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Preparation of Calcined Kaolin by Efficient Decarburization of Coal-Series Kaolinite in a Suspended Bed Reactor

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Abstract: The reaction process, mechanism, and kinetics of the decarbonation of coal-series kaolinite (CSK) were investigated using the thermal analysis (TG)–infrared spectrum analysis (IR) coupling method. A pilot test was performed using a suspended calcination system. Further, the carbon content, phase composition, whiteness, oil-absorbed value, and micromorphology of calcined kaolin were characterized. Results showed that the decarburization reaction of CSK was a two-step reaction that mainly occurred in the ranges of 593 °C–836 °C. The mechanism of the decarburization reaction was a phase-boundary reaction (unreacted-core shrinking model) with an activation energy of 214.56 kJ/mol. Calcination at 900 °C or 950 °C for ~3.3 s in a suspension reactor resulted in the decarburization rate of CSK becoming >99.9%. The whiteness of calcined kaolin was mainly positively associated with the decarburization rate, and increasing the calcination temperature aided in increasing the whiteness. The oil-absorbed value of calcined kaolin was positively correlated with the specific surface area. Insufficient or over-calcination decreased the oil-absorbed value of calcined kaolin products. The calcined kaolin product with a whiteness of 89.3% and an oil-absorbed value of 76.1 g/100 g was obtained via suspension calcination process, which meets the requirements of calcined kaolin for paper-making.

Keywords: coal-series kaolinite; calcined kaolin; decarburization kinetics; suspension reactor; whiteness; oil-absorption value



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1. Introduction

High-quality kaolin is the most commonly used white pigment in the paper industry [1–3]. Worldwide, the paper industry consumes 12–15 million tons of high-quality kaolin annually, accounting for more than 75% of its total consumption [4–6]. Recently, China's high-quality kaolin clay has been facing depletion after a long history of consumption and large-scale mining. However, China has the world's richest coal-series kaolinite (CSK) resources, with proven reserves of 1.673 billion tons and predicted reserves of up to 18 billion tons [7,8]. Moreover, the chemical composition of CSK is similar to that of high-quality kaolinite; thus, it is an ideal resource for replacing high-quality natural kaolin [9,10]. Therefore, conducting technical research on CSK to replace natural kaolin is of great practical importance.

CSK is a coal gangue with kaolinite as its main component, which contains more than 80% of kaolinite [11,12]. CSK is usually associated with coal; it contains coal with some impurity components, which make its color typically gray and black. Compared with natural kaolin, CSK contains many impurities and has poor color; thus, it cannot be used directly in the paper industry [13–15]. However, CSK can obtain a whiteness comparable to that obtained using high-quality natural kaolin after undergoing sufficient decarbonization under an oxidizing atmosphere. Moreover, the large number of pores formed by the dehydroxylation of kaolinite during calcination considerably enhances the ink adsorption capacity of the product [8,16,17]. Therefore, high-quality calcined kaolin products can completely replace natural kaolin for several industrial applications, including paper and

coatings [2]. The key technology associated with CSK processing is carbon removal [8,16]. However, the carbon in CSK exhibits complex fugacity, and many carbon particles are encapsulated inside the kaolinite particles, making CSK decarbonization extremely difficult [16]. Currently, the rotary kiln process is usually used for the calcination of CSK. Nonetheless, complete decarburization requires several hours of calcination in a rotary kiln, affording low calcination efficiency and high energy consumption [18–20]. During the calcination of CSK, kaolinite decomposition and complex phase-transformation reactions occur [8,16]. These reactions overlap and interact with each other, so the calcination of CSK cannot be regarded as the combustion process of low-quality coal [21,22]. Therefore, an in-depth study of the mechanism and reaction kinetics of carbon removal from CSK is necessary to develop a high-efficiency calcination technology.

Thermal analysis is usually used in studying reaction kinetics [23,24]. The reaction conversion rate was calculated using the mass or heat data of the sample, and then the reaction mechanism and kinetics were subsequently analyzed [25]. During the calcination of CSK, decarburization reactions, kaolinite decomposition, and phase-transformation reactions occur simultaneously, and the mass and heat are superimposed [21]. Therefore, it is difficult to determine the decarbonation reaction of CSK using the conventional method. However, the gas products released by carbon combustion and kaolinite decomposition include CO_2 and $\text{H}_2\text{O}_{(\text{g})}$, exhibiting significant infrared (IR) absorption effects. Therefore, CO_2 and $\text{H}_2\text{O}_{(\text{g})}$ can be detected and separated using the TG–IR method [21]. Previous studies have confirmed the effectiveness of the characterization of CO_2 and $\text{H}_2\text{O}_{(\text{g})}$ released by the calcination of CSK [21,26]. The release flow of CO_2 is directly related to the combustion reaction of carbon, and the infrared absorption intensity can be used for the quantitative analysis of gas products. Therefore, the conversion rate of the decarbonization reaction can be calculated using the release curve of CO_2 . The kinetics calculated from the release characteristics of CO_2 products exhibit the intrinsic kinetics associated with the decarbonization reaction of CSK, providing a basis for analyzing the decarbonization reaction mechanism and control.

Herein, CSK obtained from Junggar coalfield, Inner Mongolia, China, was used as raw material. The reaction process, gas products, reaction mechanism, and kinetics of CSK during calcination were studied using the TG–IR method. A new method for calculating kinetics based on gas products was proposed. The CO_2 release flow data were used to calculate the conversion rate of the decarbonization reaction. The kinetic equation of the decarbonization reaction was calculated using the general integral method and the Kissinger method. The kinetic equation was used to predict the effect of temperature and time on the decarbonization reaction of CSK. A pilot test was conducted on the suspension calcination system, and the carbon content, phase composition, whiteness, oil-absorbed value, and micromorphology of the product were characterized. Thus, a systematic method for the suspension calcination of CSK was established, and the results provided a basis for developing new technology and production control.

