Research Article

Pengfei Li, Jian Zhang, Biwei Luo, Yan Li, Jun Ji, Dongsheng He, Qifeng Tian*, and Yichang Chen*

Kinetics of Carbothermal Reduction Process of Different Size Phosphate Rocks

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Abstract: The effects of particle size on the apparent kinetics of carbothermal reduction process of phosphate rock were studied by non-isothermal thermogravimetric analyses. Phosphate rock of various particle size was reacted with coke and silica under high purity argon atmosphere. The apparent kinetic model and parameters of carbothermal reduction reaction of phosphate rock with different particle sizes were derived by combination of model-free (Flynn–Wall–Ozawa, Kissinger–Akahira–Sunose, Tang, Starink) and model-fitting (Coats–Redfern, Master-plots) methods. The results showed that the obtained apparent activation energy of reaction reduces from 371.74 kJ/mol to 321.11 kJ/mol as the particle size of phosphate rock decreasing from 100–150 μm to 38–48 μm . The reaction apparent kinetics was found to follow shrinking-core model and the conversion degree function equation is $G(\alpha) = 1 - (1 - \alpha)^{\frac{1}{2}}$ (α is conversion degree and $G(\alpha)$ is integral form of conversion degree function).

Keywords: phosphate rock; particle size; carbothermal reduction; apparent kinetics model; non-isothermal thermogravimetric analyses; apparent activation energy

1 Introduction

Phosphate rock is the main form of phosphorus in nature. Phosphate ore, one of the most important strategic resources of China, is the material basis for making phosphate fertilizer and fine phosphorus chemical products, and it plays an extremely important role in phosphorus chemical industry and agricultural production. China is an important producer and consumer of phosphate resources in the world. With the rapid development of the phosphate fertilizer industry and the increasing consumption of phosphate resources, it is predicted to run out of rich minerals of China around 2025 [1]. There are three types of traditional methods of making phosphoric acid from phosphate rock: wet process, thermal process, and kiln process [2]. The wet process requires higher grade of phosphate rock, and the prepared phosphoric acid contains many impurities. Kiln process is still in the research stage because its technology is not mature yet [3]. Middle and low-grade phosphate rock can be directly utilized via thermal processing, while its disadvantage is high energy consumption. The main reaction equation is shown in the follow Eq. (1) [4]:

However, the middle and low-grade of the phosphate rock in China is abundant and its utilization rate is low at present. Therefore, strengthening exploitation and utilization of middle and low-grade phosphate rock resources is vital to sustainable development of phosphorus industry [5].

In the phosphoric acid industry, phosphate ores with different particle sizes present different reaction activities.

***Corresponding Author: Qifeng Tian:** School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, Wuhan 430205, China; Key Laboratory of Green Chemical Process of Ministry of Education & Key Laboratory of Novel Reactor and Green Chemical Technology of Hubei Province, Wuhan Institute of Technology, Wuhan 430205, China; National Engineering Research Centre of Phosphate Resource Development and Utilization & Engineering Research Centre of Phosphate Resource Development and Utilization, Ministry of Education, Wuhan 430074, China; Email: qftian@wit.edu.cn

***Corresponding Author: Yichang Chen:** Hubei Research and Design Institute of Chemical Industry, Wuhan 430074, China; Email: hb_chem@126.com

Pengfei Li, Biwei Luo, Yan Li: School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, Wuhan 430205, China

Jian Zhang: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Jun Ji: School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, Wuhan 430205, China; Key Laboratory of Green Chemical Process of Ministry of Education & Key Laboratory of

Novel Reactor and Green Chemical Technology of Hubei Province, Wuhan Institute of Technology, Wuhan 430205, China

Dongsheng He: Xingfa School of Mining Engineering, Wuhan Institute of Technology, Wuhan 430074, China; National Engineering Research Centre of Phosphate Resource Development and Utilization & Engineering Research Centre of Phosphate Resource Development and Utilization, Ministry of Education, Wuhan 430074, China

Wang *et al.* [6] found that phosphate rock with smaller particle size holds larger specific surface area, which is conducive to increasing leaching rate. Phosphate rock with larger particle size has a limited contact area between reactants. As a result, the reaction cannot be proceeded fully, which reduces the decomposition rate of dolomite. Therefore, it is of great significance to study the influence of particle size on the industrial process of phosphoric acid.

