Kinetic modelling of the reaction rate of quartz and carbon pellet

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Abstract

Kinetic modelling of quartz- and carbon- pellet at temperature of 1898K(1625 °C),1923K(1650 °C) and 1948K(1675 °C) are investigated in this study. The carbon materials used were charcoal, coke, coal and pre-heated coal. The overall SiC producing reaction can be described by the reaction $SiO_2 + 3C = SiC + 2CO$. In the SiC producing step the reaction rate of quartz- and carbon- pellet can be expressed as the following.

$$\frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot F_C \cdot \%) \cdot A \cdot \exp(-\frac{E}{RT})$$

Carbon factor F_C describes the various reactivity for different carbon materials. For charcoal, coke, coal and pre-heated coal the Carbon factor F_C are 0.83, 0.80, 0.94 and 0.83 respectively. The pre-exponential factor A for the above four carbon materials are 1.06×10^{16} min^{-1}, 4.21×10^{15} min^{-1}, 3.85×10^9 min^{-1} and 1.00×10^{25} min^{-1} respectively. The activation energy E of quartz and charcoal, coke, coal and pre-heated coal pellets at SiC-producing step are 570 kJ/mole, 563 kJ/mole, 336 kJ/mole and 913 kJ/mole. After the comprehensive study, activation energy E 307 kJ/mole could be applied for simplifying the modelling with acceptable deviation.

I. INTRODUCTION

Reactions in quartz- and carbon- pellets can be divided into two steps, the SiC-producing step and SiO-producing step[1]. In the SiC-producing step, SiO_2 and C are reacting according to the reaction:

$$SiO_2(s) + 3\ C(s) = SiC(s) + 2\ CO(g) \qquad \Delta H°_{1773K(1500\ °C)} = 163.8 \text{Wh/mol} \qquad (1)$$

During the SiO-producing step, the main reaction is between SiO_2 and SiC. The reaction rate at this step is quite slow and has a constant reaction rate. It is also believed that the SiC-formation reaction (equation 1) in the quartz and carbon pellet can be divided into following two steps: SiO formation (equation 2) and SiO capture (equation 3).

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \qquad \Delta H°_{1773K(1500\ °C)} = 184.6 \text{ Wh/mol} \qquad (2)$$

$$SiO(g) + 2\ C(s) = SiC(s) + CO(g) \qquad \Delta H°_{1773K(1500\ °C)} = -20.8 \text{ Wh/mol} \qquad (3)$$

Tab. 1- Reaction rates k(T) and activation energy E summarized in previous studies for reaction 1[2] .

Carbon material	d/μm	E/kJ/mol	T/K(°C)	k/min^{-1}
Coke breeze	--	552	1673(1400)	0.66
			1723(1450)	0.84
			1773(1500)	1.50
Coke	0.198	299	1773(1500)	0.55
			1873(1600)	1.86
			1973(1700)	3.72
			2073(1800)	9.60
Charcoal	70	544	1623(1350)	0.03
			1643(1370)	0.06
			1673(1400)	0.09
			1703(1430)	0.23

			1713(1440)	0.24
Carbon black	0.187	251	1773(1500)	1.02
			1873(1600)	3.48
			1973(1700)	4.56
			2073(1800)	12.6
Carbon black	0.385	288	1773(1500)	0.47
			1873(1600)	1.68
			1973(1700)	3.72
			2073(1800)	7.80
Carbon black	0.017	287	1573(1300)	0.06
			1673(1400)	0.34
			1773(1500)	0.90
Carbon black	0.03	382	1848(1575)	0.72
			1898(1625)	1.20
			1948(1675)	3.72
			1973(1700)	5.34
			1998(1725)	7.80
Carbon black	0.218	154	2173(1900)	5.52
			2273(2000)	9.00

Weimer [2] summarized the reaction rates k(T) and activation energy E of reaction between quartz and coke, charcoal and carbon black (Table 1) for β-SiC manufacture. The activation energy for different carbon materials is different. This might be caused by the difference of the other parameters, like particle size of quartz, type of quartz and contact between quartz and carbon etc. The reaction rate k(T) for the same carbon at the same temperature are generally consistent with each other.