2. Materials and Methods

2.1. Raw Materials

CSK samples were obtained from Junggar coalfield (the largest open-pit coal mine in Asia) in Ordos, Inner Mongolia, China. The collected sample is the exposed rock layer near the coal mine, also known as “white gangue”. Its mineralization conditions are similar to those of coal gangue in coal seams; however, its coal content is lower, making it suitable for the preparation of calcined kaolin. The original ore is a massive CSK with grayish-white color, dense structure, weak bonding, and smooth cross-section. About 10 tons of CSK samples were collected, and the same batch of material was used for the analysis and pilot test. The CSK samples were crushed to 3–5 mm using a jaw crusher and then ground in a ball mill. After grinding, the material was sieved with a standard 200-mesh sieve, and the sieved material was readded to the ball mill. The particle size of CSK after grinding is $d_{50} = 53.28 \mu\text{m}$. Subsequently, the ground product was encapsulated in nylon bags.

A D/MAX-2200 X-ray diffractometer from RIKEN Japan was used to analyze the minerals of CSK. The test conditions were as follows: Cu target K α rays, tube voltage (45 kV), and tube current (40 mA). The X-ray diffraction (XRD) pattern of the raw material is shown in Figure 1.

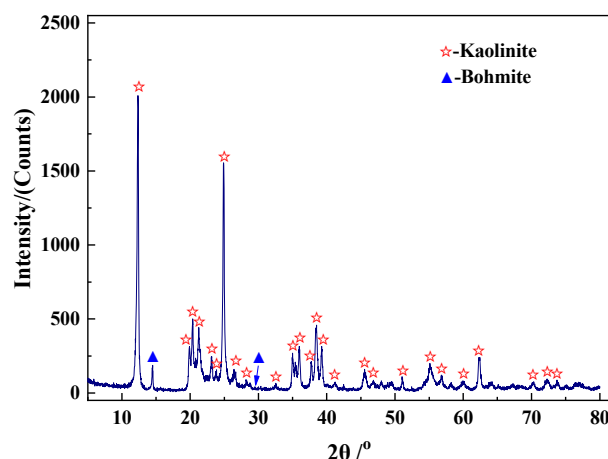


Figure 1. XRD analysis spectrum of CSK.

Figure 1 shows that the main minerals in the CSK samples are kaolinite and boehmite. The XRD characteristics of other minerals are not obvious.

The chemical composition of CSK was analyzed by X-ray fluorescence spectroscopy (XRF, S4PIONEER, Bruker, Germany) operated at X-ray tube parameters of 4.2 kW, 60 kV (max), and 140 mA (max). The results of the XRF analysis are shown in Table 1.

Table 1. Chemical composition of raw materials (wt.%).

Elements	SiO ₂	Al ₂ O ₃	CaO	TiO ₂	Fe ₂ O ₃	K ₂ O	MgO	SO ₃	P ₂ O ₅
Content	45.26	36.74	2.21	1.21	0.65	0.12	0.07	0.06	0.10

The chemical composition of CSK was obtained via semiquantitative calculations based on the results of Figure 1 and Table 1, as shown in Table 2. In Table 2, the coal content was analyzed according to the industrial analysis method of coal (GB/T212-2008).

Table 2. Chemical composition of CSK sample (wt.%).

Chemical Composition	Kaolinite	Boehmite	Quartz	Rutile	Hematite	Coal
Percentage content	87.32	5.70	2.37	1.35	0.36	2.78

As shown in Table 2, the contents of kaolinite and boehmite in CSK were 87.32 and 5.70 wt.%, respectively. The less abundant elements (Si, Ti, and Fe) were present as stable oxides, such as SiO₂, TiO₂, and Fe₂O₃, with converted contents of 2.37, 1.35, and 0.36 wt.%, respectively. The coal content was 2.78 wt.%. TiO₂, Fe₂O₃, and coal adversely affected the whiteness of calcined kaolin products [1,2].

2.2. TG-IR Experiments

In the combined TG-IR system, the thermal analyzer used was STA 409PC manufactured by NETZSCH (Germany), and the IR spectrometer was FTIR-7600 manufactured by Bruker (Germany). The wave number of the infrared detector was 4000–400 cm^{−1}. Kinetic experiments were performed using the multiple heating rate method [27]. The heating rates were 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. The sample mass was 6.0 ± 0.5 mg, the atmosphere was air, and the flow rate was 75.0 mL/min. The reaction process of CSK

during calcination was analyzed using the collected TG and IR data. The IR absorption data of CO₂ produced by CSK were collected, and the CO₂ release flow curve was obtained via deconvolution calculation. The decarbonation reaction characteristics, reaction mechanism, and kinetics of CSK were further analyzed.

2.3. Kinetic Methods

The kinetic equation for thermal analysis in integral form is [23,28]

$$G(\alpha) = A \exp(-E/RT) t \quad (1)$$

where α is the reaction conversion, $G(\alpha)$ is the mechanism function, A is the prefactor, s⁻¹, E is the activation energy, kJ/mol, R is the gas constant, 8.314 J/mol, T is the temperature, K, and t is the time, s.

The reaction conversion rate α is defined as the fraction of the recently completed reaction. The equation for calculating the conversion rate α using the CO₂ gas release flow data is

$$\alpha = S_T / S_{total} \quad (2)$$

In Equation (2), S_T is the integrated area of the CO₂ release curve, and S_{total} is the total integrated area of the CO₂ release curve. The conversion rate α represents the percentage of CO₂ currently released in the total released CO₂.

