Kinetic Modeling of CO₂ and H₂O Gasification Reactions for Metallurgical Coke Using a Distributed Activation Energy Model

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ABSTRACT: A distributed activation energy model (DAEM) was applied to the kinetic analysis of CO₂ and H₂O gasification reactions for pulverized metallurgical coke. The results of the scanning electron microscopy observations and CO₂ gas adsorption suggested that the gasification reaction occurs at the particle surface. Therefore, a grain model was employed as a gasification reaction model. The reaction rates of CO₂ and H₂O gasification were evaluated based on the DAEM. The activation energy changed as the reaction progressed and hardly depended on the particle size. The activation energies were 200–260 kJ/mol in CO₂ gasification and 220–290 kJ/mol in H₂O gasification. The frequency factor of H₂O gasification was approximately 10 times larger than that of CO₂ gasification, regardless of the progress of the reaction. At the same activation energy level, the frequency factor showed a higher value with a decrease in the particle size. This result was consistent with the theory of the grain model and indicated that the gasification reaction of the pulverized coke with a micrometer scale occurs on the surface of the coke particle. Furthermore, the value predicted by the DAEM was in good agreement with the experimental one.

1. INTRODUCTION

Metallurgical coke is the reducing agent for iron ore and gets converted to CO or CO₂ by various gasification reactions. In addition, it acts as a spacer in a blast furnace, and hence, its strength is important. The iron-making industry emits a large amount of CO₂ gas—a major greenhouse gas. Therefore, many countries are trying to supply H₂ gas into a blast furnace in an effort to reduce the production of CO and/or CO₂ gases. As part of this endeavor, Japan has started a national project “COURSE50 (CO₂ Ultimate Reduction System for Cool Earth 50)”. The aim of this is to reduce the CO₂ gas emission from a blast furnace by approximately 30% by 2050 using H₂ gas converted from coke oven gas (COG). However, H₂O gas is generated by the oxidation of H₂ gas, and the gas atmosphere in the furnace is different from that of conventional furnaces. Therefore, any change in the gas atmosphere would affect coke gasification.

Coke gasification is the reaction to convert solid fuels into a heat source and a reducing agent such as H₂ or CO gases. Hence, the reactivity of coke is a very important property. Although the coke reactivity index (CRI) expresses the apparent reaction rate of a coke lump and is affected by gas diffusion, the CRI has been widely used as a parameter for evaluating gasification reactivity.1–6 Pusz and Buszkó focused on the difference between the mean maximum and minimum reflectances, the CRI. They showed that the crystallinity greatly affected the reactivity.4 Morga et al. analyzed severalokes produced at 1223 K by Raman spectroscopy and suggested that the CRI of the coke produced under these conditions can be predicted based on the half-widths of the G and D2 bands.5,6 These studies also showed that the reactivity of coke gasification and carbon crystallinity are closely related. Also, the crystal structure of carbon changed by gasification and thermal treatment.7–9 Moreover, carbon matrices with various reactivities would exist in coke.

To evaluate the intrinsic reaction rate, thermogravimetric analysis (TGA) is widely used for the kinetic analysis of coal and biomass gasification. Roberts et al. investigated the intrinsic reaction rate of the gasification reaction of coal char by measuring the reaction rate of gasification with various reactant gases.10–13 Specifically, they calculated the reaction rate per unit surface area by measuring the surface area by the Brunauer–Emmett–Teller (BET) method; they also evaluated the effect of ambient pressure on the reaction rate of coal char gasification.10 In addition, they calculated the adsorption rate

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of CO$_2$ gas from the reaction rate measured by TGA based on the Langmuir–Hinshelwood mechanism and reported that the adsorption rate almost corresponded to that obtained by CO$_2$ gas adsorption based on the BET method at an ambient pressure of <30 atm. Following this study, both competition and inhibition between reactant gases were examined based on the Langmuir–Hinshelwood mechanism under a mixed atmosphere of CO$_2$ and H$_2$O. These investigations indicated that the data accuracy obtained from TGA is sufficient to discuss on the basis of the reaction mechanism. Thus, to evaluate reactivity of coke gasification accurately, it is necessary to measure the reaction rate under the condition that the effect of gas diffusion was removed and to employ the model that considers spatial distribution of reactivity.

