K min<sup>-1</sup>, **d** 30 K min<sup>-1</sup>,  $\dots d\alpha_s/dT$ ,  $\dots d\alpha_a/dT$



**Table 1** Characteristic kinetic parameters of carbon gasification reaction at different heating rates

Reaction stage		Heating rate ( $\beta$ )/K min <sup>-1</sup>	Activation energy ( $E$ )/kJ mol <sup>-1</sup>	Pre-exponential factor ( $A$ )/s <sup>-1</sup>	Reaction order ( $n$ )	Correlation coefficient ( $r$ )
Slow gasification	Adsorption	5	40.16	0.30	1.08	0.9939
		10	34.57	0.26	1.05	0.9946
		20	29.13	0.21	1.02	0.9941
		30	23.69	0.17	1.01	0.9928
	Interface reaction via adsorption	5	213.52	$2.69 \times 10^8$	1.39	0.9931
		10	204.18	$6.27 \times 10^7$	1.27	0.9918
		20	191.69	$4.12 \times 10^6$	1.14	0.9943
		30	183.46	$1.36 \times 10^6$	1.08	0.9927
Fast gasification	Interface reaction	5	187.42	$3.20 \times 10^7$	0.71	0.9973
		10	172.33	$8.80 \times 10^6$	0.62	0.9986
		20	157.24	$5.51 \times 10^5$	0.51	0.9967
		30	142.15	$1.56 \times 10^5$	0.43	0.9959

The kinetic parameters  $n$ ,  $A$ , and  $E$  calculated with the Freeman–Carroll method [14] are listed in Table 1.

Table 1 shows that, in slow gasification stage, the activation energy of adsorption  $E_a$  is 23.69–40.16 kJ mol<sup>-1</sup>, and the activation energy of interface reaction via adsorption  $E_c$  is 183.46–213.52 kJ mol<sup>-1</sup>. In slow gasification stage, the activation energy of interface reaction  $E_r$  is 142.15–187.42 kJ mol<sup>-1</sup>.

**Discussions**

In graphite, layers of carbon atoms overlap each other, with only weak bonds existing between the layers. The unsaturated carbon atoms, and the unsaturated edge carbon atoms in particular, have high adsorptive capabilities. The

adsorption rate of CO<sub>2</sub> on the surface of carbon particle surface can be expressed as

$$r_a = \frac{1}{\beta} k_{CO_2} \theta_{\sigma_c}^n = \frac{1}{\beta} k_{CO_2}^0 \exp\left(-\frac{E_a}{RT}\right) \theta_{\sigma_c}^n \tag{19}$$

where  $k_{CO_2}$  is the adsorption rate constant of carbon particle surface,  $k_{CO_2}^0$  is the pre-exponential factor of adsorption rate constant, and  $\theta_{\sigma_c}$  is the number of the active sites which can adsorb CO<sub>2</sub> on unit surface area of carbon particle.

Equation 19 shows that for a given value of  $\theta_{\sigma_c}$ , adsorption rate increases with increasing temperature and  $k_{CO_2}$ .

The adsorption of CO<sub>2</sub> takes place at the adsorption sites on the carbon particle surface, probably as well as at the desorption vacancies left by the desorption of the product (CO) of interface reaction. The adsorption rate increased

first to a certain extent and then decreased till it disappeared. This can be attributed to the decrease of  $\theta_{\sigma_c}$  till its extinction. There are two reasons why  $\theta_{\sigma_c}$  decreased. One is that the controlling step of carbon gasification is interface reaction via adsorption, where the adsorption rate is higher than the desorption rate. The other is that the sites on the carbon particle have no longer any adsorption capability after desorption. The interface reaction via adsorption reduced the adsorption sites. The reason why the adsorption step disappeared is that the adsorption sites disappeared completely, and thus adsorption can no longer take place.

The rate of the interface reaction via adsorption can be expressed as follows:

$$r_c = \frac{1}{\beta} k_c \theta_{\text{CO}_2}^n = \frac{1}{\beta} k_c^0 \exp\left(-\frac{E_c}{RT}\right) \theta_{\text{CO}_2}^n \quad (20)$$

where  $k_c$  is the rate constant of the reaction,  $\theta_{\text{CO}_2}$  is the number of sites where  $\text{CO}_2$  is adsorbed on unit surface area of carbon particle,  $k_c^0$  is the pre-exponential factor.

Equation 20 shows that the rate of carbon gasification reaction increased with increasing temperature and  $\theta_{\text{CO}_2}$ . In the increasing stage of adsorption rate, gasification reaction rate increases with increasing the adsorption rate. In the decreasing stage of adsorption rate, however, the gasification reaction rate does not decrease but begins to increase when adsorption rate decreases to a certain extent.

