Analysis of Coal Gasification Reactivity, Kinetics, and Mechanism with Iron-Based Catalyst from Coal Liquefaction

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ABSTRACT: In this work, the effect of an iron-based catalyst from coal liquefaction on coal gasification was studied. Two catalyst loading methods and three catalyst loading contents were taken into consideration. Besides, the carbon structure, surface morphology, and element distribution of coal char and gasified semi-char were investigated, and the interactions between the catalyst and internal minerals of coal were studied. The results showed that the coal char prepared by wet impregnation had higher reactivity than that prepared by a dry mixing method. From the perspective of improving the coal reactivity, the optimal addition method should be wet impregnation with a 2% catalyst. The model-free and model-fitting methods were applied to study the catalytic gasification kinetics. The iron-based catalyst would be broken during wet impregnation, and the catalyst fragments could stick to the surface of coal char, resulting in higher reactivity. The graphitization of char increased with the addition of the iron-based catalyst. This can imply that the carbon structure cannot effectively represent the gasification reactivity in the presence of the iron-based catalyst. The Iron-based catalyst can accelerate the gasification rate alone and can also provide higher catalytic activity with the internal minerals of coal.

1. INTRODUCTION

Gasification technology offers one of the cleanest ways for different carbonaceous feedstocks. Since the 21st century, the C-1 chemical industry based on syngas has developed rapidly under the promotion of large-scale coal gasification technology, especially in a country rich in coal resources.1 With the development of gasification technology, the feedstock of gasifiers gradually expanded from coal to petroleum coke, biomass, and solid waste.2,3 The diversified selection of raw materials makes the gasification technology have wide application potential in both chemical engineering and the energy field.

Recently, utilization of solid waste from the chemical industry has attracted much attention. Coal liquefaction residue is the solid waste from the liquefaction system and accounts for about 25–30% of the feed.4 Thermal conversion through gasification is a better way to deal with this residue, which is of great significance in economical efficiency.5 It should be noted that iron-based catalysts are widely used in coal liquefaction, as they are cheap and have low volatility, and thus, iron-based catalysts always exist in liquefaction residues.6 It is necessary to study the effects of iron-based catalysts on coal gasification, especially the catalysts used in the coal liquefaction process.

The effect of different metal catalysts on coal gasification performance has been reported in the literature. Some researchers pointed out that the active order of the catalysts was K > Na > Ca > Fe > Mg.7 The electronegativity of iron was higher than those of alkali and alkaline earth metals (AAEMs), resulting in lower catalytic activity for gasification.8 Nevertheless, much attention has been paid to investigate the application potential of iron-based catalysts because of their low cost, low environmental pollution, easy availability, and wide distribution.6,9,10 However, iron with different valence states would have different catalytic functions. Iron would be oxidized during gasification, and the catalytic effect changes accordingly.10 The catalytic activity of an iron-based catalyst was also affected by the anions. For example, Lahijani et al. pointed out that the order of iron-based catalysts for coal gasification was Fe(NO3)3 > FeCl3 > Fe2(SO4)3.11 Moreover, the iron can be combined with other metal elements to form a composite catalyst.12 These combined AAEMs can also affect the valence of iron.12,13 Monterroso et al. studied the catalytic effect of FeCO3–Na2CO3 on coal gasification, and a higher syngas yield was observed with the addition of a composite catalyst.14 The carbon structure is another important aspect that affects the gasification reactivity. Qi et al. found that iron-based catalysts could inhibit the graphitization of coal char during gasification, and the increase of amorphous carbon promoted the gasification rate,14 whereas Feng et al. pointed out that carbonaceous around the iron particles would become locally ordered.15 Xu et al. believed that the addition of the iron-based
catalyst can promote the formation of both graphitic and turbostratic carbon.\textsuperscript{16} Liu et al. found that a small amount of the iron-based catalyst loading would result in the disordering of coal char, while a large amount of the catalyst would cause graphitization.\textsuperscript{17} Besides, the good reducing property of iron can easily lead to the cracking of char and affect the pore structure.\textsuperscript{18} Therefore, the reaction mechanism of coal gasification with the addition of the iron-based catalyst needs to be further studied, especially the carbon structure evolution.