The Kissinger method and the general integration method were used for kinetic analysis [29,30]. Specifically, we first assumed the $G(\alpha)$ function, and then performed a linear fit to the α - T curve to determine A and E . The Kissinger method is as follows [29].

$$\ln \left(\frac{\beta_i}{T_{pi}^2} \right) = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T_{pi}}, \quad i = 1, 2, 3, 4 \quad (3)$$

where β_i is the rate of temperature rise (°C/min) and T_{pi} is the peak temperature on the CO₂ release curve.

The general integral is expressed as follows [30].

$$\ln \left[\frac{G(\alpha)}{T^2} \right] = \ln \left\{ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right\} - \frac{E}{RT} \quad (4)$$

Hu and Shi systematically summarized a total of 41 $G(\alpha)$ functions suitable for characterizing solid-state reactions [31]. Each of the 41 $G(\alpha)$ functions was selected, and a linear fit was made to the α - T data. The appropriate mechanism function was determined using the linear correlation coefficient r . For the correct mechanism function, the value of r was kept close to 1. E and A were obtained from the slope and intercept of the fitting straight line, respectively. The kinetic equations for the decarbonation reaction of CSK were obtained by substituting A , E , and $G(\alpha)$ into Equation (1).

2.4. Pilot System for Suspension Calcination

A new process system was designed for efficient decarburization of coal series kaolin. A schematic of the suspension calcination pilot system is shown in Figure 2. The system is composed of a hot blast stove, feeder, suspension reactor, preheater, cooling cyclone, product bin, dust collector, and centrifugal fan. The preheater comprises two cyclones, C1 and C2, connected in series. The material was added from the C1 cyclone inlet and passed through C1 and C2 for preheating. The preheated material entered from the bottom of the suspension reactor and reacted therein. The calcined material was separated by the C3 cyclone. The material coming out of C3 was divided into two parts. One part was readmitted to the reactor (to extend the residence time), while the other part went to the cooling cyclone, where it cooled before being discharged to the product bin. The energy for the system was provided using a hot blast stove, which was fueled by pulverized coal. The temperature and air supply of the hot blast stove were strictly controlled during the pilot

test to ensure the full combustion of pulverized coal to prevent any effect on the whiteness of the calcined kaolin products. The hot air from the hot blast stove was discharged after passing through the suspension reactor, C3→C1 cyclone, dust collector, and centrifugal fan.

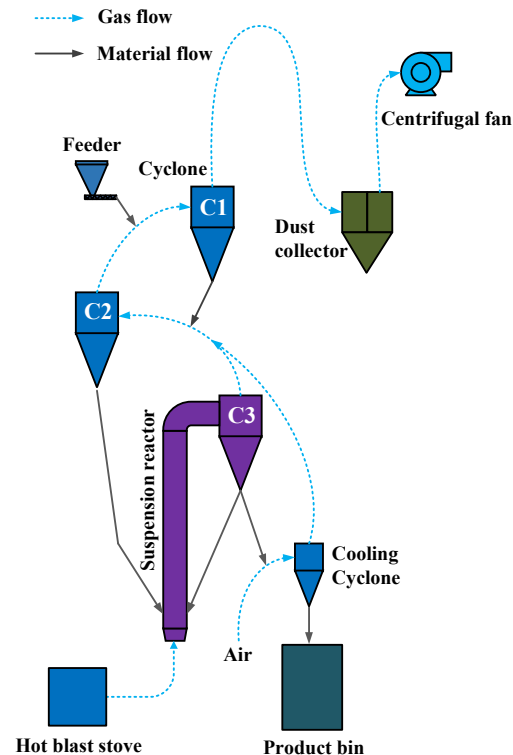


Figure 2. Schematic showing the suspension calcination pilot system.

The test parameters were as follows: the temperature in the middle of the suspension reactor was 700 °C–950 °C (with an interval of 50 °C) and the O₂ content in the outlet gas was >10%. The pressure at the outlet of the C1 cyclone was controlled from −3200 to −2800 Pa. The effective residence time of the material in the suspension reactor and in C5 was ~3.3 s. The test was run continuously for 24 h at a charge rate of 50 kg/h. Six temperature parameters (700 °C–950 °C, with an interval of 50 °C) were set in the pilot test, and each temperature was run steadily for 3 h. Samples were taken at 30-min intervals. Six samples were extracted at each temperature for analysis.

2.5. Characterization of Calcined Kaolin

A high-sensitivity high-frequency IR carbon/sulfur analyzer (CS-910, Chuangxiang, China) was used to analyze the amount of residual carbon in calcined kaolin. The measurement range of the instrument is 0.0001–99.99%. The whiteness of calcined kaolin was determined by an intelligent whiteness tester; the instrument is WSB-V1 (the method refers to GB/T5950-2008). The oil-absorbed value of calcined kaolin is referred to as GB-T5211.15-2014. XRD, scanning electron microscopy (SEM), and the Brunner–Emmet–Teller (BET) measurement method were used to evaluate the microstructure of calcined kaolin products.

3. Results and Discussions

3.1. Thermal Analysis

The TG and differential thermogravimetry (DTG) curves of the thermal analysis of CSK are shown in Figure 3a,b, respectively.

