Influence of Zinc on Nonisothermal Gasification Kinetics of Coke in a Blast Furnace

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ABSTRACT: The effect of zinc on the kinetics of coke gasification was studied by a nonisothermal method. The results indicated that with the increase of zinc content, coke gasification tended to move to the low-temperature zone, it occurred earlier, and the reaction rate increased. The main curve fitting method was used to analyze the mechanism function of coke gasification before and after adding zinc. The modified shrinking core model was found to be the optimal mechanism function for coke gasification, with which the kinetic parameters obtained showed that the pre-exponential factor and apparent activation energy of coke gasification decreased significantly with the increase of zinc adsorption amount. Moreover, a kinetic compensation effect was found to exist in the effect of zinc on coke gasification. Combined with X-ray diffraction (XRD) and the peak fitting technique, it was found that the difference in the catalytic effect of zinc on coke gasification was attributed to the carbon structure.

1. INTRODUCTION

With the continuous development of blast furnace ironmaking, the emergence and application of coke have opened up a new era. As one of the raw materials, coke plays an irreplaceable role. It can be used as a heating agent to provide heat for ironmaking, reducing agent to reduce iron ore, carburizing agent for increasing the carbon content in the hot metal, and framework to support the burden.1−4 The role of coke in the first three aspects can be partially replaced by pulverized coal. However, it supports the burden and provides a porous layer as pillar framework, which is the unique characteristic of coke.5−8 Gas permeability and liquid permeability determine the smooth operation and output of the blast furnace.9,10 Therefore, the supporting role of coke in a blast furnace is particularly important.

Many studies11−15 have found that the carbon dissolution reaction of coke is the main cause of coke cracking and pulverization, which leads to the decrease of lump size and strength of coke, further affecting the porosity and permeability between solid charges. Moreover, serious coke degradation hampers the smooth operation of the blast furnace.16 However, the harmful elements circulated and enriched in the blast furnace can aggravate the coke dissolution reaction.17−20 Zinc is loaded into the blast furnace mainly as oxide (ZnO), ferrite (ZnO-Fe3O4), silicate (2ZnO-SiO2), and sulfide (ZnS) as components of the sinter ore. The thermodynamic simulation confirms that zinc compounds can be directly reduced to metallic zinc in the high-temperature region (1373−1773 K). The zinc vapor rising with the gas stream condenses and oxidizes on the charge in the upper part of the blast furnace. Then, part of the zinc-bearing charge descends into the high-temperature zone. The reoxidized zinc is reduced to zinc vapor. Therefore, the enrichment of zinc in the furnace is mainly concentrated in the temperature range of 1173−1523 K, which corresponds to the middle of the lumpy zone to the upper end of the soft melting zone. This is also the region where the coke gasification reaction mainly occurs.21,22

A series of researches have been carried out on the effect of zinc on the thermal properties and microstructure of coke. Mu et al.23,24 conducted simulation experiments using zinc vapor adsorption. The results showed that zinc could improve the...
Table 1. Proximate and Ultimate Analyses of Coke

| samples   | moisture | ash  | volatile | fixed carbon | C   | H  | O   | N  | S  |
|-----------|----------|------|----------|--------------|-----|----|-----|----|----|
| coke A    | 1.00     | 13.16| 2.60     | 83.24        | 84.12| 0.13| 0.44| 0.52| 0.63|
| coke B    | 0.59     | 12.86| 1.42     | 85.13        | 84.76| 0.11| 0.48| 0.48| 0.72|

“Calculated by difference, wt %.

Table 2. Ash Component (Oxide Form) Analysis (wt %)

| samples   | SiO2    | Al2O3 | Fe2O3   | CaO   | MgO   | K2O | Na2O | TiO2 | SO3 | P2O5 |
|-----------|---------|-------|---------|-------|-------|-----|------|------|-----|------|
| coke A    | 54.30   | 21.65 | 7.42    | 5.72  | 2.76  | 0.74| 0.58 | 1.51 | 4.00| 0.41 |
| coke B    | 53.19   | 31.60 | 4.37    | 3.22  | 1.14  | 0.39| 0.69 | 1.53 | 2.14| 0.43 |

2. EXPERIMENTAL SECTION

2.1. Preparation of Samples. Zinc acetate dihydrate (chemical reagent) used in the experiment was from Sinopharm Co., Ltd. Group. The two kinds of coke used in the experiment were from a steel company, which were recorded as coke A and coke B. The proximate and ultimate analyses of coke are shown in Table 1. Table 2 shows the ash composition of coke. It can be found that the main components of ash composition are SiO2 and Al2O3.