The kinetics study has always been the focus of the research on coal gasification. A thermal gravimetric analyzer (TGA) was widely used in solid−gas kinetic analysis,\textsuperscript{19,20} including catalytic gasification.\textsuperscript{21} Based on noncatalytic gasification, researchers had put forward many reaction models,\textsuperscript{12,23} such as the random pore model (RPM), the grain model (GM), the volume model (VM), etc. However, catalytic gasification featured different properties, and thus the applicability and reliability of these models should be studied in depth. Lahijani et al. pointed out that the RPM can better describe the gasification process in the presence of the iron-based catalyst.\textsuperscript{11} However, Zhang et al. believed that iron particles were attached to the coal char surface, where the gasification occurred, and thus, the shrinking core model (SCM) had better fitting performance.\textsuperscript{12} Recently, the model-free method was adopted by researchers for kinetic analysis, which can obtain kinetic parameters without assuming the reaction model in advance.\textsuperscript{24} Few studies have compared and evaluated different kinetic approaches for coal gasification, especially considering the addition of the iron-based catalyst.

In this work, coal gasification with the addition of the iron-based catalyst from a liquefaction plant was carried out. The gasification reactivity was tested in the TGA, with the considerations of different loading methods and contents. Both model-free and model-fitting methods were adopted for the catalytic kinetic study. Furthermore, the carbon structure evolution, surface morphology, and catalyst distribution were investigated. The interactions between the iron-based catalyst and inner minerals of coal was explored. These detailed analyses can help us comprehensively understand the effect of iron on coal gasification and provide support for the gasification of the coal liquefaction residue, which contains a lot of waste iron-based catalyst.

2. MATERIAL AND METHODS

2.1. Sample Preparation. In the present work, Hami (HM) coal was selected as the raw material, which was the feedstock of the industrial liquefaction plant in Xinjiang, China. The raw coal was crushed and sieved to 120−180 mesh. The proximate and ultimate analyses of raw coal are summarized in Table 1, based on the Chinese standard GB/T 212-2008 and GB/T 31391-2015. Table 2 shows the coal composition of HM coal using an X-ray fluorescence spectrometer (XRF, ARL Advant’X Intellipower TM-3600) based on the GB/T 1574-2007. The catalyst was from the coal direct liquefaction plant, and the composition of the iron-based catalyst was also determined using XRF. The results showed that the content of iron was approximately 70%. In addition, it contained silicon, transition elements, and alkaline earth metal elements.

Two catalyst loading methods, i.e., wet impregnation and dry mixing, were used to prepare coal with the catalyst. The loading contents were set as 1, 2, and 3 wt %. Specifically, for dry mixing, the coal and catalyst powders were directly mixed in a certain proportion, whereas for wet impregnation, approximately, 8 g of the coal powder with a certain proportion of the catalyst was dissolved and stirred in 100 mL of ultrapure water at 80 °C. After the liquid volume was reduced to 20 mL as a slurry, the solid−liquid mixture was kept in an oven for drying at 105 °C for 12 h. The raw and pretreated coal was devolatilized in a laboratory fixed bed reactor to prepare coal char. The detailed scheme of the fixed bed reactor can be found in ref 24. The pyrolysis (devolatilization) temperature was 800 °C, and the residence time was 30 min. The raw coal char was named HMC. The coal char with the catalyst was named by the catalyst loading method and content. For example, the char from wet impregnation and dry mixing with a 1 wt % catalyst was named HMWC1 and HMDC1, respectively.

2.2. Gasification Test. The gasification test was performed in a TGA (NETZSCH STA2500). In the present work, gasification was carried out under isothermal conditions. The specific steps were as follows: First, 8 ± 0.2 mg of coal char was weighted accurately and put into a crucible. Then, the sample was heated and gasified according to the heating procedure. The sample was heated from room temperature to the gasification temperature under a N₂ atmosphere. Once the desired temperature was reached, the purge gas was switched from N₂ to CO₂. The temperature was kept until the mass had no change. The gasification temperatures were set as 800, 850, 900, and 950 °C, and the flow rate of CO₂ was 120 mL/min.