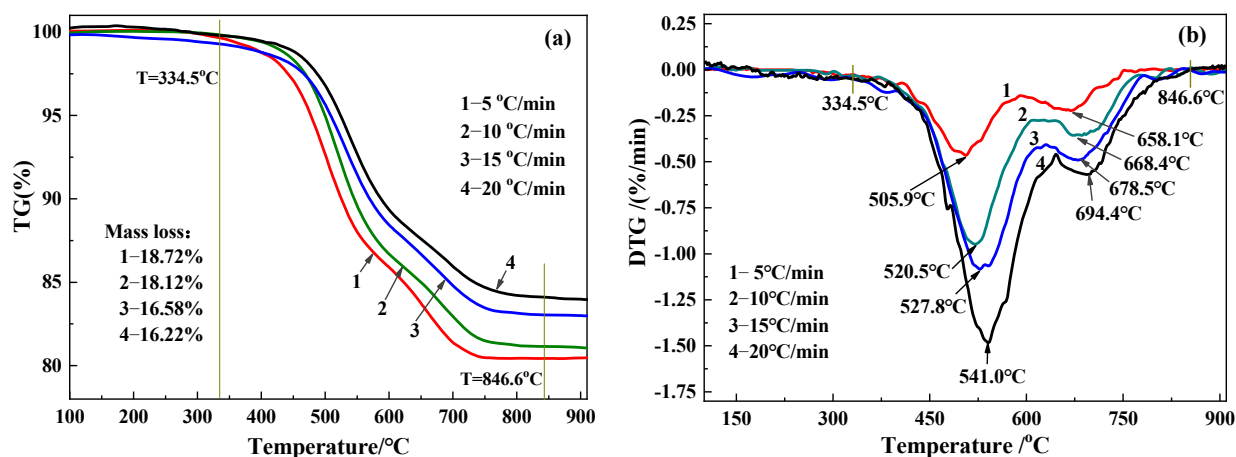


Figure 3. Thermal analysis of (a) TG and (b) DTG curves of CSK.

As shown in Figure 3a,b, the mass loss of TG from CSK started at ~ 334 °C and ended at 846 °C, with the mass loss ranging from 16.22% to 18.72%. The appearance of two peaks on the DTG curve indicated that the reaction contained two phases, and the area of the left peak was approximately twice that of the right peak. The overlapping of the two peaks indicated that the calcination of CSK was a complex reaction and the two phases cannot be separated.

3.2. IR Spectral Analysis

The IR absorption spectra of the gaseous products released from CSK during calcination are shown in Figure 4.

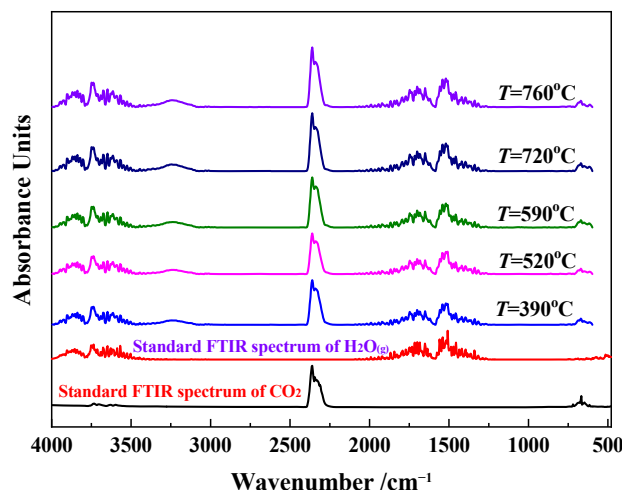
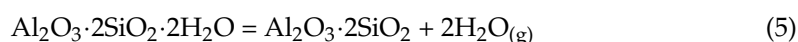
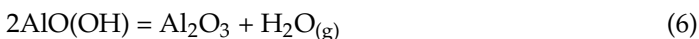


Figure 4. Infrared absorption spectrum of gas products (5 °C/min).

Figure 4 shows that the gas products released from CSK during calcination produced IR absorption mainly in three bands: 4000–3500 cm^{-1} , 2400–2250 cm^{-1} , and 2000–1300 cm^{-1} . Based on the standard spectral library, the gas product was observed to mainly contain two groups: hydroxyl and carbonyl. Furthermore, 4000–3500 cm^{-1} and 2000–1300 cm^{-1} were the absorption bands associated with hydroxyl groups, and the corresponding gas product was $\text{H}_2\text{O}_{(\text{g})}$. The absorption band for carbonyl groups was 2400–2250 cm^{-1} , and the corresponding gas product was CO_2 . Based on the chemical analysis of CSK, it was inferred that $\text{H}_2\text{O}_{(\text{g})}$ was a gaseous product of kaolinite and boehmite decomposition, while CO_2 was a gaseous product of coal combustion. The reaction is as follows.





According to the Lambert–Beer law, the absorbance was positively related to the concentration of the gaseous product, so the quantitative analysis of the gaseous product can be performed using IR absorption spectroscopy [32]. The release flow curves of $\text{H}_2\text{O}_{(\text{g})}$ and CO_2 were quantitatively resolved using the IR spectral data in Figure 4 and are shown in Figure 5a. The release flow curves of CO_2 at the four heating rates are compared in Figure 5b.

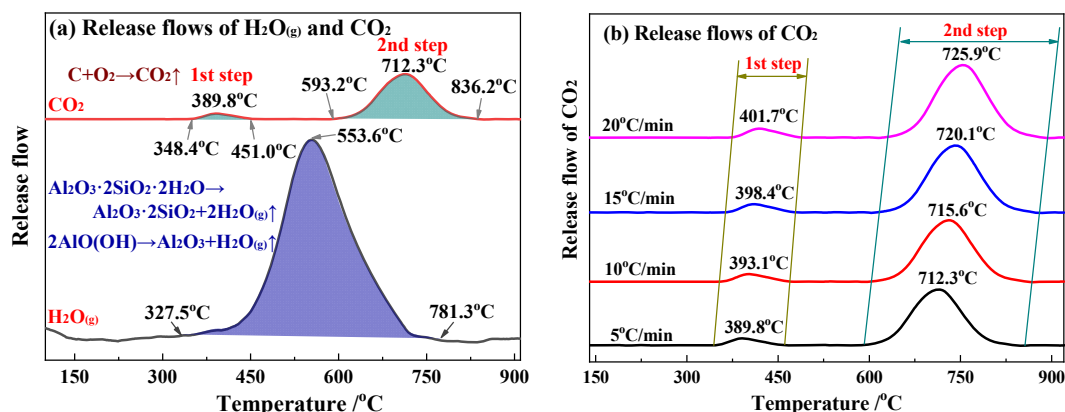


Figure 5. Release flow curve of gas products.