Thermal analysis is a widely used research tool. In recent years, the most active field of thermal analysis is thermal analysis kinetics [7]. Luo *et al.* [8] studied the nitriding reaction kinetics of metal manganese powders with different particle sizes by thermogravimetric analysis, and found that the apparent activation energy of nitriding reaction decreased from 189.2 kJ/mol to 115.2 kJ/mol when the particle size of metal manganese powder was reduced from 40 mesh to 100 mesh. Peng *et al.* [9] utilized thermogravimetric analysis to investigate the thermal decomposition process of magnesite with different particle sizes, and they reported that the activation energy of thermal decomposition of magnesite decreasing with increase of the size of magnesite, owing to the rate-determining step of magnesite thermal decomposition process is gradually changed from chemical reaction to heat transfer and CO₂ diffusion inside the particle. Noboru *et al.* [10] studied the kinetics of vapor phase dephosphorization, found that a shorter residence time at a high temperature resulted in a smaller reduction fraction of tri-calcium phosphate (TCP). The effects of particle size on the pyrolysis characteristics of oil shale were explored by Yu *et al.* [11] with thermogravimetric-infrared analyzer. Their results showed that pyrolysis activation energy increased from 65.57 kJ/mol to 266.38 kJ/mol as the particle size of oil shale increased from 76 μm to 290 μm . Lu *et al.* [12] revealed that the activation energy of pyrolysis of coals reduces as the coal particle size decreasing by non-isothermal thermogravimetric method. Gong *et al.* [13] investigated hydrogen reduction of copper oxide with different particle sizes by thermal analysis, and they demonstrated that the reaction peak temperature increased with the increase of copper oxide particle size. When the copper oxide particle size increased from 50 nm to 400 nm, the activation energy of the reaction raised from 173.39 kJ/mol to 534.80 kJ/mol. The above studies showed that the particle size has a significant effect on the activation energy of the reaction. At present, there is little systematic research about apparent kinetics study of phosphate rock carbothermal reduction reaction with different particle size. In this paper, thermogravimetric (TG) and differential thermogravimetric (DTG) of phosphate rock with different particle sizes were measured by non-isothermal

thermogravimetry. Combining the model-free and model-fitting method, the kinetic model and parameters of phosphate rock carbothermal reduction with different particle sizes were derived to supplement theoretical basis of thermal processing of middle and low-grade phosphate rock.

2 Materials and Methods

2.1 Experimental instruments and reagents

The thermogravimetric data of samples with phosphate ore of different particle sizes were measured by a SDT-Q600 thermogravimetric analyzer (TA Corporation, USA). The phosphate ore comes from Mabian, Sichuan Province, and the main compositions and their contents in the phosphate ores were analyzed by X-ray fluorescence spectroscopy. The results are shown in Table 1. SiO₂ (A.R.) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) as fluxing agent and reactant. The industrial analysis results of reducing agent coke is shown in Table 2.

Table 1: Mass fraction of each chemical component of phosphate rock % (wt.)

Substance	P ₂ O ₅	CaO	SiO ₂	MgO
Content	24.9	52.18	9.4	6.64
Substance	Fe ₂ O ₃	Al ₂ O ₃	F	
Content	1.52	1.13	2.52	

Table 2: Industrial analysis results of reducing agent coke % (wt.)

Ingredient	Fixed carbon	Volatile matter	Ash	Moisture
Content	82.03	4.15	9.27	4.55

2.2 Experimental method

Reducing agent coke and fluxing agent SiO₂ were both passed through a 200-mesh sieving to diminish the influences of their sizes. Phosphate rock particles was screened out different sizes by 100, 150, 200, and 300 sample-sieving screens for later use. The three reagents (phosphorus rock, SiO₂ and coke) were accurately weighed and

fully mixed in stoichiometric ratio, pressed into pieces, and then placed in an oven at 60°C to dry to constant weight. Four groups of samples were prepared for non-isothermal thermogravimetry with different particle sizes of phosphate rock: (a) 38–48 µm; (b) 48–75 µm; (c) 75–100 µm; (d) 100–150 µm. The thermogravimetric data of samples with different particle sizes were measured with high-purity argon as protective gas. According to the capacity of the precision crucible, the mass of each sample is 5.5 mg ± 0.05 mg. It can be seen from the preliminary work of our group [14] and previous research [15, 16], the gas flow rate was determined as 100 mL/min. The temperature range is from room temperature to 1400°C, and heating rate is 5K/min, 10K/min, 15K/min and 20K/min, respectively.