The carbon conversion was calculated based on the TG curve\textsuperscript{25}
\[
X = \frac{w_0 - w_f}{w_0 - w_i}
\]
where \(w_0\), \(w_f\), and \(w_i\) were the initial, instantaneous, and final masses during gasification. To compare the gasification reactivity of different coal chars, the reactivity index \(K\) was calculated based on eq 2\textsuperscript{24}
\[
K = \ln \frac{4}{\Delta t}
\]
where \(\Delta t\) is the time interval of conversion from 0.2 to 0.8. The larger the index \(K\), the higher the gasification reactivity.

| Table 1. Proximate and Ultimate Analyses of HM Coal\textsuperscript{ad} |
|-----------------|-------------|-------------|-------------|-------------|-------------|
| sample         | M           | V           | A           | FC          | [C]         |
| HM             | 4.51        | 46.56       | 6.90        | 42.03       | 65.65       |
|                 |             |             |             |             | 5.93        |
|                 |             |             |             |             | 15.48       |
|                 |             |             |             |             | 0.83        |
|                 |             |             |             |             | 0.70        |

\textsuperscript{ad} air-dried basis.

| Table 2. Composition of HM Coal Ash |
|-----------------|-------------|-------------|-------------|-------------|
|                 | CaO         | SO₃         | SiO₂        | Al₂O₃       | Fe₂O₃       | Na₂O        | MgO         | P₂O₅        | TiO₂        | K₂O         | others |
|                 | 26.89       | 16.80       | 16.06       | 15.46       | 14.28       | 5.32        | 2.97        | 0.40        | 0.30        | 0.27        | 1.25    |

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The solid–gas reaction rate can be expressed as a function of temperature and conversion:

$$\frac{dX}{dt} = k(T)f(X)$$

(3)

where the subfunction $f(X)$ represents the model that the gasification followed, such as the RPM, GM, VM, etc. The subfunction $k(T)$ can be expressed according to the Arrhenius relationship:

$$k(T) = k_0 e^{-E_a/RT}$$

(4)

where $k_0$ is the pre-exponential factor and $E_a$ is the activation energy.

2.3. Structure Analysis. A Raman spectrometer (DXR, ThermoFisher) was used to characterize the carbon structure of coal char and gasified semi-char. The TGA can accurately record the change in weight over time, and thus chars with different carbon conversions can be collected from the interrupted TGA experiment. In the present work, the gasified semi-chars at the conversions of 0.2 and 0.8 were prepared, and the gasification temperature was 800 °C. The Raman spectrum with a wavelength range of 800–2000 cm$^{-1}$ was collected. The graphitization degree and the relative content of the amorphous carbon structure of char were evaluated by the peak fitting method. To reduce the experimental error, 10 sampling points were selected for each sample and the average spectrum was obtained.

The surface morphology and element distribution of coal char and gasified semi-char were analyzed by scanning electron microscope and energy dispersive spectrometer (SEM–EDS, SU-1510, Hitachi), respectively. To improve the reliability of the experimental results, 20 sampling points or surfaces were randomly selected for testing and analysis.

3. RESULTS AND DISCUSSION

3.1. Gasification Reactivity. 3.1.1. Effect of the Catalyst Loading Method and Content. The effect of the catalyst loading method on coal char gasification was investigated first. Figure 1 compares the gasification reactivities of HMC, HMDC3, and HMWC3. It was found that the coal char prepared from wet impregnation (HMWC3) had higher gasification reactivity at both 800 and 900 °C. The coal char using the dry mixing method with the catalyst had a slightly higher reactivity at the late stage of gasification. It can be concluded that the gasification reactivity can be improved efficiently through wet impregnation.
loading content of the wet method on coal char reactivity was studied, as shown in Figure 2. It was found that the reactivities of HMWC2 and HMWC3 were similar and significantly higher than that of HMWC1. Therefore, the optimal loading mode was the 2 wt % catalyst using the wet impregnation method. Generally, the activity of the iron-based catalyst was low due to higher electronegativity, and the gasification reactivity was not promoted too much compared with the AAEM rich catalyst.