In this study, kinetic modelling of pellets pelletized by different carbon materials, like charcoal, coke, coal and quartz and heated to different temperatures, is investigated. The simplified reaction rate expression is obtained after comprehensive study the previous data.

II. EXPERIMENTAL

The experimental part is thoroughly described in [1], and in this paper a short summary of it will be done. Quartz used is of high purity [1]. Charcoal, coke, coal and pre-heated coal were pelletized with quartz. Quartz, charcoal, coke, coal and pre-heated coal are crushed by tungsten carbide crusher and 20-mesh sieve is used to collect the powders smaller than 20 mesh. The particle size distributions of quartz and carbon materials are demonstrated in figure 1.

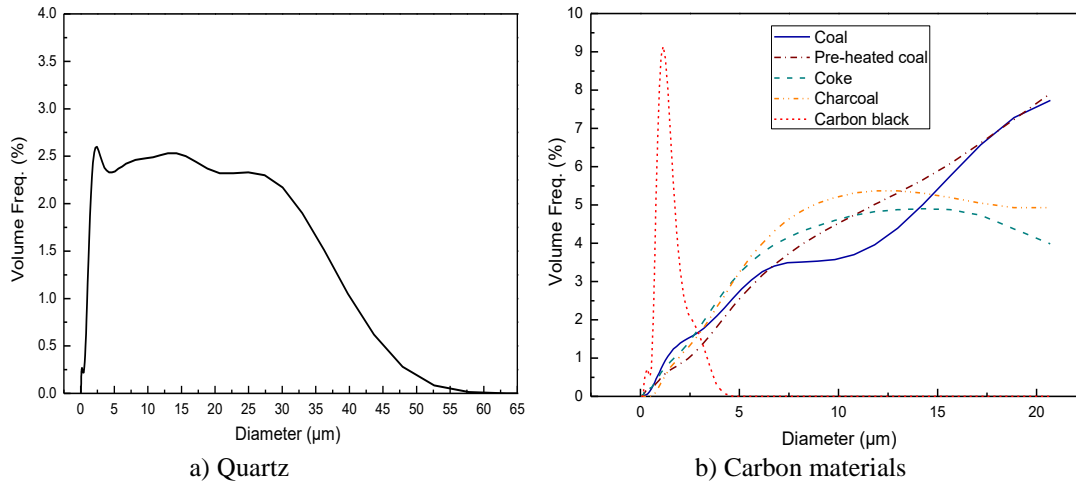a) Quartz   b) Carbon materials

Fig. 1 - Particle size distribution of quartz and carbon materials [x]

The pellets were made by the following procedure: quartz and carbon powder were mixed in the shaker mixer for 8 hours. Then the mixture is pelletized into 1-3 mm pellets using water as binder. For the last step, the pellets were heated in a drying oven at 373K(100°C) for 12 hours to vaporize the water in pellets. Content of carbon materials in the pellets is 15 $wt\%$.

Kinetic modelling was done from the point the pellets was heated to the holding temperatures to the end of SiC-producing step. Kinetic modelling is conducted with isoconversional method [3-11]. Equation 4 is the reaction rate expression. $f(\%)$ is the first order physio-geometric kinetic model(solid-state) describing the reduction of the rate as more of the pellet is transformed. % is here given as weightpercent of of original particle consumed, % = wt(t)/wt(org.1773K)100. Gas-solid interface factor $n = 0.40 \cdot X_{fix-C}^{-0.86}$ is defined to modify the solid-state reaction model making it suitable for the solid-state reaction occurs via the gas intermediate. X_{fixC} is the wt% of fix C in the particle. The temperature dependence $k(T)$ is expressed by the Arrhenius equation. A is a pre-exponential factor, E is the activation energy and R is the general gas constant, 8.3145 J/mol·K, T is absolute temperature in Kelvin.