3 Kinetic studies

The apparent kinetics of carbothermal reduction process of phosphate rock with different sizes using a combination of single heating rate and multiple heating rate method. The conversion degree α is calculated by weight loss of the mixed sample [17]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_e} \times 100\% \quad (2)$$

In formula (2), m_0 , m_t , and m_e are the mass of the sample at the initial time, the time t , and the end of the reaction, respectively.

According to the theory of non-isothermic dynamics, the differential equation of indefinite temperature dynamics is shown in formula (3) [18]:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = K(T)f(\alpha) \quad (3)$$

In formula (3), $f(\alpha)$ is the differential form of conversion degree function, dimensionless. $K(T)$ is the temperature dependence of the rate of weight loss and often modeled successfully by the Arrhenius equation (4):

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

In the formula (3) and (4), α is the conversion degree as defined in Eq. (2), dimensionless; t is reaction time, min; T is temperature, K; β is heating rate, K/min; A is pre-exponential factor, min⁻¹; E is apparent activation energy, kJ/mol; R is Gas Constant, 8.314 J/mol·K⁻¹. By combining Eq. (3) and (4), one can get Eq. (5):

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

The integral form of conversion degree function $G(\alpha)$ can be drawn in Eq. (6):

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} p(x) \quad (6)$$

The meanings of β , A , E , R , T and $f(\alpha)$ in the Eq. (6) are the same as Eq. (3) and (4), $G(\alpha)$ is the integral form of conversion degree function, dimensionless. x is equal to E/RT , which does not have analytical solution. The function $p(x)$ has no exact solution. Using different approximation of $p(x)$ generates different iso-conversional method.

3.1 Model-free method

3.1.1 Flynn–Wall–Ozawa (FWO) method

Flynn–Wall–Ozawa (FWO) method is an iso-conversional integral method and is based on the following equation using Doyle's approximation ($\ln p(x) \cong -3.315 + x$). Substituting Doyle's approximation into Eq. (6) results in FWO equation (7) [19–23]. The meaning of β , A , E , R , T and $G(\alpha)$ in the Eq. (7) is the same as Eq. (6). $[\beta]$ is the unit of heating rates β . Thus, for $\alpha = \text{constant}$, the plot $\lg \beta$ versus $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line, whose slope can be used to evaluate the apparent activation energy.

$$\lg\left(\frac{\beta}{[\beta]}\right) = \lg \frac{AE}{RG(\alpha)} - 2.315 - 0.4567 \frac{E}{RT} \quad (7)$$

3.1.2 Kissinger–Akahira–Sunose (KAS) method

Kissinger–Akahira–Sunose (KAS) method [24, 25] is based on the Coats–Redfern approximation of and Eq. (6) now can be simplified to KAS equation (8).

$$\ln\left(\frac{\beta}{T^2}\right) = \ln \frac{AR}{EG(\alpha)} - \frac{E}{RT} \quad (8)$$

Where the meaning of β , A , E , T , $G(\alpha)$ and R in the Eq. (8) is the same as Eq. (6). Using equation (8) the apparent activation energy can be obtained from a linear slope of the plot of $\ln(\beta/T^2)$ versus $1/T$ for various conversion degree α by the least square method, which is independent of the values of $G(\alpha)$ and A .

3.1.3 Tang method

The Tang *et al.* [26, 27] method is based on the approximate formula [27] which introduced into Eq. (6). Taking the log-

arithms of both sides, Eq. (9) is obtained as:

$$\ln \left(\frac{\beta}{T^{1.894661}} \right) = \ln \frac{AE}{RG(\alpha)} + 3.635041 - 1.894661 \ln E - 1.00145 \frac{E}{RT} \quad (9)$$

Where the meaning of β , A , E , T , $G(\alpha)$ and R in the Eq. (9) is the same as Eq. (6). The plots of $\ln(\beta/T^{1.894661})$ versus $1/T$ give a group of straight lines. The apparent activation energy E can be obtained from the slope of the regression line.

3.1.4 Starink method

Starink method [28] is one of the most suitable, accurate and advanced method, based on the recommendations of the International Confederation for Thermal Analysis and Calorimetry [29]. The equation of Starink method is presented as Eq. (10):

$$\ln \left(\frac{\beta}{T^{1.92}} \right) = C - 1.008 \frac{E}{RT} \quad (10)$$

Where C is a constant and the other symbols are the same as the above equations. In this method the apparent activation energy is determined from plots of $\ln \beta/T^{1.92}$ versus the inverse of T for various conversion degrees.

