Research Article

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Effect of CaO on catalytic combustion of semi-coke

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Abstract: Generally, adding a certain amount of an additive to pulverized coal can promote its combustion performance. In this paper, the effect of CaO on the combustion characteristics and kinetic behavior of semi-coke was studied by thermogravimetric (TG) analysis. The results show that adding proper amount of CaO can reduce the ignition temperature of semi-coke and increase the combustion rate of semi-coke; with the increase in CaO content, the combustion rate of semi-coke increases first and then decreases, and the results of TG analysis showed that optimal addition amount of CaO is 2 wt%. The apparent activation energy of CaO with different addition amounts of CaO was calculated by Coats–Redfern integration method. The apparent activation energy of semi-coke in the combustion reaction increases first and then decreases with the increase in CaO addition. The apparent activation energies of different samples at different conversion rates were calculated by Flynn–Wall–Ozawa integral method. It was found that the apparent activation energies of semi-coke during combustion reaction decreased with the increase in conversion.

Keywords: semi-coke, catalytic combustion, chemical reaction dynamics

1 Introduction

At present, it has become a routine technology for blast furnace ironmaking to replace coke with pulverized coal. It plays an important role in saving coke, reducing consumption, adjusting furnace conditions, reducing pig iron costs, and reducing environmental pollution [1]. The commonly used pulverized coal for blast furnace injection includes bituminous coal and anthracite. Because of its high volatility and flammability, bituminous coal is widely used in blast furnace injection [2,3]. Bituminous coal has good flammability, but it contains a lot of harmful substances such as S and P [4–6]. Anthracite has the characteristics of high fixed carbon and low S and P impurity content, but its combustion performance is poor [7,8]. To increase the amount of coal injected into the blast furnace and ensure that the coal powder is burned as much as possible inside the blast furnace, anthracite is generally mixed with bituminous coal for mixed injection [9,10]; this not only makes use of the high fixed carbon content and high calorific value of anthracite, but also takes advantage of the low ignition point and good combustion characteristics of bituminous coal. With the increasing price of anthracite, the cost of blast furnace ironmaking is also increasing, and therefore it is necessary to find another pulverized coal to replace anthracite. As a new type of carbon material, semi-coke has huge reserves in China [11]. It has the advantages of low ash, low sulfur, low phosphorus, and high fixed carbon. Its pore structure is complex, its combustion performance is good, and its price is lower than anthracite; therefore, the use of semi-coke combined with bituminous coal can further reduce the cost of blast furnace coal injection. However, at present, the blending amount of semi-coke in mixed injection pulverized coal is limited. After excessive addition, the combustion performance of mixed pulverized coal will be reduced, and the unburned

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pulverized coal will increase, which is not conducive to the blast furnace going forward.

Zhang *et al.* [12] found that in the mixture of semi-coke and bituminous, when semi-coke accounts for 20%, it has a certain promotion effect on the entire combustion process. Yang *et al.* [13] used thermogravimetric (TG) analysis to study the co-firing behavior of Fushun low-calorie oil shale and semi-coke. The results showed that with the increase in oil shale mass fraction and oxygen concentration, the combustion characteristics of the sample were improved. Yao *et al.* [14] used TG analysis to study the combustion characteristics and kinetics of the blend in an oxygen-rich atmosphere. Finally, it was found that CO₂ instead of N₂ can significantly improve the burnout behavior of semi-coke under the same oxygen concentration. Yang *et al.* [15] used TG analysis to study the mixed combustion process of several kinds of coal and semi-coke, and found that as the heating rate increased, the combustion performance of mixed coal powder and semi-coke was improved. All the above studies are about the mixed combustion of semi-coke and other combustible materials, and the experimental study on the effect of combustion promoters on their catalytic combustion has not been carried out.