In the process of preparing zinc-rich coke, because coke has the characteristics of porous structure and large specific surface area, it can be used as an effective adsorbent using the liquid-phase adsorption method. In this paper, zinc acetate dihydrate was dissolved in water to prepare a solution of different concentrations. Because zinc acetate dihydrate is soluble in water, and crystal water can be removed below 473 K, anhydrous zinc acetate begins to decompose at 515 K, and completely decomposes into ZnO at 643 K. Therefore, zinc acetate dihydrate has been completely decomposed and generates ZnO before coke gasification, which can effectively simulate the catalytic effect of zinc on coke gasification in the blast furnace.

Coke (20 g) that had been crushed and sieved to 23–25 mm was weighed and soaked in 500 mL of zinc acetate dihydrate solution of different concentrations for 24 h. For the two added experiments, the 24% zinc acetate solution was heated to boiling for 1 h for the purpose of loading more zinc on the coke. Then, the coke was taken out from the solution and put into the drying oven with a temperature setting at 453 K for 2 h. After drying, the coke was weighed, and the increase in its weight was the zinc acetate content. Further, the zinc content (wt %) in coke could be calculated by the molecular formula of zinc acetate. Table 3 shows the zinc loading experimental scheme. Finally, the coke was ground and sieved for 30 min to ensure uniform mixing. At the same time, the powder with the particle size less than 74 μm (200 mesh) was selected for the experiment to eliminate the influence of the particle size factor on the experimental process. Figure 1 shows the specific area of two kinds of coke. The BET specific surface areas of coke A and coke B are 2.427 and 2.423 m²/g, respectively, indicating that the contact areas of the two

Figure 1. Specific area of coke A and coke B.
kinds of coke with gas are similar in the process of coke gasification.

2.2. Experimental Equipment and Process. The experiments were conducted using thermogravimetric (TG) analyzer HCT-3, produced by Beijing Henven Co., Ltd., as shown in Figure 2. The equipment includes the heating furnace, control cabinet, computer, balance, and air supply device. The control cabinet inherits the gas flow control and temperature control to realize full automatic management. The experimental data is transmitted to the computer for real-time collection and recording, and the computer collects the data of temperature, time, weight, and heat at the same time.

The heating rate was kept at 5 K/min and increased from normal temperature to 1673 K for eliminating the influence of heat conduction and thermal gradient on coke gasification.27 In each experiment, 5 mg of coke sample was weighed and put into the corundum crucible (7.5 mm in diameter and 1.8 mm in height). After the sample was placed in a differential thermal balance, the heating program of the heating furnace was set. The temperature was raised to 673 K in 50 mL/min N2 atmosphere, and then CO2 gas with a purity of 99.9% was introduced at a flow rate of 50 mL/min. For each sample and experimental condition, two repetitive TG curves were obtained to ensure reproducibility of the results, as shown in Figure 3.

3. KINETIC ANALYSIS

Thermogravimetric analysis has been widely used to measure the loss of mass with temperature and time to determine the kinetic parameters.28−33 To ensure that all of the weight loss is caused by the reaction consumption of carbon and CO2, the coke samples must be dried for 2 h in N2 atmosphere at 1073 K. The carbon conversion in coke gasification can be expressed as below

\[ x = \frac{m_i - m_f}{m_i} \]  

(1)

where \( m_i \) (mg) is the initial mass of the sample after drying at 1073 K in N2 atmosphere, \( m_f \) (mg) is the mass of the sample at time \( t \), and \( m_f \) (mg) is the mass of the sample at the end of the reaction. The conversion rate \( \frac{dx}{dt} \) is a function of the rate constant \( k(T) \) and the mechanism function \( f(x) \) for heterogeneous solid reactions, as shown in eq 2

\[ \frac{dx}{dt} = k(T)f(x) \]  

(2)

where \( t \) (s) is the time, \( T \) (K) is the temperature, and \( k(T) \) can be expressed by the famous Arrhenius equation

\[ k(T) = A \exp\left(-\frac{E}{RT}\right) \]  

(3)

where \( A \) (s\(^{-1}\)) is the pre-exponential factor, which is proportional to the reaction rate. \( E/\text{mol}\cdot\text{K} \) is the apparent activation energy of the coke gasification reaction, reflecting the difficulty of the gasification reaction. It is the minimum energy required for the molecule of reactants to change from the initial stable state to the activated molecule. \( R \) is the standard molar gas constant, which is 8.314 J/mole\cdotK. Substituting eq 3 into eq 2, we get eq 4

\[ \frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)f(x) \]  

(4)

Coke gasification is a heterogeneous gas–solid reaction. The most common mechanism functions of gas–solid reactions are shown in Table 4.