3.2 Model-fitting method

3.2.1 Coats-Redfern (CR) method

Coats-Redfern method [30] belongs to a model-fitting method which by asymptotic approximation and rearranging Eq. (6), the following CR equation (11) can be deduced based on the supposition in the Doyle approximation [19, 31]. The conversion degree function equation was established by Coats-Redfern (CR) method [32–41] that is a commonly method used for solid-solid reaction kinetics calculation.

$$\ln \left(\frac{G(\alpha)}{T^2} \right) = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (11)$$

The meaning of β , A , E , R , T and $G(\alpha)$ in the Eq. (11) is the same as Eq. (6). The different forms of conversion degree function equation $G(\alpha)$ in formula (11) was selected from reference [18]. According to solid-solid reaction kinetics theory, $\ln(G(\alpha)/T^2)$ and $1/T$ have a linear relationship under a constant heating rate. The results of CR method can be used as a comparison with those of master-plots method.

3.2.2 Master-plots method

The reaction models can be determined by using the master-plots method [27, 42–46]. Master-plots are reference theoretical curves depending on the kinetic model but generally independent of the kinetic parameters of the process [47]. The experimental TG data is easy to be transformed into master-plots form, then the experimental master-plots data can be compared with theoretical master-plots curves assumed by different reaction models, allowing the selection of appropriate reaction model. Taking the conversion point $\alpha = 0.5$ as reference point, the following Eq. (12) can be obtained from Eq. (6)

$$\frac{g(\alpha)}{g(0.5)} = \frac{p(x)}{p(x_{0.5})} \quad (12)$$

where $T_{0.5}$ means the absolute temperature where conversion degree reaches 50%. To draw the experimental master-plots of $p(x)/p(x_{0.5})$ versus α from experimental data obtained under different temperatures, an approximate formula [48] of $p(x)$ with high accuracy was used. Consequently, the master-plots method was used to determine reaction models in this paper.

4 Results and Discussion

4.1 TG-DTG thermal analysis of phosphate rock

The photos of compressed sample after carbothermal reduction in the tubular furnace are presented in Figure 1, which indicated that the carbothermal reduction started at about 90 min after heating temperature is reached and obvious segregation occurred with extended reaction time.

Figure 1: The slag after different reaction time at temperature of 1300 °C (a): 30 min, (b): 60 min, (c): 90 min, (d): 120 min, (e): 150 min, (f): 180min

Figure 2: TG and DTG Curves of carbothermal reduction of phosphate rock with different particle sizes. (a): 38–48 μm ; (b): 48–75 μm ; (c): 75–100 μm ; (d): 100–150 μm

Figure 2 is series of TG and DTG curves of four groups of samples with different particle sizes at various heating rates of 5K/min, 10K/min, 15K/min, and 20K/min, respectively. It can be seen from the TG curves that the first weight-loss stage is between 600–800°C, which is caused by thermal decomposition of dolomite [49], an impurity mineral in phosphate rock. The second obvious weight-loss stage begins at about 1160°C, which is the initial of carbothermal reduction reaction of the phosphate rock. The starting temperature of reaction was thought as the inflection point of the second weight-loss stage on the TG curve [17]. The two obvious peaks of DTG curves are equivalent to the two weight-loss parts of TG curves. The peak temperature increases with heating rate or particle size increasing, which will lead to larger temperature gradient between the out-

side and inside layer of sample and thermal hysteresis phenomenon is aggravated, and consequently the combined effects of heat and mass transfer limitations are very important for the reaction. The change in the kinetics characteristics might be due to the heat and mass transfer limitations within the large particles, which means the studied kinetics in this paper is apparent kinetics [50, 51]. The effects of heating rate and particle size on TG responses are consistent with results in the literature [9, 42–55]. Wang *et al.* [56] studied the thermal decomposition of phosphate rock by TG-DSC combined technology and found that the first weight-loss temperature decreases, and weight-loss rates increases as phosphate rock particle size decreasing. In addition, they also reported the initial temperature, peak temperature, and ending temperature of the de-

composition process of phosphate rock are significantly shifted to high temperature as heating rate augmenting. The decomposition rate of impurity dolomite decreases with increasing particle size, which is consistent with the results by Wang *et al.* [56]

4.2 Model-free analysis

Kinetic parameters calculations were elucidated with phosphate rock and its particle size is 48–75 μm . Figure 3 showed that the linear plots of KAS, FWO, Tang and Starink methods generated a correlation coefficient (R^2) higher than 0.98 for all of α values. The variation of apparent activation energy of carbothermal reduction of phos-

phate rock with conversion degree α calculated by KAS, FWO, Tang and Starink methods were shown in Figure 4.