Alkaline earth metals such as Ca, Mg, Ba, and other compounds can promote the interfacial reaction of carbon and oxygen and have a high reactivity. In particular, Ca compounds are very cheap combustion-supporting catalysts. CaO, CaCO₃, CaCl₂, and other Ca-based catalysts have been widely studied by scholars [16,17]. Jayasekara *et al.* [18] studied the influence of Ca and Fe content on the reactivity of coke with CO₂. Compared with the addition of Fe, the reactivity of Ca added to coke was doubled. Cheng *et al.* [19] studied the catalytic effects of Na-rich and Ca-rich industrial wastes on coal ignition. The results show that both metals have good catalytic effect on coal ignition, but Na has higher catalytic activity on coal ignition than Ca. Abbasi-Atibeh *et al.* [20] used TG analyzers to study the effects of K, Ca, and Fe on the catalytic pyrolysis and combustion characteristics of low-calorie Turkish lignite. The results show that the combustion tests conducted under O₂/CO₂ environmental conditions show that the relative activity of the catalyst is Fe ≫ K > Ca and Fe > Ca ≫ K at O₂ concentrations of 30% and 35%, respectively. In addition, potassium catalysts have higher reaction rates at all oxygen concentrations. The above results show that the combustion promoters have good catalytic effect on coal, but there is no specific experimental study on the catalytic combustion of semi-coke.

To reduce the cost of pig iron in blast furnace and reduce environmental pollution, increasing the amount

of semi-coke in the mixed pulverized coal injection is an effective method. At present, there are many studies on the co-combustion characteristics of semi-coke and other combustible substances, but there are few studies on the effect of combustion-supporting additives on the catalytic combustion performance of semi-coke. Although alkali metals such as Na and K have a good catalytic effect on combustion, after being added, they easily cause corrosion to the combustion equipment, which is not conducive to long-term use of the blast furnace [21,22]. Because CaO has obvious combustion-supporting effect on coal powder, the price is cheap and easy to obtain, and it will not cause corrosion to the blast furnace. In this paper, the catalytic combustion of semi-coke was studied using CaO combustion aid, which has certain guiding significance for increasing the amount of semi-coke in mixed injection coal powder.

2 Experimental

2.1 Sample preparation

The semi-coke used in the experiment was obtained from a smelting company in Yunnan, China. First, use a ball mill to grind the semi-coke to 200 meshes, then dry it to a constant weight at 80°C in a constant temperature oven, and then store it in a sealed bag. The industrial analysis of semi-coke is presented in Table 1. The preparation of the experimental sample was as follows: weigh 10 g semi-coke, put it into a beaker, and then add 2 wt% CaO and 150 mL anhydrous ethanol; the mixture was magnetically stirred at room temperature for 1 h, then the sample was dried at 105°C for 24 h, and then taken out and ground for 5 min. The above operation was repeated to prepare mixed semi-coke samples having CaO addition amounts of 0, 2, 4, 6, and 8 wt%, which were designated as K1, K2, K3, K4, and K5, respectively.

Table 1: Proximate and ultimate analysis results of semi-coke, wt%

Proximate analysis				Ultimate analysis				
M _{ad} %	V _{ad} %	A _{ad} %	FC _{ad}	C _{ad}	H _{ad}	O _{ad}	N _{ad}	S _{ad}
5.28	17.57	8.69	70.28	83.74	3.43	0.76	0.72	0.4

Note: ad – air dry basis; M – moisture; V – volatile matter; FC – fixed carbon.

2.2 Sample characterization

The combustion characteristics of the mixed samples were analyzed by a thermal analyzer model STA6000/8000. The temperature deviation of the thermal analyzer was $\pm 0.1^\circ\text{C}$, and the sensitivity deviation of the balance was less than $0.1\ \mu\text{g}$. In this experiment, the sample was raised to $1,000^\circ\text{C}$ at room temperature at a heating rate of $10^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$, $30^\circ\text{C}/\text{min}$, and $40^\circ\text{C}/\text{min}$ under an air flow rate of $50\ \text{mL}/\text{min}$.