To analyze the reaction rate of coke gasification taking into consideration the spatial distribution of reactivity, the distributed activation energy model (DAEM), which is often used for the release of volatile matter from coal, can be used because the change in carbon crystallinity by oils, occur simultaneously. For metallurgical coke, although the coal samples by applying the method to the experimental properties and discussed the ratio of volatile matter present in CO$_2$ gasi. The calculated value corresponded to the experimental one. These studies show that the prediction accuracy of the reaction rate determined with the obtained Arrhenius parameters, and the validity of the analysis was evaluated by comparing the result obtained with the experimental values.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation and Analysis of Sample Properties. Metallurgical coke produced in a coke oven was used as the sample. The properties of the sample—obtained by proximate analysis (JIS M 8812), ultimate analysis (JIS M 8819, JIS M 8813 (O)), and ash composition analysis—are listed in Table 1. The coke sample was pulverized and sieved based on JIS Z 8801. The aperture sizes were set to 32–53 μm (Coke S), 75–100 μm (Coke M), and 125–150 μm (Coke L). To evaluate the accuracy of sieving, the particle size distributions of the samples were measured with a laser diffraction particle size analyzer (Microtrac HRA, NIKKISO). Figure 1 shows the particle size distribution of the samples. The refractive indices of the solvent and the sample were set to 1.33 and 1.51, respectively, which were those of water and glass, respectively.

![Figure 1. Particle size distributions of Coke S, Coke M, and Coke L.](https://doi.org/10.1021/acsomega.1c00443)
The measurement time and the number of measurements were 30 s and 2, respectively. As shown in Figure 1, all samples showed unimodal particle size distributions, and the volume median diameter followed the order Coke L, Coke M, and Coke S. Hence, the particle size distribution was different for different samples, and the average diameter followed the order Coke L, Coke M, and Coke S.

2.1.2. Observation of the Surface of Coke Samples Using SEM. To evaluate the surface structure of coke samples, the sample surface was observed by SEM (S-4800, Hitachi High-Technologies, Inc.). The acceleration voltage was set to 3.0–5.0 kV.

2.1.3. Measurement of the Pore Surface Area and Pore Size Distribution Based on the Gas Adsorption Method. To quantitatively evaluate the surface structure of the particles in the coke samples, their specific surface area and pore size distributions were measured using an automatic specific surface area/pore size distribution measurement instrument (AS1-MP, Quantachrome Instruments). The specific surface area was estimated based on the BET method. The pore size distribution was obtained by fitting the adsorption isotherm curve calculated by density functional theory (DFT) to the experimentally obtained curve. The calculated adsorption isotherm curve was obtained by assuming a slit pore. Both the fitting based on the non-local density functional theory (NLDFT) method and the one based on the Monte Carlo models were conducted, and the fitting errors of the two methods were compared. Herein, the pore size distribution by the NLDFT method was used because it produces a smaller error than the Monte Carlo model.

2.2. Gasification Experiments. Gasification experiments of CO₂ and H₂O were conducted using a thermogravimetry analyzer (STA 449 F1 Jupiter, NETZSCH) and one (TG/DTA-2000SA, Bruker AXS K.K.) equipped with a steam generator (HC9700, NETZSCH, Japan), respectively. The reaction rate of gasification was analytically calculated by the weight loss. Before the gasification experiment, 1.00 ± 0.05 mg of the coke sample was measured and placed in an alumina crucible. To avoid the stacking of coke particles, they were dispersed in the crucible. Next, the crucible was placed on the sample carrier of the thermogravimetry analyzer. The furnace temperature was increased under a nonactive atmosphere. The heating rate was set to 5, 10, or 15 K/min because the values calculated by the above method to eq 4, and the obtained value was compared with the experimental values.

\[
\ln\left(\frac{a}{T}\right) = \ln\left(\frac{kR}{E_a}\right) - \ln\left(\int_0^X \frac{1}{f(X)} \, dX\right) - \frac{E_1}{RT}
\]

(2)

Here, \(a\) is the heating rate, \(f(X)\) is the equation of the reaction model, \(R\) is the gas constant, and \(T\) is the sample temperature. Note that \(f(X)\) is expressed in the grain model by eq 3.

\[
f(X) = (1 - X)^{2/3}
\]

(3)

To investigate the validity of the obtained Arrhenius parameters, the reaction rate was analytically calculated by assigning the activation energy and frequency factor obtained from the above method to eq 4, and the obtained value was compared with the experimental values.

\[
\frac{dX}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right) f(X)
\]

(4)

In eq 4, the assigned activation energy and the frequency factor are the values obtained at the conversion of \(X\). The activation energy and frequency factor values at each conversion were obtained by linear interpolation between discrete points because the values calculated by fitting were discontinuous. The calculated value of the conversion was defined using eq 5.

\[
X_n = X_{n-1} + \frac{dX}{dt} \Delta t
\]

(5)

where \(n\) is the time step and the time increment \(\Delta t\) was set to 0.1 s. The calculated value did not change when the time increment was set to under 0.1 s.