From Figure 4 one can find the same trend of E versus α curves were obtained by different iso-conversional methods. In addition, it is obvious that the values of apparent activation energy calculated by KAS, FWO, Tang and Starink method are very close, which proves the reliability of calculated apparent activation energy. It can be seen from Figure 4 that as the reaction proceeds, the apparent activation energy of the reaction gradually decreases. Because the carbothermal reduction reaction of phosphate rock is a solid-solid reaction, there is no melting state in the early stage of reaction. The large diffusion resistance leads to high activation energy of at this stage. As the reaction temperature increases, the melt is formed gradually

Figure 3: Linear fit of apparent activation energy of phosphate rock with particle size 48–75 μm at different conversion degrees. (a): FWO; (b): KAS; (c): Tang; (d): Starink

Figure 4: Variation of apparent activation energy E with α for carbothermal reduction of phosphate rock with particle size 48-75 μm by different method

in the system, which reduces the diffusion resistance and the activation energy accordingly. When the conversion degree is up to 0.65, the apparent activation energy of the reaction is the lowest in the whole reaction. When the phosphate rock conversion degree reaches 0.90, the reaction driving force is weakened due to consumption of reactants, that is why apparent activation energy is larger in the end of reaction.

All applied iso-conversional methods can not suggest a direct way of evaluating either the pre-exponential factor or the integral form of the reaction model, which was established by model-fitting analysis.

4.3 Model-fitting analysis

The iso-conversional model-free method can only give the value of apparent activation energy but fail to obtain reaction model. Table 3 shows commonly used thirty reaction conversion degree function, where m is the index of different conversion degree functions under the same model. With CR method, the kinetics parameters and linear coefficients of fitted models for carbothermal reduction of phosphate rock under four heating rates were listed in Table 4. The results in Table 4 demonstrated that the fitting results by CR method are greatly dependable on the model selection.

From Table 4, one can see that there are six different models A1 and A1/2 (Avrami-Erofeev), R2 (Shrinking-core model), D5 (Diffusion), P1 (Maple power law), and C1 (Chemical reaction) gave a higher correlations coefficients (R^2) at all heating rates. On the other hand, according to Table 4, it could be found that the values of apparent activation energy corresponding to the reaction model R2 is the

Table 3: Differential and integral expressions of common reaction conversion degree function

NO.	Code	Reaction model	Differential $f(\alpha)$	Integral $G(\alpha)$
1–8	Am	Avrami-Erofeev	$m(1-\alpha)[- \ln(1-\alpha)]^{(m-1)/m}$	$[- \ln(1-\alpha)]^{1/m}$
		$m = 1, 2, 3, 4, 3/2, 1/4, 1/3, 1/2$		
9–14	Rm	Shrinking-core model	$m(1-\alpha)^{(m-1)/m}$	$1 - (1-\alpha)^{1/m}$
		$m = 2, 3, 4, 1/4, 1/3, 1/2$		
	Dm	Diffusion		
15	D1	1-D diffusion	$1/2\alpha^{-1}$	α^2
16	D2	2-D diffusion(Valensi)	$[- \ln(1-\alpha)]^{-1}$	$\alpha + (1-\alpha) \ln(1-\alpha)$
17	D3	2-D diffusion(Jander)	$(1-\alpha)^{1/2} [1 - (1-\alpha)^{1/2}]^{-1}$	$[1 - (1-\alpha)^{1/2}]^2$
18	D4	3-D diffusion(anti-Jander)	$3/2(1+\alpha)^{2/3} [(1+\alpha)^{1/3} - 1]^{-1}$	$[(1+\alpha)^{1/3} - 1]^2$
19	D5	3-D diffusion(Z-L-T)	$3/2(1-\alpha)^{4/3} [(1+\alpha)^{-1/3} - 1]^{-1}$	$[(1-\alpha)^{-1/3} - 1]^2$
20	D6	3-D diffusion(Jander, $n=2$)	$3/2(1-\alpha)^{2/3} [1 - (1+\alpha)^{1/3}]^{-1}$	$[1 - (1-\alpha)^{1/3}]^2$
21	D7	3-D diffusion(Jander, $n=1/2$)	$6(1-\alpha)^{2/3} [1 - (1+\alpha)^{1/3}]^{1/2}$	$[1 - (1-\alpha)^{1/3}]^{1/2}$
22	D8	3-D diffusion(G-B)	$3/2[(1+\alpha)^{1/3} - 1]^{-1}$	$1 - 2/3\alpha - (1-\alpha)^{2/3}$
23–27	Pm	Maple power law	$M\alpha^{(m-1)/m}$	$\alpha^{1/m}$
		$m = 1, 2, 3, 4, 2/3$		
	Cm	Chemical reaction		
28	C1	Reaction order($n=2$)	$(1-\alpha)^2$	$(1-\alpha)^{-1} - 1$
29	C2	Reaction order($n=3/2$)	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$
30	C3	Reaction order($n=3$)	$1/2(1-\alpha)^3$	$(1-\alpha)^{-2}$