3 Results and discussion

3.1 Combustion performance

Five samples of K1, K2, K3, K4, and K5 were tested by thermal analyzer. The TG and DTG curves of combustion tests for different samples are shown in Figure 1. It can be

Figure 1: TG–DTG curves of the sample at the temperature rise rate of $20^\circ\text{C}/\text{min}$: (a) TG and (b) DTG curves.

seen from the TG curve that the combustion temperature range of the mixed semi-coke sample is between 400°C and 750°C . Ignition temperature (T_i) of the samples can be determined by TG-DTG tangent method, that is, the vertical point of the X-axis is made at the peak point of the DTG curve, and the TG curve is intersected at one point, and the tangent of the TG curve is made at this point, and the tangent of the point where the initial mass is unchanged on the TG curve, the intersection of the two tangent lines is the ignition point of the samples. T_i reflects the ignition performance of the sample, and the smaller the T_i , the easier the sample is to catch fire [23]. The burnout temperature (T_b) indicates the temperature at which the combustibles in the samples are completely burned out within a certain temperature range, and usually the TG curve tends to a horizontal straight line, corresponding to the temperature at which the DTG curve is close to zero. T_i and T_b reflect changes in combustion performance throughout the combustion process [24]. The burnout temperature and ignition temperature of the sample are presented in Table 2. After the addition of CaO, the burnout temperature and ignition temperature of the semi-coke are reduced. After adding 2 wt% CaO, the ignition temperature of the semi-coke decreased by 23.70°C , and the burnout temperature decreased by 7.23°C . As the amount of CaO added continues to increase, although the ignition temperature of semi-coke is somewhat reduced, the reduction is much smaller than that of semi-coke with 2 wt% CaO.

By analyzing the TG curve, the combustion rate of the sample at different temperatures can be obtained. For the convenience of analysis, the combustion rate of the samples at the combustion temperatures of 500°C , 600°C , 700°C , and 800°C is generally selected. The combustion rate calculation formula is as follows:

$$R = \frac{W_i - W_t}{W_i \times \eta} \times 100\%, \quad (1)$$

where W_i is the initial mass of the sample, g; W_t is the mass after the sample is burned t min, g; η is the weight loss rate when the sample is completely burned without additives; and R is the combustion rate of the sample.

In the combustion process, integrated combustion characteristic index (S) is generally used to reflect the whole process of burnout and ignition of the sample. The larger the S , the better the combustion characteristics of the sample. The calculation formula is as follows:

$$S = \frac{\left[\left(\frac{dw}{dt} \right)_{\max} \times \left(\frac{dw}{dt} \right)_{\text{mean}} \right]}{T_i^2 \times T_b}, \quad (2)$$

Table 2: Combustion parameters of mixed semi-coke samples

Sample	T_i (°C)	T_b (°C)	Combustion rate (%)				$S \times 10^9$ (% ² min ⁻² °C ⁻³)
			500°C	600°C	700°C	800°C	
K1	439.15	757.52	5.36	24.52	91.99	99.99	0.44
K2	415.45	750.29	6.15	29.47	89.16	99.82	0.69
K3	428.38	753.68	5.53	24.61	87.24	96.96	0.63
K4	428.96	751.48	4.25	22.57	80.21	94.49	0.42
K5	430.96	754.29	4.24	21.71	76.53	91.53	0.35

where $\left(\frac{dw}{dt}\right)_{\max}$ is the maximum combustion rate of pulverized coal, %/min; and $\left(\frac{dw}{dt}\right)_{\text{mean}}$ is the average combustion rate, %/min.

Comprehensive combustion characteristic index and combustion rate of different samples at different temperatures are presented in Table 2. It can be seen from Table 2 that the combustion rates at the combustion temperatures of 500°C and 600°C are improved when the addition amount of CaO in the semi-coke is 2 wt% and 4 wt% compared with the semi-coke without the additive. With the further increase in CaO addition, when the added amount of CaO in the semi-coke is 6 wt% and 8 wt%, the combustion rates between 500°C and 800°C are lowered. It shows that CaO can promote the combustion of semi-coke, but adding too much of CaO will inhibit its combustion. With the increase in the amount of CaO, the comprehensive combustion characteristics of the samples first increase and then decrease; when the amount of CaO added is 2 wt%, the ignition temperature and burnout temperature of the sample are the lowest, probably because CaO will adsorb the macromolecular volatile components in the semi-coke, which will cause the fixed carbon to locally overheat, resulting in a decrease in the fixed carbon ignition temperature [25,26]. Therefore, the oxidation reaction is more likely to occur, but excessive CaO will inhibit the combustion of semi-coke.