3.1.2. Effect of Gasification Temperature and Conversion.

According to the optimal catalyst loading conditions, the gasification reactivities of HMC, HMDC3, HMWC1, and HMWC2 were further investigated herein. The reactivity index $K$ based on eq 2 was calculated at different temperatures for the four samples, as shown in Figure 3a. The index $K$ considered the time interval of the 60% conversion and thus can represent the overall reactivity. It was found that the index $K$ increased with the increase of temperature, and the HMWC2 had the highest index $K$ at the same gasification temperature. To quantitatively describe the catalytic activity, the specific index $K/K_{HMC}$ was further calculated, as shown in Figure 3b. The specific reaction index was greater than 1, indicating that the catalyst can promote gasification. The higher the value, the stronger the catalytic activity. The results showed that the catalytic activity was stronger at low temperatures for char with wet impregnation, whereas the temperature had a limited effect on catalyst activity using the dry mixing method. Especially, the specific indexes of HMWC1 and HMDC3 were very close at high temperatures.

The change in the gasification rate with conversion was further analyzed, as shown in Figure 4. It was found that the maximum reaction rate ($R_{\text{max}}$) occurred at a conversion of 0.1. On the one hand, this can be explained by the random pore model (RPM), which featured $R_{\text{max}}$ at low conversions. On the other hand, isothermal gasification in the TGA required the time to replace N$_2$ with CO$_2$, which may result in lower reaction rates at the initial stage. Overall, the reaction rate decreased with the increase of conversion. This was significantly different from catalytic gasification using a potassium-based or sodium-based catalyst, which usually had $R_{\text{max}}$ at the late stage of gasification. The gasification rate of HMDC3 was lower than that of HMWC1 at 800 °C, whereas they were pretty close at 900 °C. This was consistent with the results of reactivity index analysis.

3.2. Kinetic Analysis. 3.2.1. Model-Free Method. The changes in activation energy ($E_a$) with conversion $X$ can be obtained by the model-free method. eq 3 can be rewritten as
changes at the conversion in the range of 0.2–0.8 based on the model-free method. The average \( E_a \) values were 113.86, 114.96, 109.79, and 95.83 kJ/mol for HMC, HMDC3, HMWC1, and HMDC2, respectively. Moreover, \( E_a \) increased with the conversion for all samples, especially for HMWC2, indicating that the gasification reactivity decreased gradually. It is a fact that the more the active sites are consumed \( fi \), the more the deactivation and the volatilization of the catalyst with the conversion for all samples, especially for HMWC2, whereas the addition of the catalyst would change the \( E_a \) value than that of raw coal char. It was found that the gasification temperature had little effect on the structure parameter \( \psi \), whereas the char from wet impregnation had a lower \( \psi \). It can be speculated that the dry mixing method was larger, whereas the char from wet impregnation had a lower \( \psi \).

3.3. Catalytic Mechanism. In this section, a comparative study of chemical structure evolution between the raw and gasified semi-char has been carried out to explore the catalytic mechanism using the iron-based catalyst during gasification. Specifically, the catalytic element content and distribution together with the carbon structure were analyzed, with the emphasis on the different loading methods. Moreover, the deminimalized coal was prepared by NH4AC washing to remove the active AAEMs. By comparing the catalytic effect of the iron-based catalyst on raw and deminimalized coal, the interactions between the catalyst and inner minerals of coal can be implied. The catalytic effect is more dependent on the chemical structure evolution than the physical structure. The physical structure analysis of the micropore structure can be found in the Supporting Information.

3.3.1. Surface Morphology and Catalyst Distribution. The surface morphology of gasified semi-char was observed by SEM. Figure 7a1–a4 shows that the catalyst would break and spread over the char surface during wet impregnation, whereas the catalyst remained intact as spherical particles in char swarm using the dry mixing method (Figure 7b3,b4), and the fragments on the char surface were mainly carbonaceous and
Figure 6. Determination of the pore structure parameter $\psi$ for RPM.