3. RESULTS AND DISCUSSION

3.1. Difference in the Physical Structure between Coke Samples. To select the reaction model, the external surface of the coke samples was qualitatively evaluated. Figure 3 shows the SEM images of Coke S and Coke L before the
reaction \((X = 0)\). As can be seen in the low-magnification images shown in Figure 3a,c, the external surface of the particle had hardly any microscale pores; as a result, the surface was smooth. This is because the pores that existed inside the coke samples were eliminated by pulverization. The higher-magnification images (Figure 3b,d) show that although the external surface was rough and fine particles attached to the external surface, micrometer-scale pores were not observed. Therefore, the gasification reaction is expected to occur on the external surface of the coke sample.

Pores smaller than macropores of size \(0.1–1000 \mu m\) could not be distinguished in the SEM images. To quantitatively evaluate the smaller pores, the pore size distributions of Coke S and Coke L before the reaction were obtained by the gas adsorption method (Figure 4). Each sample had pores smaller than 1.4 nm with a cumulative pore volume of \(2.0 \times 10^{-9}–3.2 \times 10^{-9} \text{ m}^3/\text{g}\). The total volume of the sample is calculated to be \(1 \times 10^{-9} \text{ m}^3/\text{g}\) by assuming that the bulk density of the coke sample is 1000 kg/m\(^3\). From this result, the volume fraction of the pores of size <1.4 nm in the coke sample is calculated to be approximately 0.001 vol\% and, thus, there were hardly any pores in the coke samples. Table 2 shows the specific surface areas of Coke S and Coke L before the reaction. The specific surface area of Coke S was larger than that of Coke L because the former had smaller particles than the latter. This result is similar to the trend shown in the SEM images and the pore size distribution. Therefore, it can be suggested that the reaction model in which the reaction occurs on the sample surface is suitable for the gasification reaction of metallurgical coke pulverized to a micrometer scale. In this study, the grain model was employed as the reaction model for kinetics analysis.

![Figure 3. SEM images of (a,b) Coke S and (c,d) Coke L with (a,c) low and (b,d) high magnification before reaction \((X = 0)\).](image-url)

![Figure 4. Pore size distributions of (a) Coke S and (b) Coke L before reaction.](image-url)

| Table 2. Specific Surface Areas of Coke S and Coke L before Reaction |
|---------------------------------------------------------------|
| sample     | specific surface area [m\(^2\)/g] |
| Coke S     | 9.01                             |
| Coke L     | 8.50                             |
3.2. Difference in Gasification Reactivity According to Particle Size and Reactant Gas. Figure 5 shows changes in the conversion and reaction rate as the reaction progresses. For each reactant gas, the reaction time decreased with an increase in the heating rate. When the time elapsed was the same, the reaction temperature was high when the heating rate was high. Thus, the reaction rate of gasification increased with the heating rate when the time elapsed was the same, and the reaction time became shorter with an increase in the heating rate. The reaction time tended to decrease with an increase in the particle size of the sample. This tendency was particularly remarkable for CO₂ gasification. As shown in Figure 5b, the reaction rates are almost equal regardless of the particle size when the reaction temperature was below 1300 K. However, at 1300−1500 K, the reaction rate increased with a decrease in the particle size. This result is consistent with that obtained from the SEM images, the pore size distribution, and the specific surface area. Especially, the specific surface area increased with a decrease in the particle size as shown in Table 2, and then, the reaction rate was proportional to the specific
Figure 6. Relationship between \(\ln\left(a/T^2\right)\) and \(1/T\) at each conversion for CO\(_2\) gasification and H\(_2\)O gasification of (a) Coke S, (b) Coke M, and (c) Coke L.
surface area. This result suggested that the reaction occurred at the external surface of the particle, and the effect of nanosized pores on the reaction rate was small. In addition, when the reaction temperature was over 1500 K, the reaction rate monotonically decreased in each case because the reaction surface area of the sample decreases as the reaction progresses. In addition, in the case of H2O gasification, the reaction rate increased with a decrease in the particle size at 1250−1400 K. As these results show, the reaction rate depended on the particle size at the middle stage of the reaction, and thus, the reaction time decreased with decreasing particle size. Moreover, a comparison of the reaction time between CO2 gasification and H2O gasification showed that the reaction time for H2O gasification was approximately 1.3 times shorter than that of CO2 gasification. This tendency is common1,2,3,23,33 and is probably caused by the difference in the reactivity of the reactant gas.