3.2 Impact of heating rates

Considering the impact of different heating rates of the thermal analyzer on the samples, the K1, K2, K3, K4, and K5 were tested in air atmospheres with heating rates of 10°C/min, 20°C/min, 30°C/min, and 40°C/min. The combustion process of the mixed samples having similar trends at different heating rates is shown in Figures 2–6, which indicates that the variation trend of combustion process of mixed samples is similar under different heating rates, but it has little impact on the whole combustion reaction process of pulverized coal. The TG curve

is constantly shifting to the right as the rate of temperature rises, causing T_i and T_b to increase accordingly. For K3 sample, when the heating rate rises from 10°C/min to 40°C/min, the T_i of the sample rises from 428.38°C to

Figure 2: TG–DTG curves of K1 sample at different heating rates: (a) TG and (b) DTG curves.

Figure 3: TG–DTG curves of K2 sample at different heating rates: (a) TG and (b) DTG curves.

450.25°C, and the T_b rises from 753.68°C to 836.27°C. This is because the propagation and heat transfer of the medium take some time. If the heating rate of the program is too fast, the time for the combustion reaction of the sample will be insufficient, and then the entire TG curve will shift to the high temperature area. It can be obtained from the DTG curve that the mass loss rate of the sample also decreases as the rate of temperature rises. With the increase in the heating rate from 10°C/min to 40°C/min, the maximum weight loss rate of the sample decreases from 0.91% to 0.36% per degree Celsius.

3.3 Dynamic analysis results

The Coats–Redfern integration method belongs to a single scan rate method and is a method for kinetic

Figure 4: TG–DTG curves of K3 sample at different heating rates: (a) TG and (b) DTG curves.

analysis of data results of a TG curve measured by an experiment at a fixed heating rate [27]. According to Arrhenius's law, if the initial mass of the coal powder involved in the reaction is m_0 , the mass after the reaction t time is m , and the final mass is m_∞ after the reaction is completed, the expression of the reaction rate can be obtained as follows:

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp\left(-\frac{E_\alpha}{RT}\right) f(\alpha), \quad (3)$$

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}, \quad (4)$$

where A refers to the pre-exponential factor, min^{-1} ; α is the conversion rate of coal powder; n is the reaction order; E_α is the activation energy, kJ/mol; and R is the gas constant.

Figure 5: TG–DTG curves of K4 sample at different heating rates: (a) TG and (b) DTG curves.

If the rate of temperature raises, $\beta = \frac{dT}{dt}$ is brought to Eq. 3, and a temperature approximation is made, then there is:

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{AR T^2 \left(1 - \frac{2RT}{E_a}\right) \exp\left(-\frac{E_a}{RT}\right)}{\beta E_a}. \quad (5)$$

After Eq. 5, the Coats–Redfern equation can be obtained: when $n \neq 1$,

$$\ln \left[\frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR \left(1 - \frac{2RT}{E_a}\right)}{\beta E_a} \right] - \frac{E_a}{RT}, \quad (6)$$

when $n = 1$,

Figure 6: TG–DTG curves of K5 sample at different heating rates: (a) TG and (b) DTG curves.

$$\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR \left(1 - \frac{2RT}{E_a}\right)}{\beta E_a} \right] - \frac{E_a}{RT}. \quad (7)$$

In the combustion process of pulverized coal samples, the result of $\frac{E_a}{RT}$ is much larger than 1; therefore, the result of $1 - \frac{2RT}{E_a}$ is about equal to 1, that is, the expression of the first term on the right-hand side of the Coats–Redfern equation is independent of temperature. When $n = 1$, in Eq. 7, $\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right]$ is plotted against $\frac{1}{T}$, and the graph is approximated as a straight line, $-\frac{E_a}{R}$ is the slope, and $\ln \left[\frac{AR}{\beta E_a} \right]$ is the intercept. Therefore, in the end, the value of the exponential pre-factor and the activation energy of the combustion reaction of the semi-coke mixed sample can be obtained.