The heating rate remains unchanged in the reaction process as follows

\[ \frac{dT}{dt} = \beta \]  

(5)

| code | reaction model | \( f(x) \) |
|------|----------------|-----------|
| A1   | nuclei production (\( n = 1 \)) | \( 1 - x \) |
| A2   | Avrami–Erofeev (\( n = 2 \)) | \( 2(1 - x)[\ln(1 - x)]^{1/2} \) |
| C1   | phase boundary reaction (\( n = 2 \)) | \( (1 - x)^2 \) |
| C2   | phase boundary reaction (\( n = 3/2 \)) | \( 2(1 - x)^{3/2} \) |
| D1   | one-dimensional diffusion | \( \frac{1}{2\pi} \) |
| D2   | two-dimensional diffusion | \( [\ln(1 - x)]^{-1} \) |
| D3   | three-dimensional diffusion (Jander) | \( 3/2(1 - x)^{1/3}[1 - (1 - x)^{1/3}]^{-1} \) |
| R1   | shrinking core model | \( 2(1 - x)^{1/2} \) |
| R2   | shrinking core model | \( (1 - x)^{1/3} \) |
| R3   | shrinking core model (\( n = 2 \)) | \( 1/2(1 - x)^{-1} \) |
By substituting formula (5) into formula (4), the following results can be obtained

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right)f(x)$$

(6)

The conversion rate ($\frac{dx}{dT}$) can be regarded as a function of conversion ($x$) and temperature ($T$). Different mechanism function curves can be obtained by the nonlinear fitting method of the least-squares method, which was realized on the program written by the author in C++ programming language, and the kinetic parameters can be obtained. Meanwhile, the mechanism function corresponding to the maximum $R^2$ value is taken as the optimal mechanism function.

4. RESULTS AND DISCUSSION

4.1. Effect of Zinc on Gasification Characteristics of Coke. Differential thermal experiments were carried out on coke A and coke B with different zinc contents prepared by the liquid-phase adsorption method. The curves of coke conversion and conversion rate are shown in Figure 4. It shows that the coke conversion and conversion rate curve generally move to the low-temperature zone with the increase of zinc content. Moreover, the maximum conversion rate increases with the increase of zinc loading, and the corresponding temperature also decreases significantly, as shown by the arrow in Figure 4. The results reveal that zinc has a positive catalytic effect on coke gasification.

Furthermore, the catalytic effect is enhanced with the increase of zinc content.

To quantitatively analyze the effect of zinc on coke gasification, the initial reaction temperature $T_s$ is defined as the temperature when carbon conversion is 1% according to the literature. $T_{\text{max}}$ and $T_f$ are the temperature at the maximum carbon conversion rate and the temperature at 99% carbon conversion, respectively. The variation law between the characteristic temperature of coke gasification and zinc-rich content is shown in Figure 5. It shows that the characteristic
temperatures $T_i$ and $T_{\text{max}}$ decrease with the increase of zinc content, especially $T_{\text{max}}$ (the maximum decrease is about 200 K). However, the reaction termination temperature $T_i$ has no obvious change. In conclusion, with the increase of zinc content in coke, the coke gasification reaction gradually moves to the low-temperature region, the gasification reaction occurs earlier, and the reaction rate accelerates, which proves that zinc has a positive catalytic effect on coke gasification. Moreover, the catalytic capacity is enhanced with the increase of zinc adsorption.

### 4.2. Effect of Zinc on Gasification Kinetics of Coke

Ten mechanism functions in Table 4 are introduced into eq 6, and ten kinetic control equations are obtained. The kinetic control equations are used as fitting functions to carry out nonlinear fitting of the experimental data successively, and the kinetic parameters ($E$ and $A$) of the gasification reaction of coke with different zinc content can be obtained. The fitting results are shown in Table 5, where the greater the $R^2$ value, the better the fitting degree.