Table 4: Calculating results of CR method on kinetic parameters of carbothermal reduction of phosphate rock with particle size 48–75 μm

$G(\alpha)$	$\beta = 5 \text{ K/min}$			$\beta = 10 \text{ K/min}$			$\beta = 15 \text{ K/min}$			$\beta = 20 \text{ K/min}$		
	Apparent activation Energy $E/\text{kJ}\cdot\text{mol}^{-1}$	$\ln A$	R^2	Apparent activation Energy $E/\text{kJ}\cdot\text{mol}^{-1}$	$\ln A$	R^2	Apparent activation Energy $E/\text{kJ}\cdot\text{mol}^{-1}$	$\ln A$	R^2	Apparent activation Energy $E/\text{kJ}\cdot\text{mol}^{-1}$	$\ln A$	R^2
1	457.66	7.95	0.97	326.07	18.43	0.96	405.63	22.21	0.95	448.84	25.54	0.96
2	216.21	25.53	0.96	344.09	15.98	0.95	189.69	5.28	0.95	211.18	7.13	0.96
3	135.73	22.68	0.96	364.42	12.85	0.94	117.72	/	0.94	131.96	0.78	0.95
4	95.49	8.66	0.95	387.49	9.11	0.94	81.73	/	0.93	92.35	/	0.95
5	296.69	26.85	0.96	334.82	17.31	0.95	261.67	10.99	0.95	290.40	13.34	0.96
6	1906.32	28.71	0.97	313.85	19.16	0.96	1701.22	120.66	0.96	1874.81	132.8	0.97
7	1423.43	58.77	0.97	315.16	19.22	0.96	1269.36	88.03	0.96	1399.48	97.28	0.97
8	940.54	28.71	0.97	317.81	19.17	0.96	837.49	55.27	0.96	924.16	61.56	0.97
9	215.33	2.37	0.74	336.38	17.23	0.74	206.70	6.38	0.75	220.00	7.55	0.77
10	161.76	26.32	0.62	339.99	16.78	0.62	156.28	2.43	0.64	165.54	3.33	0.65
11	125.59	25.92	0.53	342.93	16.38	0.52	121.47	/	0.54	128.56	0.38	0.55
12	322.60	17.46	0.98	325.90	17.92	0.98	328.08	17.98	0.99	336.29	18.29	0.97
13	405.03	27.48	0.95	327.64	17.94	0.94	359.02	17.29	0.93	407.44	21.09	0.95
14	424.95	45.47	0.96	326.86	17.93	0.95	370.07	17.91	0.94	426.27	22.31	0.95
15	630.40	0.46	0.88	320.54	18.92	0.88	594.13	35.60	0.88	641.56	39.07	0.90
16	740.98	19.45	0.92	319.46	18.90	0.91	659.16	40.20	0.91	729.65	45.40	0.92
17	770.51	2.16	0.94	319.15	18.90	0.94	702.39	43.00	0.93	779.11	48.64	0.95
18	569.10	28.05	0.86	321.41	18.51	0.86	537.90	28.76	0.86	579.56	31.82	0.88
19	1059.51	7.60	0.98	317.00	19.05	0.97	943.57	61.59	0.97	1039.81	68.52	0.97
20	835.38	28.39	0.96	318.55	18.85	0.95	744.27	45.57	0.94	841.40	52.76	0.95
21	189.86	54.65	0.95	347.62	15.11	0.94	166.39	2.75	0.92	190.45	4.85	0.94
22	747.01	28.34	0.93	319.36	18.80	0.93	687.02	40.95	0.92	756.53	46.04	0.94
23	56.65	14.13	0.79	418.61	4.58	0.78	51.31	/	0.77	56.98	/	0.81
24	83.97	19.34	0.82	385.67	9.80	0.82	77.15	/	0.81	84.82	/	0.84
25	138.61	23.75	0.85	356.89	14.21	0.85	128.85	0.06	0.84	140.49	1.19	0.87
26	302.54	27.26	0.87	331.83	17.72	0.87	283.94	12.19	0.87	307.51	14.09	0.89
27	466.47	28.13	0.88	324.22	18.59	0.88	439.04	23.96	0.88	474.53	26.65	0.89
28	656.64	28.56	0.98	321.27	19.02	0.96	582.88	36.58	0.96	642.04	40.98	0.97
29	142.28	24.60	0.79	352.52	15.06	0.76	123.23	0.51	0.76	136.51	1.79	0.75
30	644.82	28.91	0.82	319.75	19.36	0.81	571.63	37.55	0.81	625.46	41.55	0.80

nearest approximation of the values obtained by model-free analysis.