Figure 7: Coats–Redfern method plots of different samples at 20°C/min.

The Flynn–Wall–Ozawa integration method belongs to the multiple scan rate method, which analyzes the experimental data obtained by samples at different heating rates [28,29]. The basic equation of the model is as follows:

$$\ln \beta = \ln \left(\frac{AE_a}{G(\alpha)} \right) - 5.331 - 1.052 \frac{E_a}{RT}. \quad (8)$$

At different heating rates, if the same conversion rate is chosen, integral form of reaction mechanism mode function $G(\alpha)$ is a fixed value, plotted as $\ln \beta$ versus $\frac{1}{T}$, the data is fitted by least squares method, and the activation energy of the reaction can be determined from the slope.

Assume that the combustion reaction of the sample in this experiment is a first-order reaction, that is, $n = 1$. Figure 7 shows the Coats–Redfern kinetic analysis curve of different samples at a programmed temperature rate of 20°C/min. The activation energy and pre-exponential factor calculation results are presented in Table 3.

It can be seen from Figure 7 that the linearity of the curve of $\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right]$ with $\frac{1000}{T}$ is very good, indicating that it is reasonable to assume that the combustion reaction of the sample under the experimental conditions is a

Table 3: Combustion kinetic parameters of different samples

Sample	E_a (kJ/mol)	A (min^{-1})	R^2
K1	93.74	3.70×10^5	0.998
K2	82.86	1.16×10^7	0.998
K3	87.24	1.36×10^5	0.998
K4	87.25	3.56×10^4	0.999
K5	93.58	2.72×10^5	0.996

first-order reaction. It can be obtained from Table 3 that the activation energy of semi-coke has a certain degree of reduction after adding CaO. When the addition amount is 2, 4, 6, and 8 wt%, the activation energy is reduced by 10.88, 6.50, 6.49, and 0.16 kJ/mol. This indicates that CaO promotes the combustion of semi-coke, and the activation energy is also relatively reduced. When the CaO addition amount is 2 wt%, the reaction activation energy is the smallest, which is consistent with the K2 sample combustion characteristics of the mixed sample obtained above.

The kinetic analysis of different samples was performed by multi-scan FWO integration method. This

Figure 8: FWO method plots of sample K1 in different conversion degrees.

Figure 9: FWO method plots of sample K2 in different conversion degrees.

method is to fit the experimental data by the conversion rate α within a certain range. In the experiment, α is between 0.1 and 0.7, and the fitting data exceeding this range are discarded because it is unreasonable. Figures 8–12 show the FWO kinetic analysis curves of the different samples reacted at different temperature programmed rates, and Tables 4–8 present the activation energy calculation and pre-exponential factor calculation results.

As shown in Figures 8–12, the straight line fitted by the FWO integral method agrees well with the original data, which indicates that the linearity of the kinetic curve obtained by this method is high and the result is reliable. Moreover, the slope of the fitted straight line changes with the change in α of the conversion, that is,

Figure 10: FWO method plots of sample K3 in different conversion degrees.

Figure 11: FWO method plots of sample K4 in different conversion degrees.

Figure 12: FWO method plots of sample K5 in different conversion degrees.

the reaction activation energy also changes. It can be seen from Tables 4–8 that the activation energy decreases with the increase in conversion in the same sample. This is because the whole experimental process is carried out under programmed temperature. As the temperature rises gradually, the gas–solid reaction will transition from the initial power control zone to the diffusion control zone, and finally the resulting activation energy is reduced [30,31].