It can be found that the optimal mechanism function for coke gasification without adding zinc is the $R_1$ model. Under the conditions of adding zinc, the $R_1$ model also shows a good correlation for the gasification reaction at Zn-1 and Zn-2 concentrations. However, the $R_2$ model is the optimal mechanism function at the concentration of Zn-3, and the correlation coefficients are all above 0.95. The results show that under the catalysis of zinc, the mechanism of coke gasification does not change, which is the shrinking core model (SCM). Xu et al.\(^{40}\) also found that the shrinkage core model could better characterize the catalytic steam gasification process of Jiaozuo anthracite. Meng et al.\(^{41}\) concluded that the shrinking core model was suitable for the kinetic analysis of the alkali carbonate catalyst for coal gasification. Zhang et al.\(^{42}\) indicated that the experimental results of anthracite char gasification with steam and carbon dioxide could be well described by the shrinking core model.

The shrinking core model supposes that the reaction of solid-gas occurs from the outside to the inside. Compared with the diffusion model and nuclei production model, which assumes that the reaction occurs homogeneously throughout the volume of the particle without considering changes in the structure, the shrinking core model can better describe the coke gasification process due to the compactness of the coke structure. However, due to the complexity of catalysis (e.g., the release of internal catalysts and the catalysis of endogenous minerals), some modified models\(^{43-45}\) have been developed. One of them is the modified shrinking core model (MSCM) whose function is shown in eq 7. It is a semiempirical model based on the shrinking core model and is an empirical constant.\(^\text{1}\)

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1 - x)^n$$  \quad (7)

The correlation coefficients ($R^2$) calculated by the shrinking core model (SCM) and modified shrinking core model (MSCM) are shown in Table 6. It can be found that the modified shrinking core model shows a better correlation between the experimental and calculated data, and the $R^2$ values are all above 0.99.

### Table 6. Correlation Coefficient Calculated Using Two Kinds of Models

| samples       | model   | $R^2$  |
|---------------|---------|--------|
| coke A Zn-0   | SCM     | 0.95408 |
|               | MSCM    | 0.996686 |
| coke A Zn-1   | SCM     | 0.95125 |
|               | MSCM    | 0.99616 |
| coke A Zn-2   | SCM     | 0.96529 |
|               | MSCM    | 0.99577 |
| coke A Zn-3   | SCM     | 0.98435 |
|               | MSCM    | 0.99015 |
| coke B Zn-0   | SCM     | 0.96654 |
|               | MSCM    | 0.99736 |
| coke B Zn-1   | SCM     | 0.95173 |
|               | MSCM    | 0.99705 |
| coke B Zn-2   | SCM     | 0.95167 |
|               | MSCM    | 0.99694 |
| coke B Zn-3   | SCM     | 0.99295 |
|               | MSCM    | 0.99553 |

Kinetic parameters of different samples were obtained using the modified shrinking core model, and the results are shown in Table 7. It can be found that the $E$ values of coke A and coke B gradually decrease with the increase of zinc content, which indicates that the catalysis of zinc can significantly reduce the apparent activation energy of coke gasification, resulting in the

### Table 7. Kinetic Parameters Calculated by the Modified Shrinkage Model

| sample label | $E$ (kJ/mol) | standard error for $E$ (kJ/mol) | $\ln A$ (s$^{-1}$) |
|--------------|--------------|---------------------------------|-------------------|
| coke A Zn-0  | 129.1397     | 3.2364                          | 36.4715           |
| coke A Zn-1  | 114.6824     | 3.1812                          | 35.2311           |
| coke A Zn-2  | 105.6882     | 2.7390                          | 34.5897           |
| coke A Zn-3  | 88.6204      | 2.5008                          | 33.4504           |
| coke B Zn-0  | 115.4411     | 4.2894                          | 35.0201           |
| coke B Zn-1  | 101.7021     | 3.4188                          | 33.8805           |
| coke B Zn-2  | 93.1615      | 2.3850                          | 33.2910           |
increase of carbon atom active number and coke reactivity. The activation energies of gasification of coke A and coke B are 129.13987 ± 3.2364 and 115.4411 ± 4.2894 kJ/mol, respectively. However, the apparent activation energy of coke A decreases significantly with the increase of zinc content, and the decrease range is larger than that of coke B, so that the activation energy of coke B (88.6204 ± 2.5008 kJ/mol) is less than that of coke A (93.1615 ± 2.3850 kJ/mol) for Zn-3. Moreover, combined with the results shown in Figure 4 that the gap between the conversion rate curves of coke A is larger than that of coke B, it can be found that coke B has better ability to resist zinc catalysis than coke A. The cause of this phenomenon is discussed below.