$$\frac{d\%}{dt} = f(\%) \cdot k(T) \tag{4}$$

$$f(\%) = 1 - n \cdot \% \tag{5}$$

$$k(T) = A \cdot \exp(\frac{-E}{RT}) \tag{6}$$

III. RESULTS and DISCUSSION

3.1 Experimental results of rate of reaction (d%/dt) versus extent of reacted given in %

As shown in Figure 2, all the curve of d%/dt versus % for charcoal, coke, coal and pre-heated coal have the similar shape when comparing with carbon black. The experiments at 1898K(1625 °C) will not be discussed due to the slow reaction rate of quartz with coke, coal and preheated coal pellets. For experiments conducted at the temperatures of 1898K(1625 °C) and 1923K(1650 °C), the maximum reaction rate occurred when the holding experimental temperature was reached. For the experiment at 1948K(1675 °C), due to fast reaction rate, the holding temperature was obtained with the weight loss of about 12.5%. From the start of the period with the constant maximum temperature the curves show a linear decrease with % transformed, which means that equation 5 is valid.. After the SiC producing step, that is the linear area,, the SiO-producing step with the constant ratefollows. However, the lengths of constant step are not the same due to the different reactivates of carbon materials. The kinetic modelling in this paper will focus on the SiC –reaction, that is the linear area describing the reaction rate at constant temperature.
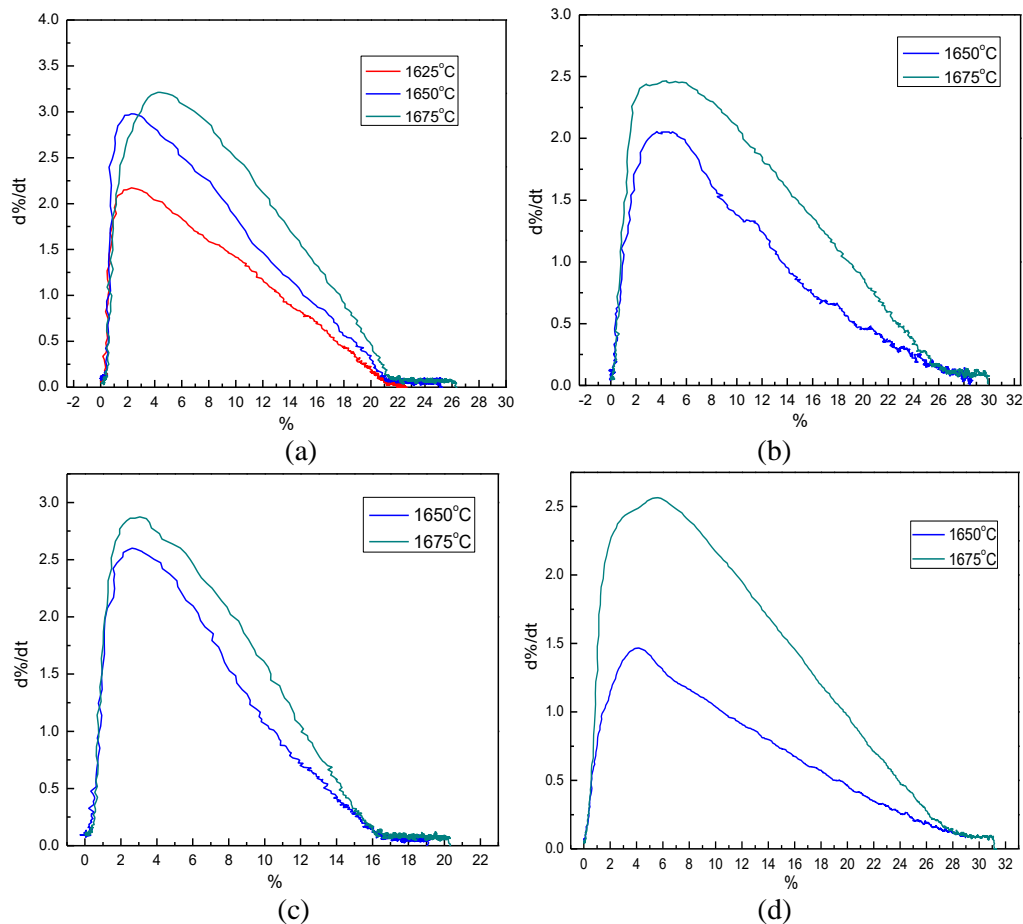
Fig. 2 - The rate versus temperature for the SiC-production from quartz with charcoal (a), coke (b), coal (c) and pre-heated coal (d) pellet.