Table 3. Kinetic Parameters and Fitting Performance for the RPM, GM, and VM

| samples   | $\psi$  | $E_a$ (kJ/mol) | SSR$^a$ | $E_a$ (kJ/mol) | SSR$^a$ | $E_a$ (kJ/mol) | SSR$^a$ |
|-----------|---------|----------------|---------|----------------|---------|----------------|---------|
| HMC       | 10.93   | 115.46         | 0.023   | 115.10         | 0.189   | 114.57         | 0.407   |
| HMDC3     | 15.64   | 116.83         | 0.028   | 116.23         | 0.245   | 115.60         | 0.480   |
| HMWC1     | 8.79    | 110.47         | 0.017   | 110.30         | 0.150   | 110.08         | 0.355   |
| HMWC2     | 8.89    | 96.28          | 0.025   | 97.70          | 0.162   | 96.81          | 0.369   |

$^a$Average value.

Figure 7. SEM and EDS for semi-char with (a) wet impregnation and (b) dry mixing. (c) Fe content.
fly ash (Figure 7b1,b2). It suggested that wet impregnation was conducive to the dispersion of the catalyst, which resulted in the high catalytic activity for gasification. The iron content on the char surface was further detected, and the results are shown in Figure 7c. The iron content of HMDC3 was close to that of HMC and was significantly lower than those of HMWC1 and HMWC2. The increase of the iron content on the char from dry mixing pretreatment was very limited even if the maximum amount of the catalyst was added. It again indicated that wet impregnation was better than dry mixing for catalyst dispersion. Besides, the iron content of char increased as the gasification procedure with the consumption of carbonaceous. Its property was similar to those of Ca and Mg and was different from that of K or Na.33

3.3.2. Carbon Structure Evolution. Raman spectroscopy is widely used to study the carbon structure of coal char. Herein, the carbon structures of the four coal chars (HMC, HMDC3, HMWC1, and HMWC2) were analyzed, together with their gasified semi-chars. It was found that all of the spectra had two obvious peaks at around 1350 and 1580 cm$^{-1}$, which were D (defect) and G (graphite) bands.34 Figure 8a shows the Raman spectra of coal char. It was found that the spectral curves of HMC and HMDC3 were similar in shape and were different from that of HMWC1 or HMWC2, especially at around the D band. Figure 8b,c shows the Raman spectra of gasified semi-chars, and the conversion was controlled accurately at 0.2 and 0.8, representing the initial and late stages of gasification. It should be noted that the same conversion for different samples required different reaction times. It was found that the intensity of D1 and the valley region were decreased significantly as the gasification proceeded.

To quantify the change in different carbon structures, the peak fitting method was adopted according to refs 2, 34. Specifically, Raman spectra was resolved into five peaks (D1, D2, D3, D4, and G), as shown in Figure 8b. The peak area ratios of $I_{D3}/I_G$ and $I_C/I_G$ were calculated herein, and the results are listed in Table 4. It was found that the value of $I_{D3}/I_G$ increased and then decreased for coal catalytic gasification, whereas it monotonically decreased for noncatalytic gasification. $I_C/I_G$ showed the opposite trends. It was worth noting that $I_C/I_G$ increased significantly for the raw coal chars of HMWC1 and HMWC2, indicating that the iron-based catalyst promoted the graphitization of coal char during the devolatilization process. Nevertheless, the gasification reactivity of the wet impregnation char was higher than that of raw coal char. The graphitization degree increased during the gasification process. On the one hand, the active amorphous carbon structure in coal char was consumed, resulting in the ordered carbon structure, especially for catalytic gasification.2,15 On the other hand, the formation and consumption of Fe$_3$C would lead to the graphitization of coal char during gasification.15 The finding in the present work was different from that concluded by Qi et al.14 and Feng et al.15 They believed that the addition of the iron-based catalyst can only promote or inhibit graphitization. Generally, the presence of the iron-based catalyst would promote the graphitization of coal char by comparing the Raman parameters of char with the same conversion. Thus, the carbon structure cannot effectively represent the gasification reactivity in the presence of the iron-based catalyst.