Figure 5a shows that the CO_2 release curve was clearly divided into two steps: the first step from 348 °C–451 °C and a peak temperature of 389.8 °C. The reaction of first step may be caused by the burning of organic matter in CSK or coal in the granular surface layer. The second step, from 593 °C to 836 °C with a peak temperature of 712.3 °C, was the main reaction process of coal combustion in CSK. The combustion temperature of coal in CSK was considerably higher than that of normal coal, indicating difficult combustion. The explanation was that coal was wrapped inside CSK particles, and the heat and oxygen required for coal combustion had to be transferred through the wrapping layer. The decomposition of kaolinite and boehmite results in heat absorption, delaying heat transfer, and the wrapping layer prevents the internal diffusion of oxygen. Thus, the decarburization of CSK cannot be simply regarded as the combustion of poor-quality coal [21,22]. A peak can be observed on the release curve of $\text{H}_2\text{O}_{(\text{g})}$ in Figure 5a, indicating that the dehydroxylation reaction of CSK is a continuous process. The temperature range of the dehydroxylation reaction was 327 °C–781 °C, with a peak temperature of 553.6 °C. Although both kaolinite and boehmite decompose during calcination to release $\text{H}_2\text{O}_{(\text{g})}$, they cannot be clearly separated. According to the comprehensive analysis of Figures 3b and 5a, the first phase of DTG includes the majority of the dehydroxylation reaction and the first step of decarburization. The second phase includes the superposition of the dehydroxylation reaction and the second decarbonization step. Therefore, the physical significance of the reaction kinetics calculated using the conventional TG method was unclear. Figure 5a shows that the second decarbonization step started from the second half of the dehydroxylation reaction. The large number of pores produced by kaolinite and boehmite decomposition created good conditions for the diffusion of oxygen and carbon dioxide during decarbonation [17].

The preparation of calcined kaolin from CSK focused on the decarburization reaction. As shown in Figure 5b, the basic characteristics of the CO_2 release curves were consistent for the four heating rates but exhibited a shift of reaction temperature toward the high-temperature region as the heating rate increased. This was because the larger the heating rate, the larger the lag between the actual temperature of the sample and the temperature of the thermal analysis furnace. These were the typical facts of thermal analysis [27,31].

In summary, by resolving the release flow curves of $\text{H}_2\text{O}_{(\text{g})}$ and CO_2 , the goal of precisely separating dehydroxylation from the coal combustion reaction in CSK was achieved. This provided a basis for further mechanistic analysis and kinetic calculations.

3.3. Kinetic Analysis

The CO_2 release flow data of the second decarbonization step in Figure 5b were integrated, and the conversion rate data were obtained according to Equation (2). The α - T curves are plotted in Figure 6.

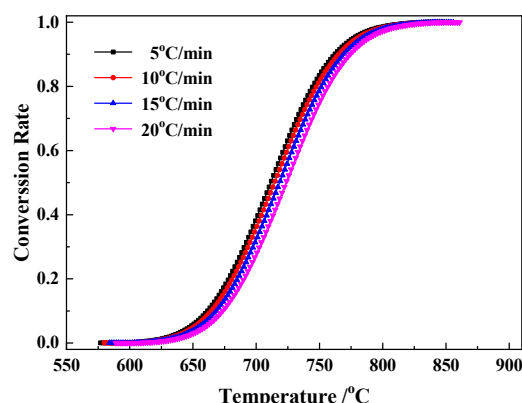


Figure 6. α - T curve of the decarburization reaction.

A linear fit of the α - T curve in Figure 6 was performed using the general integration method. The linear correlation coefficients r were ranked from the largest to the smallest, and the fitting results of 10 functions are shown in Figure 7.