3.2 Kinetic modelling

The activation energy and pre-exponential factor of different carbon materials pellets are listed in Table 2 according to equation 4-6. The activation energy of charcoal and coke are 570 kJ/mole and 563 kJ/mole, which are close to carbon black. For coal, the existence of liquid coal tar during heating increases the contact between quartz and carbon, and increases the reaction rate compared to the pre-heated coal. The coal is however not very temperature sensitive and has a lower activation energy (335 kJ/mole). Contrarily, the lack of the coal tar pitch hinders the reaction in the quartz and pre-heated coal pellet, but is very temperature sensitive. The activation energy of pre-heated coal is 913 kJ/mole.

Tab. 2 - Activation energy E and Pre-exponential factor A

Type of carbon	E / kJ·mole^{-1}	A / min^{-1}
Carbon black[20]	594	2.62E+16
Charcoal	570	1.21E+16
Coke	563	4.21E+15
Coal	335	3.85E+09
Pre-heated coal	913	1.00E+25

The relationship between gas-solid interface factor n and fix-C was obtained from experiments of quartz and carbon black[20]. As shown in Table 3, there is some deviation between the experimental and the calculated value of gas-solid interface factor. This indicates that the Gas-solid interface factor n is not only influenced by the amount of fix-C, but are also influenced

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by the type of carbon, the shape of carbon particle and the other parameters that originated from the difference of the carbon materials. In this paper, the carbon factor F_C is defined to describe the influence of different carbon materials that effect on the gas-solid interface reaction. For carbon black, carbon factor is set as 1. For the other carbon materials, F_C equals the experimental n references to the carbon black. Carbon factor F_C for charcoal is found to be 0.83, for coke 0.8, for coal 0.94 and for pre-heated coal 0.83.

$$n = 0.40 \cdot X_{fix-C}^{-0.86} \cdot F_C \tag{7}$$

Tab. 3 – Experimental and calculated Gas-solid interface factor n and Carbon factor F_C

Type of carbon	Experimental value	Calculated value	F_C
Carbon black[x]	0.038	0.039	1
Charcoal	0.045	0.054	0.83
Coke	0.038	0.047	0.80
Coal	0.061	0.065	0.94
Pre-heated coal	0.035	0.042	0.83

Equation 8 -11 show the reaction rate expression for quartz and charcoal, coke, coal and pre-heated coal pellet. The fitting results at 1898K(1625 °C),1923K(1650 °C), 1948K(1675 °C) are shown in Figure 3. The modelling results all have good consistency with the experimental results. It must be noted that in the first part of the curves the temperature is still increasing and the modelled rate is only determined at the constant holding temperature part, at the isothermal part of the experiments.

$$\text{Charcoal: } \frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot 0.83 \cdot \%) \cdot 1.21 \cdot 10^{16} \cdot \exp(-\frac{570000}{RT}) \tag{8}$$

$$\text{Coke: } \frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot 0.80 \cdot \%) \cdot 4.21 \cdot 10^{15} \cdot \exp(-\frac{563000}{RT}) \tag{9}$$

$$\text{Coal: } \frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot 0.94 \cdot \%) \cdot 3.85 \cdot 10^{9} \cdot \exp(-\frac{335000}{RT}) \tag{10}$$

$$\text{Pre-heated coal: } \frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot 0.83 \cdot \%) \cdot 1.00 \cdot 10^{25} \cdot \exp(-\frac{913000}{RT}) \tag{11}$$