Table 4: Combustion kinetic parameters of sample K1

Conversion	E_a (kJ/mol)	A (min^{-1})	R^2
0.1	58.35	2.16×10^6	0.996
0.2	57.89	0.97×10^5	0.998
0.3	56.68	3.03×10^7	0.997
0.4	56.13	3.82×10^5	0.993
0.5	55.47	3.62×10^7	0.994
0.6	54.69	2.57×10^7	0.991
0.7	53.29	1.62×10^6	0.992
Average	56.07	—	—

Table 5: Combustion kinetic parameters of sample K2

Conversion	E_a (kJ/mol)	A (min^{-1})	R^2
0.1	47.35	2.63×10^6	0.988
0.2	46.89	1.19×10^5	0.995
0.3	45.68	3.71×10^7	0.995
0.4	45.13	4.75×10^5	0.998
0.5	44.47	4.52×10^7	0.994
0.6	43.69	3.28×10^7	0.994
0.7	43.29	1.99×10^6	0.996
Average	45.21	—	—

Table 6: Combustion kinetic parameters of sample K3

Conversion	E_a (kJ/mol)	A (min^{-1})	R^2
0.1	53.25	2.35×10^6	0.995
0.2	52.39	1.07×10^5	0.993
0.3	51.79	3.28×10^7	0.995
0.4	50.22	4.27×10^5	0.997
0.5	50.47	3.98×10^7	0.995
0.6	49.61	2.89×10^7	0.994
0.7	49.18	1.76×10^6	0.996
Average	50.99	—	—

Table 7: Combustion kinetic parameters of sample K4

Conversion	E_a (kJ/mol)	A (min^{-1})	R^2
0.1	54.16	2.31×10^6	0.995
0.2	53.26	1.05×10^5	0.993
0.3	52.33	3.24×10^7	0.995
0.4	51.69	4.14×10^5	0.997
0.5	49.87	4.04×10^7	0.995
0.6	48.69	2.88×10^7	0.994
0.7	47.86	1.81×10^6	0.996
Average	51.12	—	—

Table 8: Combustion kinetic parameters of sample K5

Conversion	E_a (kJ/mol)	A (min^{-1})	R^2
0.1	59.35	2.11×10^6	0.995
0.2	58.28	0.98×10^5	0.993
0.3	57.63	2.97×10^7	0.995
0.4	56.38	3.79×10^5	0.997
0.5	55.74	3.61×10^7	0.995
0.6	54.69	2.56×10^7	0.994
0.7	53.89	1.61×10^6	0.996
Average	56.57	—	—

Five samples were tested at different heating rates, when the conversion rate α exceeds 0.7, under the condition of high temperature programming rate, the sample is not completely converted, so the subsequent fitting data are unreasonable and discarded.

4 Conclusions

In this paper, the characteristics and kinetic behavior of semi-coke mixed with CaO were studied by TG analysis. In the TG analyzer, the combustion characteristics of

semi-coke are obviously different because of the catalytic combustion supporting characteristics of CaO. The main conclusions are as follows:

- (1) The addition of a certain amount of CaO can lower the burnout and ignition temperature of the semi-coke. When the addition amount was 2 wt%, the burnout and ignition temperature of the semi-coke decreased the most, which were 23.70°C and 7.23°C, respectively. With the further increase in CaO addition, although the burnout and ignition temperature of semi-coke decreased, it was significantly lower than the semi-coke when the CaO addition amount was 2 wt%.
- (2) The combustion rate and comprehensive combustion characteristic index of different samples at different temperatures indicate that the addition of CaO can promote the combustion of semi-coke, but adding too much of CaO will inhibit its combustion.
- (3) The apparent activation energy of semi-coke with different addition amounts of CaO was calculated by Coats–Redfern integration method. In this experiment, the apparent activation energy decreases first and then increases with the increase in CaO addition. When the added amount is 2 wt%, the apparent activation energy is reduced to 82.86 kJ/mol. The apparent activation energies of different samples at four heating rates were calculated by FWO integration method. In this experiment, the apparent activation energy of the combustion reaction of different samples decreased with the increase in conversion. The calculated apparent activation energy is closer to the real activation energy at lower conversion, that is, the lower the reaction gas temperature.

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