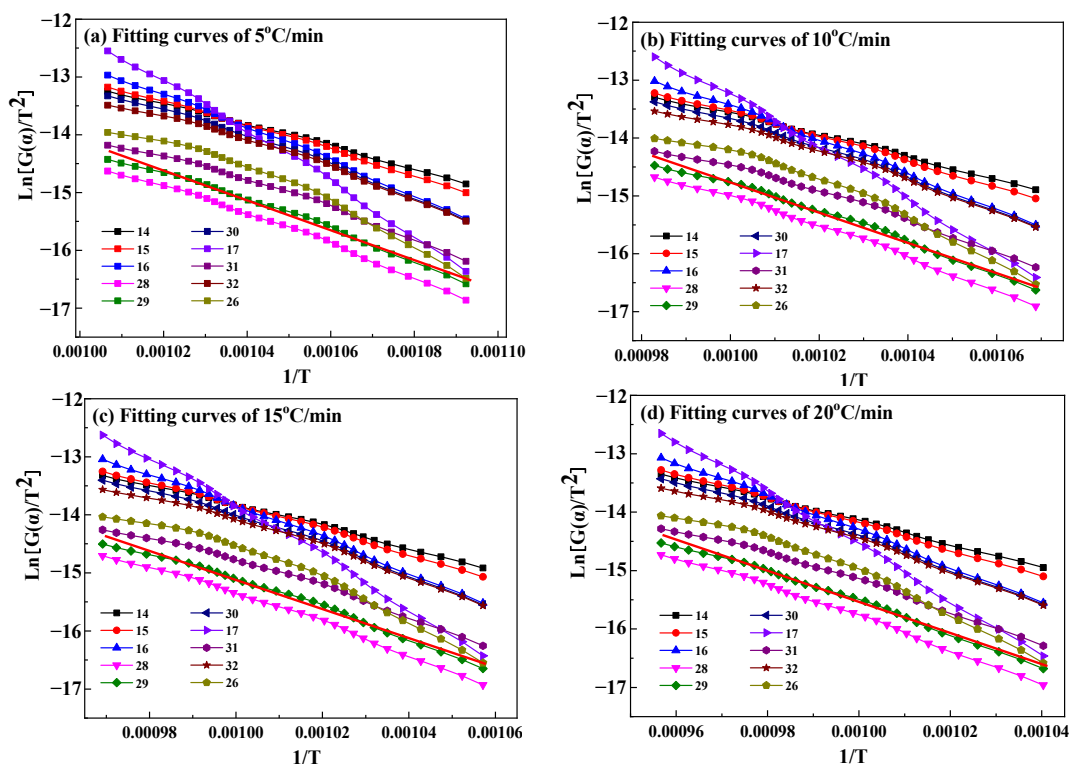


Figure 7. Kinetic fitting curve using the general integration method.

The correlation coefficients r for No. 29, 30, 31, 32, and 15 in Figure 7 exceeded 0.99. The mean values of the fitting results for the four warming rates are listed in Table 3.

Table 3. Fitting results for the top five $G(\alpha)$.

Serial Number of $G(\alpha)$	Correlation Coefficient r	Activation Energy E (kJ/mol)	Reaction Mechanism	Order
29	0.996479	214.56	Surface reaction rate controlling mechanism	1
30	0.995928	215.75		2
31	0.993684	201.76		3
32	0.993635	201.77		4
15	0.998703	182.78	Nucleation and growth rate controlling mechanism	5

Table 3 shows that the fitting results of the No. 29–32 were close and consistent with the surface reaction rate controlling mechanism. In comparison, the linear correlation coefficient r was the largest for No. 29 ($r = 0.996479$); therefore, it was adopted as the correct mechanism function. The kinetic results of No. 29 at the four heating rates are listed in Table 4.

Table 4. Kinetic results for the decarburization reaction of CSK.

Method	Heating Rate (°C/min)	Activation Energy E (kJ/mol)	Preexponential Factor A (s^{-1})	Correlation Coefficient r
General integral method	5	210.62	2.79×10^9	0.995259
	10	211.21	1.56×10^9	0.995328
	15	204.70	4.88×10^8	0.994881
	20	217.39	1.57×10^9	0.996899
	Average value	214.56	1.60×10^9	0.996479
Kissinger method		216.35	—	0.995554

The reaction mechanism of No. 29 was the surface reaction rate controlling mechanism (shrinking core model), indicating that the decarburization reaction of CSK was conducted according to the shrinking core model [31]. The kinetic equation is as follows.

$$1 - (1 - \alpha)^{\frac{1}{3}} = 1.60 \times 10^9 \exp\left(-\frac{214.56}{RT}\right) \cdot t \quad (8)$$

Equation (8) reveals the relationship between T and t on the reaction conversion rate of CSK decarburization, which can be used for the design of calcination process parameters. In Equation (8), let $\alpha = 1.0$, the essential time t for decarburization corresponding to different calcination temperatures T can be obtained. The time required for CSK decarburization at 700 °C–950 °C is shown in Table 5.

Table 5. Time required for complete decarburization was predicted using the kinetic Equation (8).

Temperature (°C)	700	750	800	850	900	950
Time (s)	205.6	56.1	17.4	5.9	2.2	0.91

Table 5 shows that only 2.2 s was needed for the decarburization of CSK at 900 °C, which was less than the residence time in the suspension reactor (~3.3 s), indicating that the temperature for the pilot test should exceed 900 °C. This provided the basis for temperature selection for the pilot test.

3.4. Product Characterization

3.4.1. Carbon Content Analysis

It was assumed that no loss of Al elements occurred during the calcination of CSK. The equation for calculating the decarburization rate η from the carbon content is

$$\eta = \frac{x_0/\text{Al}_0 - x_i/\text{Al}_i}{x_0/\text{Al}_0 - 0} \times 100\% = \left(1 - \frac{x_i\text{Al}_0}{x_0\text{Al}_i}\right) \times 100\% \quad (9)$$

In Equation (9), x_0 and Al_0 are the contents of carbon and Al in the raw materials of CSK, respectively (wt.%). x_i and Al_i are the contents of carbon and Al in calcined kaolin products, respectively (wt.%). Table 6 shows the analytical data of Al, carbon content, and decarburization rate of calcined kaolin. The variation curve of carbon content according to Table 6 is shown in Figure 8a. The experimental data of decarburization rate compared with the predicted results using the kinetic equation (Equation (8)) are shown in Figure 8b.

Table 6. Analysis results of decarburization rate of calcined kaolin products.

Temperature (°C)	Al ₂ O ₃ (wt.%)	C (wt.%)	Decarburization Rate (%)	
			Experimental Data	Forecast Data
Raw ore	36.74	2.78	0.00	0.00
700	37.79	2.6318	7.97	4.74
755	38.35	2.3105	20.37	16.59
800	41.36	1.5839	49.39	46.85
850	42.35	0.2726	91.49	91.14
900	42.63	0.0023	99.93	100.0
950	42.70	0.0007	99.98	100.0