At 1650 °C the k will be xx, xx, xx, xx for charcoal, coal, coke and preheated coal respectively, showing that charcoal and coal have a higher reduction rate compared to coke and pre-heated coal. The previous investigation [x] showed that the k(1650 °C) with carbon black was lower than ……, even though the carbon black had a much higher reaction area due to the fine particles.
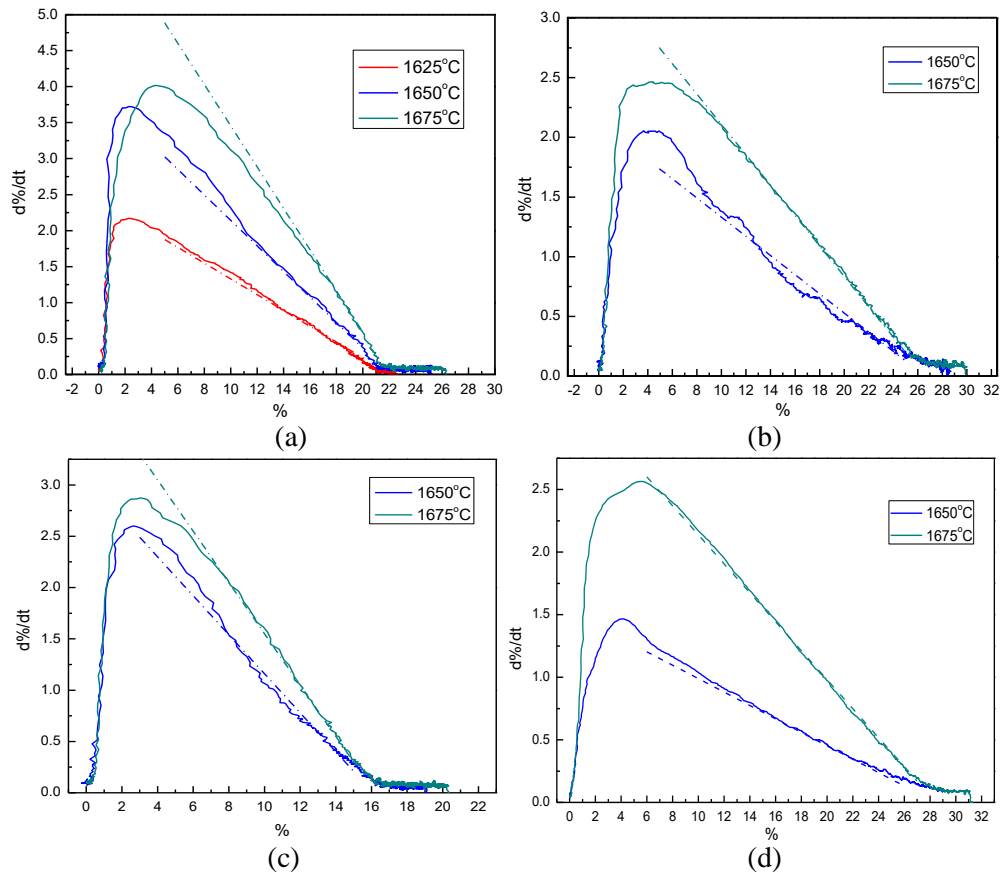
Fig. 3 - The rate versus temperature for the SiC-production from quartz with charcoal (a), coke (b), coal (c) and pre-heated coal (d) pellet. (Solid lines – experimental rates, dotted lines – modelled rates)

When comparing to previous studies it is seen that the activation energy for carbon black, charcoal and the coke are in the same area as summarised in Table 1 by Weimer [13] of 544 kJ/mole for charcoal and 552 kJ/mole for coke breeze. For the carbon black, it is higher compared to the literature which is in the area of 154-382 kJ/mole. The difference may be contributed to type of carbon black and type of quartz. The pre-exponential factor, which reflects how often the molecules collide during the reaction, is consistent with the value of activation energy.