In the slow carbon gasification stage, the adsorption activation energy (23.69–40.16 kJ mol<sup>-1</sup>) is much lower than the activation energy of the interface reaction via adsorption (183.46–213.52 kJ mol<sup>-1</sup>). This shows that the interface reaction via adsorption needs to overcome the lower energy barrier than that of carbon gasification. The controlling step of carbon gasification reaction may be the interface reaction via adsorption.

The activation energy of the interface reaction via adsorption (183.46–213.52 kJ mol<sup>-1</sup>) is about 22.52–12.22% higher than that of interface reaction (142.15–187.42 kJ mol<sup>-1</sup>). This shows that the interface reaction via adsorption needs to overcome higher energy barrier than that of interface reaction.

## Conclusions

- (1) Under non-isothermal conditions, the entire carbon gasification process can be divided into an exothermic slow gasification stage during the initial period and an endothermic fast gasification later.
- (2) In the slow gasification stage, carbon gasification reaction is mainly an interface reaction via adsorption. The net exothermic effect is the combined effects of exothermic adsorption and endothermic interface reaction via adsorption. The controlling step

of carbon gasification reaction may be the interface reaction via adsorption.

- (3) In the fast gasification stage, the heat effect is equivalent to the heat of carbon gasification reaction. After desorption, the sites on the carbon particle have no longer the adsorption capability any more. The adsorption step stopped. The gasification process can be expressed by a simple interface reaction.
- (4) The interface reaction via adsorption needs to overcome a higher energy barrier than that of the sole interface reaction.

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## References

1. Von Fredersdorff CG. Reactions of carbon with carbon dioxide and with steam. *Inst Gas Technol Chicago Res Bull.* 1955;19:75–82.
2. Ergun S. Kinetics of the reaction of carbon dioxide with carbon. *J Phys Chem.* 1956;60:480–5.
3. Chen SG, Yang RT, Kapteijn F, Moulijn JA. A new surface oxygen complex on carbon toward a unified mechanism for carbon gasification reactions. *Ind Eng Chem Res.* 1993;32(11):2835–40.
4. Stenseng M, Zolin A, Cenni R, Frandsen F, Jensen A, Dam-Johansen K. Thermal analysis in combustion research. *J Therm Anal Calorim.* 2001;64:1325–34.
5. Barkia H, Belkbir L, Jayaweera SAA. Non-isothermal kinetics of gasification by  $\text{CO}_2$  of residual carbon from timahdit and tarfaya oil shale kerogens. *J Therm Anal Calorim.* 2004;76:623–32.
6. Amaya A, Piriz J, Tancredi N, Cordero T. Activated carbon pellets from eucalyptus char and tar TG studies. *J Therm Anal Calorim.* 2007;89:987–91.
7. Feroso J, Arias B, Pevida C, Plaza MG, Rubiera F, Pis JJ. Kinetic models comparison for steam gasification of different nature fuel chars. *J Therm Anal Calorim.* 2008;91:779–86.
8. Fangxian L, Shizong L, Youzhi C. Thermal analysis study of the effect of coal-burning additives on the combustion of coals. *J Therm Anal Calorim.* 2009;95:633–8.
9. Nakanishi M, Ogi T, Fukuda Y. Thermogravimetric analysis in steam and oxygen with gas chromatograph mass spectrometry for basic study of biomass gasification. *J Therm Anal Calorim.* 2010;101:391–6.
10. Nowicki L, Antecka A, Bedyk T, Stolarek P, Ledakowicz S. The kinetics of gasification of char derived from sewage sludge. *J Therm Anal Calorim.* 2010. doi:10.1007/s10973-010-1032-1.
11. Lizzio AA, Piotrowski A, Radovic LR. Effect of oxygen chemisorption on char gasification reactivity profiles obtained by thermogravimetric analysis. *Fuel.* 1988;67(12):1691–5.
12. Feng B, Bhatia SK. On the validity of thermogravimetric determination of carbon gasification kinetics. *Chem Eng Sci.* 2002; 57(15):2907–20.
13. Molina A, Mondragon F. Reactivity of coal gasification with steam and  $\text{CO}_2$ . *Fuel.* 1998;77(15):1831–9.
14. Freeman ES, Carroll B. The application of thermoanalytical techniques to reaction kinetics: the thermogravimetric evaluation of kinetics of the decomposition of calcium oxalate monohydrate. *J Phys Chem.* 1958;62:394–404.