The knowledge of α as a function of temperature and the value of the apparent activation energy are essential in order to calculate the experimental master-plots of $p(x)/p(x_{0.5})$ against α from experimental data under a defined heating rate. Figure 5 showed the scattered experimental master-plots points of $p(x)/p(x_{0.5})$ against α and the theoretical master-plots curves corresponding to the $g(\alpha)$ functions for A1, A1/2, R2, D5, P1, and C1 models (from Table 3) under different heating rates.

As shown in Figure 5, all experimental master-plots of carbothermal reduction process at 5, 10, 15 and 20 K/min are consistent with theoretical master-plots of R2 model. The comparison of the experimental master-plots with theoretical ones indicated that the kinetic process for the carbothermal reduction process of phosphate rock was most probably described by the shrinking-core model R2, whose conversion degree function equation is $g(\alpha) = 1 - (1 - \alpha)^{\frac{1}{2}}$.

To calculate the pre-exponential factor (A), the conversion degree function equation was introduced into Eq. (5),

Figure 5: Master-plots of theoretical $g(\alpha)/g(0.5)$ vs α for A1, A1/2, R2, D5, P1, and C1 reaction models and experimental master-plots for carbothermal reduction of phosphate rock with particle size 48–75 μm at different heating rates

and the following equation was obtained:

$$1 - (1 - \alpha)^{\frac{1}{2}} = \frac{AE}{\beta R} p(x) \quad (13)$$

Where E in Eq. (13) represent the average value of the apparent activation energy obtained by model-free analysis.

The plot of $[1 - (1 - \alpha)^{1/2}]$ versus $p(x)E/(\beta R)$ for carbothermal reduction process of phosphate rock at different heating rates was displayed in Figure 6. For R2 model with $m = 2$ and $E = 325.08 \text{ kJ/mol}^{-1}$, the pre-exponential factor was found to be $A = 3.19 \times 10^9 \text{ min}^{-1}$ ($\ln A = 21.89$) with the aid of linear least square fitting. All the values are within the limit of error.

Based on the above calculation results, the kinetic equation can be obtained as:

$$1 - (1 - \alpha)^{\frac{1}{2}} = \int_{T_0}^T 10^{21.89} \exp\left(-\frac{3.91 \times 10^4}{T}\right) dT \quad (14)$$

Following the same calculation process of above studying, the kinetic parameters of carbothermal reduc-

Figure 6: Plotting $1 - (1 - \alpha)^{1/2}$ vs $p(x)E/(\beta R)$ at different heating rates and their linear-fitting (solid line)

tion of phosphate rock with particle sizes 38–48 μm , 75–100 μm , and 100–150 μm were calculated. The results were summarized in the Table 5.

Substituting the kinetic parameters in Table 5 into Eq. (6), the kinetic equations of the carbothermal reduction process of phosphate rock with different particle sizes were obtained. The results are summarized in Table 6.

It can be seen from Table 5 that as the particle size reduces, the apparent activation energy of the reaction and the logarithm values of pre-exponential factor decreases gradually. Xiao *et al.* [54] studied the effect of particle size on adsorption kinetics of cubic nano- Cu_2O and found that the adsorption activation energy and pre-exponential factor of nano- Cu_2O lowers as particle size of nano- Cu_2O decreases. From Table 5, one can see that the pre-exponential factor is not a constant but changes with apparent activation energy. This phenomenon is called dynamic compensation effect [53]. With the decrease of particle size, the contact between reactants is more efficient and the driving force of the reaction is increased. Therefore, reducing the particle size of phosphate rock can effectively accelerate carbothermal reduction reaction rate of phosphate rock. Salem *et al.* [57] investigated the effects of par-

Table 5: Kinetic parameters of carbothermal reduction process of phosphate rock with different particle sizes