Figure 4 shows the reaction rate of temperature dependence $k(T)$ expressed by Arrhenius equation from table 1 and 3. The $k(T)$ value from the references present the exponential relationship versus temperature (Figure 4, (a)). This indicates that the temperature plays the vital role regarding to the reaction rate. The $k(T)$ obtained from this study are fit to the exponential trend. Figure 4 (b) shows roughly linear relationship between $\ln(k(T))$ and $1/T$ and turns around 1998K(1725°C, $1/T=0.0005$). This implies although the difference between many types of carbon materials and quartz the reaction mechanism is the same above or below 1998K(1725°C) respectively. The 1998K(1725°C) is close to the melting point of β-cristobalite.
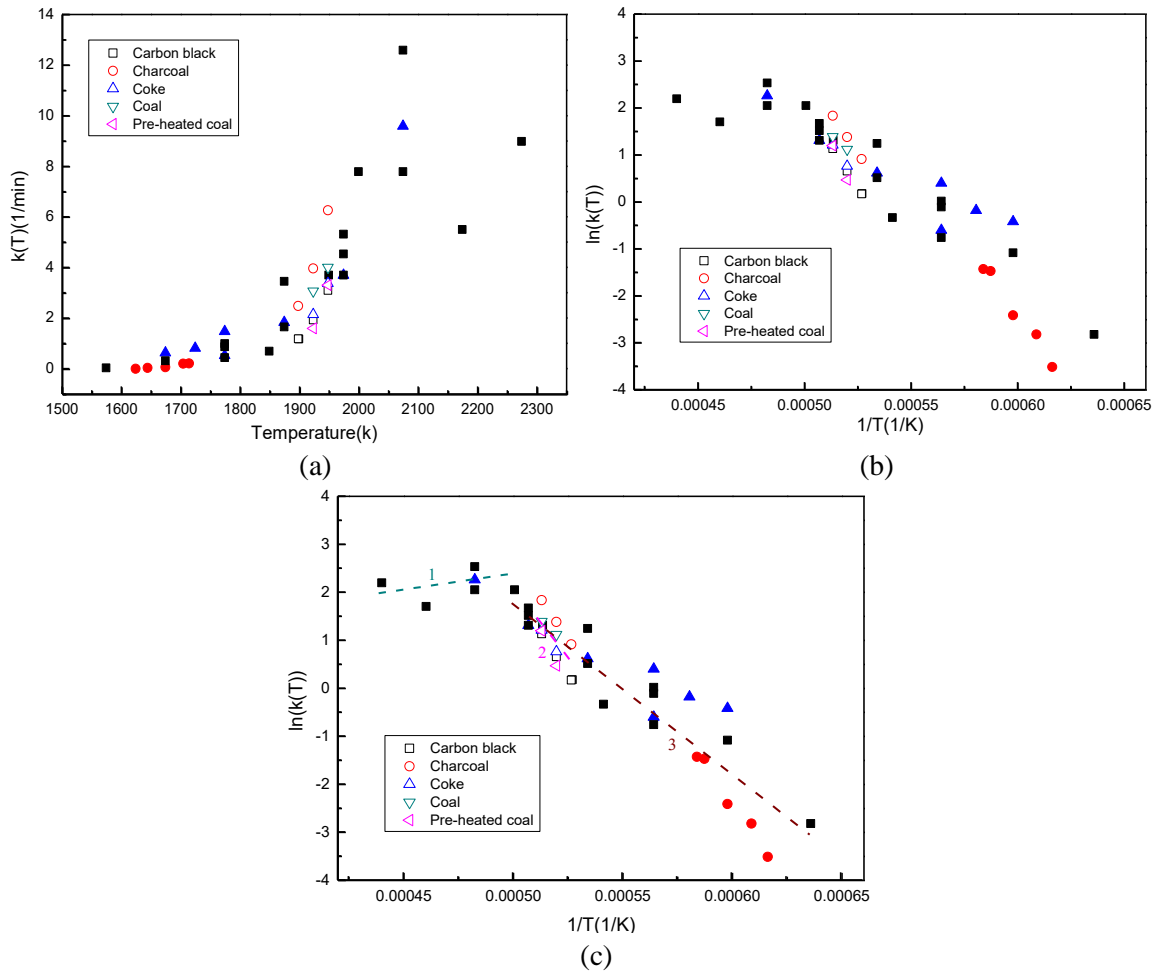
Fig. 4 - k(T) of carbon materials at different temperatures(a), ln(k(T)) versus 1/T(b) and ln(k(T)) versus 1/T(b) with trend line.(Solid icon: data from references, open icon: data from this study, dotted line: trend line.1: published data above melting of SiO_2, 2: data from present study 3: data below melting of SiO_2)

Tab. 4 - Activation energy of line 1-3 in Figure 4 (b)