The pre-exponential factor of coke gasification decreases gradually with the increase of zinc adsorption amount, indicating that the number of effective collisions decreases. It can be seen from the linear relationship between the pre-exponential factor and activation energy in Figure 6 that there is a kinetic compensation effect in the catalytic reaction of zinc on coke gasification. A significant compensation effect was also found in the catalysis of alkali carbonate on coke gasification. According to the research by Xie, in the gasification reaction, the free activated carbon is easier to connect with CO2 to generate C (O) when the E value is lower. But at the same time, the C (O) bond becomes stronger and the carbon structure becomes more stable, which limits the movement of C (O) and leads to the decrease of A value.

To further verify the reliability of the modified shrinking core model, the conversion curves of different samples can be obtained by substituting the kinetic parameters in Table 7 into the integral form of eq 7. The results shown in Figure 7 can be seen that the experimental data are in good agreement with the calculated values. Moreover, the deviation (DEV) between the calculated values and the experimental data were calculated using eq 8 to quantify the error of different kinetic models. The results are shown in Table 8. It can be found that the deviation obtained using the modified shrinking core model is smaller compared to the shrinking core model. The above analyses again show that the

| samples   | shrinking core model | modified shrinking core model |
|-----------|---------------------|--------------------------------|
| coke A Zn-0 | 4.64                | 1.24                           |
| coke A Zn-1 | 4.25                | 1.76                           |
| coke A Zn-2 | 2.93                | 0.82                           |
| coke A Zn-3 | 3.43                | 1.27                           |
| coke B Zn-0 | 5.57                | 1.54                           |
| coke B Zn-1 | 4.12                | 1.18                           |
| coke B Zn-2 | 2.18                | 0.61                           |
| coke B Zn-3 | 1.75                | 0.65                           |
modified shrinking core model has good accuracy in characterizing the coke gasification process.

\[
\text{DEV}(x)(\%) = 100 \times \left( \frac{\sum_{i=1}^{N} (x_{\text{exp},i} - x_{\text{calc},i})^2 / N}{\text{max}(x)_{\text{exp}}} \right)^{1/2}
\]

where \(\text{DEV}(x)(\%)\) is the relative error, \(x_{\text{exp},i}\) is the experimental data, \(x_{\text{calc},i}\) is the calculated value, \(\text{max}(x)_{\text{exp}}\) is the maximum conversion rate of the experiment, and \(N\) is the number of data points.

Coke gasification is a complex process. Numerous models were chosen to try to describe the gasification reaction process. Among these models, the shrinkage core model shows favorable correlations. However, the shrinkage core model has its limitations. For example, when the maximum gasification rate occurs at a high conversion, the \(R_2\) model cannot be used. Conversely, the \(R_1\) model shows poor correlation when the maximum gasification rate occurs at a low conversion. This is due to the fact that zinc accelerates the reaction, resulting in a leftward shift of extreme point of the reaction rate. Therefore, the modified shrinking core model can overcome this drawback by adjusting the model parameter \(n\).

4.3. Comparison and Causes of Effects of Zinc on the Gasification Reaction of Two Kinds of Coke. In the characteristic temperatures of coke gasification, the initial reaction temperature \(T_s\) determining the temperature limit of direct reduction and indirect reduction is the most important parameter. Figure 8 shows the effect of zinc on the initial reaction temperature of two kinds of coke.

![Figure 8](image-url)  
**Figure 8.** Comparison of the effect of zinc on the initial reaction temperature of two kinds of coke.

8 and 9, it is found that the initial reaction temperature and activation energy of gasification of coke A are higher than those of coke B, indicating that the reactivity of coke A is lower than that of coke B without adding zinc. However, compared with coke B, coke A has a greater increase in reactivity with the increase of zinc content, which reveals that the catalytic effect of zinc on the gasification of coke A is greater than that of coke B.

Kinetic analysis has revealed significant differences between the two coke gasification reactions. The carbon structure has become an important factor affecting carbon reactivity under conditions of approximately the same surface area. The X-ray diffraction (XRD) technique is one of the most commonly used techniques to study the carbon structure of carbonaceous materials. The peak of (002) indicates the degree of orientation of the aromatic carbon net in the microcrystalline structure, namely, the order of the carbon structure. The higher and narrower the peak of (002), the better the degree of lamellar orientation and the higher the graphitization degree.47–50 In this study, XPERT PRO MPD X-ray diffraction (PAnalytical Company, Netherlands) was used to conduct polycrystal diffraction, and then the carbon structure parameters were calculated according to the classic Scherrer formula,51–54 as shown in eqs 9–11

\[
d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \tag{9}
\]

\[
L_c = \frac{0.89 \lambda}{\beta_{002} \cos \theta_{002}} \tag{10}
\]

\[
N = \frac{L_c}{d_{002}} \tag{11}
\]

where \(d_{002}\) is the average layer spacing of the microcrystalline structure, \(\lambda = 1.5418 \text{ Å}, \theta_{002}\) (rad) is the incidence angle of X-ray, \(L_c\) is the stacking height of the microcrystalline structure, \(\beta_{002}\) (rad) is the half peak width of the diffraction peak, and \(N\) is the average number of layers of the microcrystalline structure.