3.3.3. Interactions between the Catalyst and Internal Minerals. The interactions between the iron-based catalyst and inner minerals of coal was explored using the demineralized coal as the reference. Coal was pretreated by NH$_4$Ac washing for 48 h and water washing. Then, the iron-based catalyst was loaded to the demineralized coal according to the optimal catalytic loading method (wet impregnation, 2 wt %), and the demineralized coal char (HM-N-C) and the char with the catalyst (HM-N-WC2) were prepared. The isothermal gasification properties at 800 and 900 °C are shown in Figure 9. It was believed that NH$_4$Ac can remove active (ion-exchanged) AAEMs.24,35 As anticipated, the gasification reactivity decreased dramatically after the pretreatment of NH$_4$Ac washing. According to the reactivity index $K$, the reactivity of HM-N-WC2 increased by 141 and 59% at 800 and 900 °C, respectively. Moreover, the $K$ values of HM-N-WC2 and HMC were very close. This part of the catalytic activity can be considered as the intrinsic activity of the iron-based catalyst. This was because some other metal substances existed in the iron-based catalyst that was used for the coal liquefaction technology. In addition, the reactivity of HMWC2 was higher than that of HM-N-WC2, especially at the low gasification temperature. This part of the catalytic activity can be considered as the synergistic effect from the interactions between the catalyst and inner minerals. This might be due to

| Table 4. Peak Area Ratio for Coal Char and Gasified Semi-Char |
|-----------------|--------|------|---------|---------|
| samples        | raw $I_{D3}/I_G$ | $I_C/I_G$ | $I_{D3}/I_G$ | $I_C/I_G$ |
| HMC            | 1.137  | 0.147 | 0.940   | 0.156   |
| HMDC3          | 1.028  | 0.159 | 1.099   | 0.148   |
| HMWC1          | 0.654  | 0.228 | 0.782   | 0.190   |
| HMWC2          | 0.751  | 0.214 | 0.778   | 0.187   |

Figure 8. Raman spectra for (a) raw char and (b, c) gasified semi-char.
the fact that the iron-based catalyst reduced the volatilization of the AAMEs, and thus the reactivity was enhanced. Moreover, these two parts of the catalytic activity decreased with the increase of gasification temperature.

4. CONCLUSIONS

In this work, the iron-based catalyst from a coal liquefaction plant was used to investigate the catalytic effect on coal char gasification. The catalyst loading method and content were taken into consideration. The char gasification kinetics were analyzed by employing the model-free and model-fitting methods. The catalytic mechanism was discussed from the perspective of catalytic element distribution, carbon structure evolution, and interactions between the inner minerals. The following conclusions can be drawn from this study.

(1) The coal char prepared from wet impregnation had higher gasification reactivity. Moreover, the best utilization pattern of the iron-based catalyst was the 2 wt% catalyst with wet impregnation in the application. This implied that the coal water slurry gasifier was preferred to reuse the coal liquefaction residue.

(2) The Ea obtained from the model-fitting method matched well to that from the model-free method. The RPM showed the best fitting performance. Moreover, wet impregnation can increase the active sites and thus reduce the Ea significantly.

(3) Through wet impregnation, the catalyst was broken and can be fully distributed on the coal char surface, which resulted in higher catalytic activity, whereas the spherical catalyst particles still existed in coal char swarm through the dry mixing method.

(4) The graphitization degree of coal char increased after the devolatilization process. Nevertheless, the iron-based catalyst can still accelerate the gasification rate. Moreover, graphitization decreased first and then increased during catalytic gasification using the iron-based catalyst.

(5) The demineralized coal char with the catalyst had lower reactivity than raw coal char. This can imply that the iron-based catalyst can work as a catalyst alone and can also interact with inner minerals (ion-exchanged AAEMs) of coal showing higher catalytic activity.
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