No.	Data	E / kJ·mole^{-1}	Trend line	R^2
1	Above melting point	-20	ln(k(T)) = 2370.2/T + 1.0099	0.034
2	From this paper	518	ln(k(T)) = -52278/T + 28.109	0.347
3	Below melting point	307	ln(k(T)) = -36939/T + 20.394	0.8246

When dividing the data in Figure 4 (b) from the melting temperature at 1998K(1725°C) into two groups and making the trend line 1 and 3 for each, the activation energies could be obtained. As shown in Figure 4(c) and Table 4, the activation energy for reaction above/below 1998K(1725°C) are - 20kJ/mole and 307kJ/mole respectively. -20kJ/mole and 307kJ/mol could be regarded as the activation energy for all the different kinds of quartz and carbon in the pellet above/below 1998K(1725°C). Apparently, the solid-state reaction between quartz and carbon below 1998K(1725°C) is more difficult than the solid-fluid reaction above 1998K(1725°C). The trend line 2 is calculated based on the results of charcoal, coke, coal, pre-heated coal and carbon black from this study and the activation energy is 518 kJ/mole.

Table 5 shows the corresponding pre-exponential factor adopting activation energy from line No.2 and 3. The reaction expressions for quartz and charcoal, coke, coal, pre-heated coal and

carbon black pellets are shown by equation 12 and 13. It could be seen when 518kJ/mole and 307kJ/mole are adopted as the activation energy the reaction rate expressions are simpler.

Tab. 5 - Activation energy E and Pre-exponential factor A from line No.2 and 3

Type of carbon	Line No.2		Line No.3	
	E / kJ·mole^{-1}	A / min^{-1}	E / kJ·mole^{-1}	A / min^{-1}
Carbon black[20]		2.26E+14		4.27E+08
Charcoal		4.65E+14		8.66E+08
Coke	518	2.57E+14	307	5.19E+08
Coal		3.34E+14		6.76E+08
Pre-heated coal		2.22E+14		4.57E+08

$$\frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot F_C \cdot \%) \cdot A \cdot \exp(-\frac{518000}{RT}) \qquad (12)$$

$$\frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot F_C \cdot \%) \cdot A \cdot \exp(-\frac{307000}{RT}) \qquad (13)$$

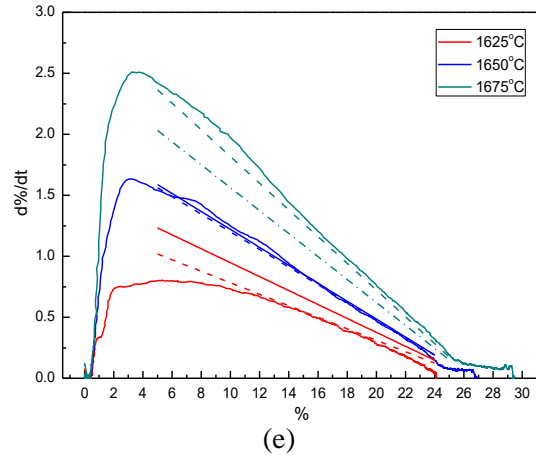(a)

(b)

(c)

(d)