Phosphate rock size / μm	Apparent activation Energy $E/\text{kJ}\cdot\text{mol}^{-1}$	$\ln A/\text{min}^{-1}$	Conversion degree function equation $G(\alpha)$
100~150	371.74	24.90	$1 - (1 - \alpha)^{1/2}$
75~100	351.13	23.69	$1 - (1 - \alpha)^{1/2}$
48~75	325.08	21.89	$1 - (1 - \alpha)^{1/2}$
38~48	321.11	21.68	$1 - (1 - \alpha)^{1/2}$

Table 6: Kinetic equations of carbothermal reduction process of phosphate rock with different particle sizes

Phosphate rock size / μm	Conversion degree function equation
100~150	$1 - (1 - \alpha)^{\frac{1}{2}} = \int_{T_0}^T 10^{24.90} \exp\left(-\frac{4.47 \times 10^4}{T}\right) dT$
75~100	$1 - (1 - \alpha)^{\frac{1}{2}} = \int_{T_0}^T 10^{23.69} \exp\left(-\frac{4.22 \times 10^4}{T}\right) dT$
48~75	$1 - (1 - \alpha)^{\frac{1}{2}} = \int_{T_0}^T 10^{21.89} \exp\left(-\frac{3.91 \times 10^4}{T}\right) dT$
38~48	$1 - (1 - \alpha)^{\frac{1}{2}} = \int_{T_0}^T 10^{21.68} \exp\left(-\frac{3.86 \times 10^4}{T}\right) dT$

ticle size distribution on barite reduction and revealed the value of activation energy decreases as particle size distribution of barite is shifted to finer sizes. Activation energy falls approximately 9.0 kcal when the barite particle range changes from (−140, +230 mesh) to (−230, +400 mesh), but more decrease in particle size has little effect on apparent activation energy. The apparent activation energies with various particle sizes of phosphorus rock in Table 5 demonstrated the similar trend as barite carbothermic reduction. Liu *et al.* [58] probed on the effects of microwave and conventional heating on the carbothermal reduction reaction of manganese ore powder and found that reducing the particle size of manganese ore powder can increase the reaction rate. The reaction rate was also significantly increased with reduction of ore particle size till 150 mesh. It was indicated that the particle size of the manganese ore powder has an optimal value. In this study, there is no significant difference in the apparent activation energy of the reaction for the particle size of the phosphate rock is reduced from 48–75 μm to 38–48 μm , which possibly due to the fact that the phosphate rock particles are too thin and some of refractory materials formed by the reaction wrapped the rock particles, which leads the reaction cannot proceed sufficiently [6].

5 Conclusions

TG and DTG data were measured at different heating rates for carbothermal reduction of phosphate rock with different particle sizes by using the combination of model-free (FWO, KAS, Tang and Starink method) and model-fitting (CR and Master-plots) method. The apparent kinetic three factors of were calculated: E , $\ln A$, and $G(\alpha)$. The main conclusions were listed in the follow:

1. The fitting results showed that the mechanisms are consistent with the shrinking-core model and reaction conversion degree function equations of different particle sizes of phosphate rock were obtained;

2. The apparent activation energy decreases from 310 kJ/mol to 350 kJ/mol, and the logarithmic value of the pre-exponential decreases from 24.90 to 21.68 as the particle size of the phosphate rock reduces from 100–150 μm to 38–48 μm ;
3. Reducing the size of the phosphate rock can increase the rate of carbothermal reduction reaction of phosphate rock.

Supplementary Materials: The analyses and fitting results of samples with particle sizes at 38–48 μm , 75–100 μm and 100–150 μm by model-free and model-fitting methods are available online at www.mdpi.com/xxx/s1, Figure S1: title, Table S1: title, Video S1: title.

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Appendix A

List of abbreviations and symbols:

α	conversion degree, dimensionless;
$G(\alpha)$	the integral form of the reaction conversion degree function, dimensionless;
m_0	the mass of the sample at the initial time, mg;
m_e	the mass of the sample at the end of the reaction, mg;
m_t	the mass of the sample at the time t, mg;
$[\beta]$	the unit of the heating rate;
β	heating rate, K/min;
E	apparent activation energy, kJ/mol;
$f(\alpha)$	the differential form of the reaction conversion degree function, dimensionless;
T	temperature, K;
x	equal to E_a/RT ;
A	pre-exponential factor, min^{-1} ;
C	a constant, dimensionless;
CR	Coats-Redfern;
FWO	Flynn-Wall-Ozawa;
$K(T)$	Arrhenius equation.
KAS	Kissinger-Akahira-Sunose;
R	Gas Constant, $8.314 \text{ J/mol}\cdot\text{K}^{-1}$;