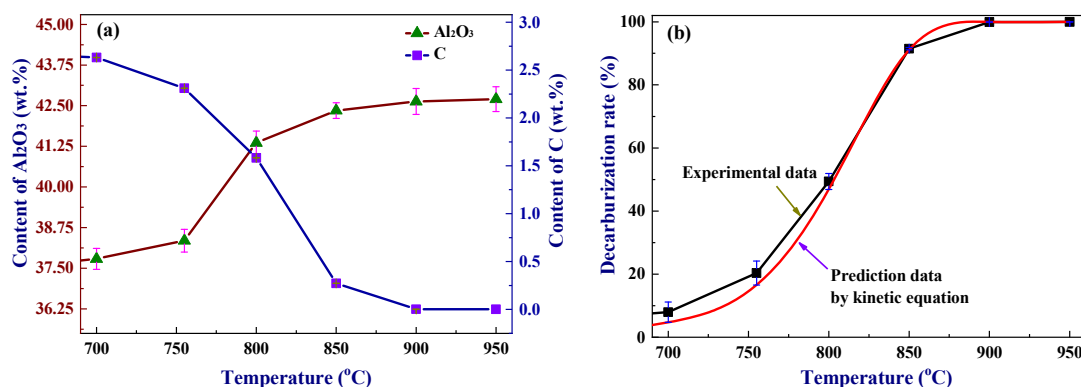


Figure 8. Graph of (a) carbon content and (b) decarburization rate of calcined kaolin.

As shown in Figure 8a, as the temperature increases, the CSK undergoes dehydroxylation and decarburization reactions, causing mass loss. Therefore, the Al_2O_3 content in the product gradually increases. However, the carbon content decreases sharply between 750 °C and 850 °C, to below 0.01 wt.% at 900 °C and 950 °C. Figure 8b shows that the predicted values were smaller than the measured values in the low-temperature region, which was because the thermal analysis conditions react in the stacked state, where the reaction rate was lower than that in the suspended state. In the late stage of decarbonization, the reaction rate decreased considerably, so the difference between the predicted and measured values narrowed. Overall, the experimental data of the decarbonization rates of products were consistent with the predicted results of the kinetic equations, confirming that the decarbonization kinetics calculated using the CO_2 release flow curves were valid.

3.4.2. XRD Analysis

The results of the XRD analysis of the calcined kaolin products are shown in Figure 9.

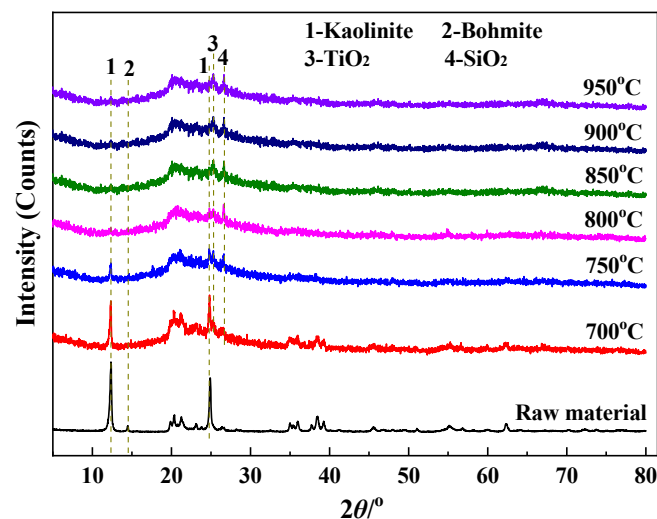


Figure 9. XRD analysis of calcined kaolin products.

Figure 9 shows that kaolinite and boehmite in CSK decompose almost completely when calcined at 800 °C. The decarburization rate in this case is only 49.39% (Table 6), indicating that the decarburization reaction was considerably slower than the dehydroxylation reaction, which was consistent with the analysis in Figure 5a. The XRD patterns of the calcined CSK products in the range of 800 °C–950 °C showed a typical indeterminate structure, indicating that the main composition of the products was metakaolin. A close observation revealed that with the formation of the amorphous structure of metakaolinite, the diffraction peaks of TiO_2 and SiO_2 could be detected. These small amounts of components were undetectable in the raw material; however, their crystal structure was not destroyed during calcination [15].

3.4.3. Analysis of Whiteness and Oil-Absorbed Value

The analysis results of whiteness and oil-absorbed value of calcined kaolin are shown in Figure 10.

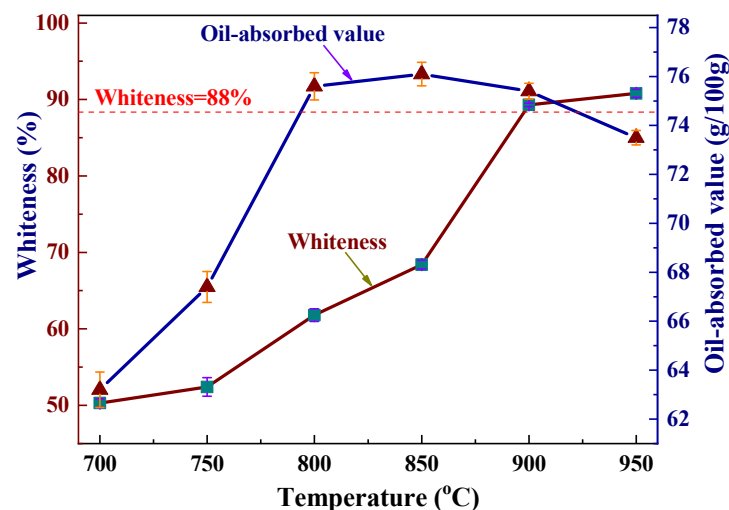


Figure 10. Analysis results of whiteness and oil-absorbed value of calcined kaolin.

Figure 10 shows that in the calcination time of ~3.3 s, the whiteness of calcined kaolin continuously increases with an increase in temperature. The trend of whiteness in Figure 10 was consistent with that of the decarburization rate in Figure 8b, confirming that the carbon content was the major influencing factor of whiteness. The whiteness of the

products calcined at 900 °C and 950 °C was 89.3% and 90.8%, respectively, which met the requirement of GB/T5950-2008 that whiteness should exceed 88%.