(e)
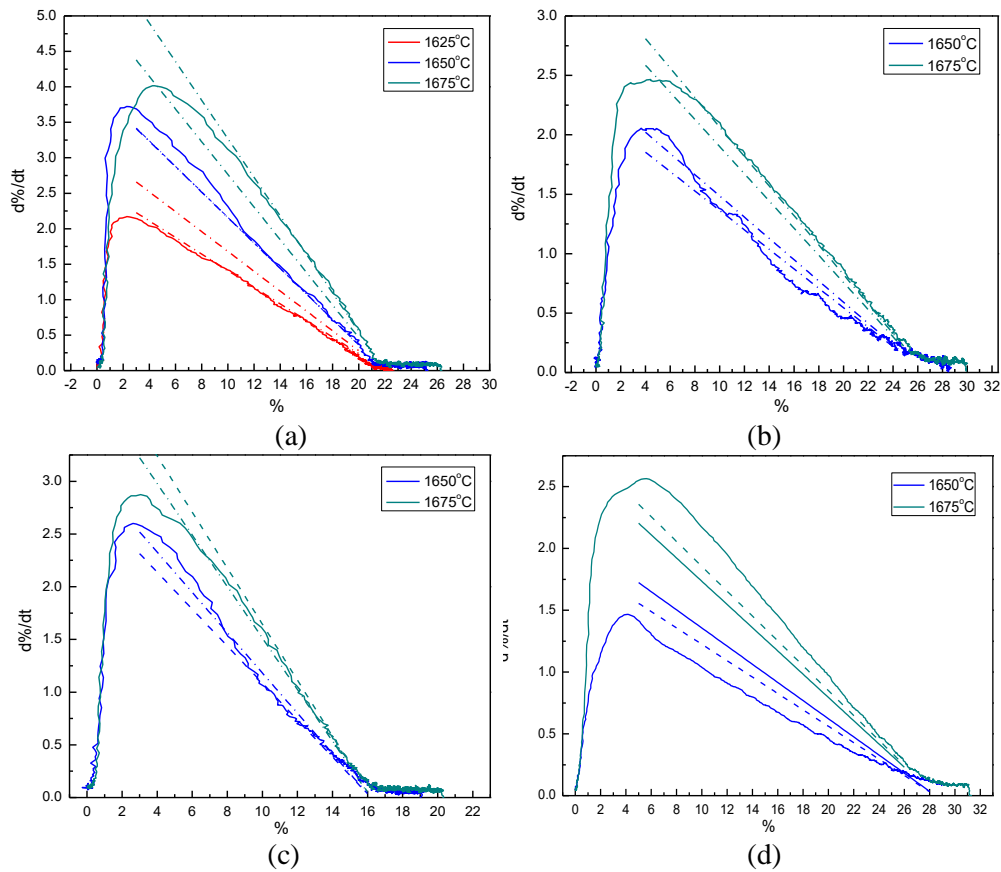
Fig. 5 - The rate versus temperature for the SiC-production from quartz with charcoal (a), coke (b), coal (c), pre-heated coal (d) pellet and carbon black [20] (e) (Solid lines – experimental rates, dotted lines – modelled rates at $E = 518$kJ/mole, dash dotted lines – modelled rates at $E = 307$kJ/mole)

The fitting results of equation 15 and 16 are shown in Figure 5. When the activation energy of is 518 kJ/mole, the modelled results still show the high consistency for charcoal, coke and carbon black. The coal and pre-heated coal present 10-20% of deviation. This could be explained the different reaction mechanism influence by volatile in coal and pre-heated coal. When activation energy is 307 kJ/mole, coal shows the high consistency again while the other materials show the 15-30% of deviation. This indicates that the parameters for example the different shape of quartz and carbon powder, the different melting point and the reaction atmosphereet al contribute these deviations. Even though several parameters are still unknown the deviations are still in the acceptable scale. This makes the equation 16 competent for the prediction of the reaction rate for the other kinds of raw materials.

IV. CONCLUSIONS

Kinetic modelling was done for at the isothermal part of the experiment to the end of SiC-producing step. The activation energy E of quartz and charcoal, coke, coal and pre-heated coal pellets at SiC-producing step are found to be 570kJ/mole, 563 kJ/mole, 335 kJ/mole and 913 kJ/mole. The pre-exponential factor A for the above four carbon materials are 1.21×10^{16}, 4.21×10^{15}, 3.85×10^{9} and 1.00×10^{25}. Carbon factor F_C for charcoal, coke, coal and pre-heated coal are 0.83, 0.80, 0.94 and 0.83.

When the published data below 1998K(1725°C) are included in a comprehensive study, the activation energy 307 kJ/mole could be used to predict the reaction rate quartz- and carbon-pellet neglecting the difference of raw materials at acceptable deviation. The reaction rate can be expressed as following simplified equation:

$$\frac{d\%}{dt} = (1 - 0.40 \cdot X_{fix-C}^{-0.86} \cdot F_C \cdot \%) \cdot A \cdot \exp(-\frac{307000}{RT})$$

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