Figure 9 shows the X-ray diffraction patterns of coke. The peak fitting technique is adopted due to the overlap of coke (002) peak and SiO2 peak, as shown in Figure 11. Compared with coke B, the (002) peak intensity of coke A is higher and the (002) peak shape of coke A is narrower, indicating that the carbon structure of coke A is more ordered and the graphitization degree is higher. The carbon structure parameters

![Figure 9](image-url)  
**Figure 9.** Comparison of effect of zinc on the activation energy of gasification of two kinds of coke.
of the two kinds of coke are shown in Table 9 using the quantitative calculation of eqs 9–11, and it is found that the $d_{002}$ value determined by the diffraction angle of (002) peak is roughly the same, whereas the graphitization stacking height $L_c$ value of coke A is greater than that of coke B. Therefore, the number of aromatic layers of coke A is greater than that of coke B (the number of aromatic layers of coke A and coke B are 6.71 and 5.34, respectively). The above analysis indicates that the graphitization degree of coke A is higher than that of coke B, and the carbon structure of coke A is more ordered compared with coke B.

In the process of coke gasification, CO$_2$ will be adsorbed by C atoms, which are more active on the surface of solid carbon. With the increase of temperature, the physical adsorption changes to chemical adsorption, and then the reaction occurs. Because the graphitization degree of coke A is higher than that of coke B, the carbon structure is more stable, so the activation energy is higher in the gasification reaction, which is consistent with the research results in Table 7. However, previous studies have shown that the catalytic effect of zinc on coke gasification is selective, namely, the higher the degree of graphitization, the stronger the catalytic effect. Therefore, the decreasing trend of activation energy of gasification of coke A is greater than that of coke B with the increase of zinc content.

The chemical reaction between the carbon matrix and CO$_2$ starts from the surface of the solid phase and progresses to the center gradually. The reaction occurs near the phase interface between the layers, and the unreacted part is inside the carbon matrix. The reaction goes through three stages. The reaction starts from some active points on the solid surface but the initial reaction rate is low due to the difficulty of the contact between the gas and solid phases. Second, with the opening of the closed pore, the gas–solid interface continues to expand toward the center, which can promote the adsorption of CO$_2$ and zinc vapor and the interfacial reaction, so the reaction rate is accelerated with the expansion of the interface. Finally, the pores begin to overlap and collide with each other when the frontier of the reaction interface developed by the pores reaches its limit, the reaction interface shrinks, and the reaction rate gradually drops until the end of the reaction.

## 5. CONCLUSIONS

1. With the increase of zinc content, the coke gasification gradually moved to the low-temperature zone, and the characteristic temperatures $T_s$ and $T_{max}$ decreased, while the reaction termination temperature $T_f$ had no obvious change. In addition, coke gasification occurred even earlier and the reaction rate accelerated under the influence of zinc, indicating that zinc had a positive catalytic effect on coke gasification, and the catalytic ability was strengthened with the increase of the adsorption amount of zinc.
Kinetic analysis revealed that the optimal mechanism function of coke gasification under the catalysis of zinc was the modified shrinking core model, which had good accuracy in characterizing the coke gasification process. Furthermore, the gasification reaction was accelerated so that the maximum reaction rate reached in advance, and the extreme point of the reaction rate shifted to the left.

The kinetic parameters obtained by the modified shrinking core model showed that zinc could reduce the apparent activation energy of coke gasification, resulting in the increase of coke reactivity. Moreover, the kinetic compensation effect between the pre-exponential factor and activation energy was confirmed in the catalysis of zinc on coke gasification.

The XRD analysis indicated that the graphitization degree of coke A was higher than that of coke B. This is the reason for the higher activation energy of gasification of coke A. However, the decreasing trend of activation energy of coke A gasification was greater than that of coke B with the increase of zinc content. This phenomenon was related to the carbon structure of coke.

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**Notes**

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