Figure 10 shows that the oil-absorbed value tended to increase initially and decrease subsequently, with a maximum value of 76.1 g/100 g at 850 °C. The oil-absorbed value reflects the adsorption properties of the product on ink, which is directly related to the specific surface area of the product. The results of the specific surface area analysis of calcined kaolin are shown in Table 7.

Table 7. Brunner–Emmet–Teller (BET) surface area of products.

Temperature (°C)	700	750	800	850	900	950
Specific surface area (m ² /kg)	17.52	18.79	20.19	20.39	20.17	19.85

As shown in Table 7, before 800 °C, the decomposition of kaolinite and boehmite and the combustion of coal in CSK produced a large number of microporous structures; therefore, the specific surface area of the product was increased. The largest specific surface area was formed at 850 °C when the dehydroxylation reaction was almost completed. When the temperature increased to 900 °C and 950 °C, the reaction time of dehydroxylation was less than 3.3 s, affording slight over-calcination. The sintering effect from over-calcination led to a partial closure of micropores, affording a reduced specific surface area and a lower oil-absorbed value. Therefore, it can be concluded that the temperature and time parameters should be strictly controlled for calcined kaolin to have good oil-absorbed performance. A comprehensive analysis revealed that 900 °C–950 °C was suitable for the suspension calcination system. Calcination at 900 °C for 3.3 s is considered the best condition, in which calcined kaolin with 89.3% whiteness and 76.1 g/100 g oil-absorbed value can be obtained, which meets the requirement of calcined kaolin for paper-making.

3.4.4. SEM Analysis

SEM photographs of calcined kaolin prepared using a suspension calcination system at 900 °C are shown in Figure 11b.

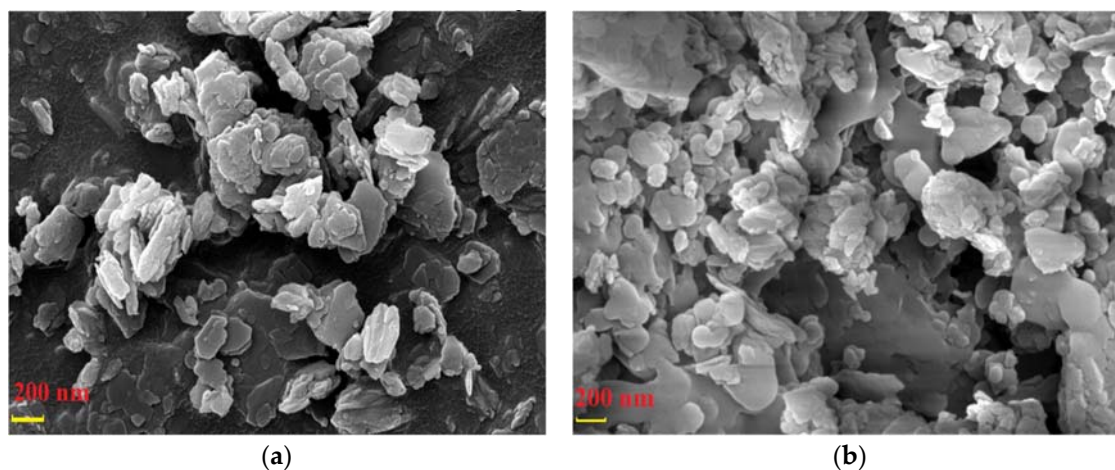


Figure 11. SEM photograph of (a) CSK and (b) calcined kaolin.

As shown in Figure 11a, kaolinite in CSK is a typical sheet structure with well-defined sheets and clear boundaries [4,10,16,17]. Figure 11b shows that after suspension calcination, the sheet structure was destroyed, the original clear boundary became blurred, and the large particles showed obvious porous characteristics [16]. After calcination at 900 °C, the particles did not exhibit a sintering phenomenon, which was the reason for the high activity and high oil-absorbed value of calcined kaolin by suspension calcination.

4. Conclusions

In this paper, a new kinetic method for decarburization of coal series kaolinite was proposed. It was used to optimize the parameters of the pilot test system, and high-quality calcined kaolin was obtained. The main conclusions are as follows.

(1) The decarburization reaction in the calcination of CSK is a two-step reaction, and the released gas product is CO₂. The temperature range for the first step is 348 °C–451 °C and that for the second step is 593 °C–836 °C. The second step is the major decarburization process caused by the combustion of coal in CSK. The decarburization reaction is considerably slower than the dehydroxylation of kaolinite and boehmite. Therefore, a combined TG–IR analysis method is used to achieve an accurate characterization of the decarburization reaction.

(2) The CSK decarburization reaction is consistent with a phase-boundary reaction mechanism (unreacted-core shrinking model), with an activation energy of 214.56 kJ/mol. The reaction is controlled by the contraction rate of the reaction interface. The predictions of the kinetic equations in case of CSK decarburization are consistent with the experimental data obtained via suspended calcination.

(3) Calcination at 900 °C or 950 °C for ~3.3 s in the suspension calcination pilot system afforded a CSK decarburization rate of more than 99.9%. The composition of calcined kaolin was dominated by metakaolin within the calcination temperature range of 800 °C–950 °C. The whiteness of calcined kaolin was mainly positively correlated with the decarburization rate. Therefore, increasing the calcination temperature aided in increasing the whiteness of calcined kaolin. The oil-absorbed value of calcined kaolin is positively correlated with the specific surface area. Insufficient or over-calcination leads to a decrease in the oil-absorption performance of calcined kaolin.

(4) The best parameter of suspension calcination is calcination at 900 °C for ~3.3 s. The calcined kaolin products with 89.3% whiteness and 76.1 g/100 g oil-absorbed value can be obtained, which meets the requirements of calcined kaolin for paper-making.

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