3.3. Evaluation of Arrhenius Parameters Obtained from the DAEM. Figure 6 shows the relationship between ln(a/T^2) and the inverse of temperature for determining the activation energy and frequency factor by the method proposed by Miura and Maki.25 In this figure, to calculate the distribution of the activation energy with high accuracy, the values are plotted with an increment of 0.025 in the conversion range between 0.1 and 0.9. At each conversion, the three different heating rates had a negative relationship; Honaker et al. also reported a similar result.24,25 Figure 7 shows the activation energy and the frequency factor calculated based on the conversion. The grain model was employed as the reaction model used for fitting by the DAEM. For each reactant gas, the activation energy first decreased and then increased with the reaction. The frequency factor also showed a similar behavior. As shown in Figure 7b, the activation energy of Coke M was minimum at a conversion
of 0.3; the frequency factor also showed a similar trend, perhaps owing to the compensation effect.\textsuperscript{34} Compared with the reactant gases, the activation energy of CO$_2$ gasification was 200–260 kJ/mol (Figure 7a) and was equivalent to that reported in previous studies.\textsuperscript{35} In contrast, the activation energy of H$_2$O gasification was 220–290 kJ/mol, which was higher than that of the CO$_2$ gasification reaction. Although this is different from the general trend,\textsuperscript{10,36,37} a previous study\textsuperscript{10} also reported a similar trend. Similar to the activation energy, the frequency factor of the H$_2$O gasification reaction seemed to be higher than that of the CO$_2$ gasification reaction. To compare the frequency factor at the same activation energy, the
change in the frequency factor for the activation energy is plotted in Figure 8. For each gasification reaction, the activation energy and the frequency factor have a positive correlation owing to the compensation effect.\(^{34}\) For each particle size, the frequency factor of the H\(_2\)O gasification reaction was always approximately 10 times larger than that of the CO\(_2\) gasification reaction. In this study, the reaction rate of H\(_2\)O gasification was larger than that of CO\(_2\) gasification because of the difference in the frequency factor. It seems that the activation energy and the frequency factor hardly depend on the particle size in each gasification reaction (Figure 7). However, when the activation energy was the same, the frequency factor increased with a decrease in the particle size (Figure 8). This tendency did not change by changing the

Figure 10. Comparison of (a) conversion and (b) reaction rate of Coke S, Coke M, and Coke L between the experimental and calculated results at heating rates of 5, 10, and 15 K/min for H\(_2\)O gasification.
reactant gas. In a previous study, the frequency factor of CO₂ gasification of a high ash coal char was larger with a smaller particle. The reaction rate also increased with a decrease in the particle size, and thus, this result was similar to our results. Moreover, the frequency factor calculated using the grain model, kg, is inversely proportional to the initial particle size, as shown in eq 8.

\[
k_g = \frac{b}{C_{B0}} \left(1 - \varepsilon_0\right) C_a^m C_s^n (8)
\]

Thus, the frequency factor could express the reaction model. This result suggested that the gasification reaction of the coke pulverized into micrometer particles is a surface reaction.

3.4. Evaluation of the Validity of the Analysis. Figures 9 and 10 show the conversion and reaction rate calculated using the DAEM with the experimental values. In the CO₂ gasification reaction, the calculated values correspond to the experimental values, and the prediction accuracy would be almost equivalent regardless of the heating rate and particle size (Figure 9). At a reaction temperature of 1400–1600 K, the calculated reaction rate of each particle size slightly overestimated the experimental value. This is because the accuracy of fitting decreased around 1400 K owing to the change in the slope of the experimental reaction rate. In addition, in the H₂O gasification reaction, the calculated value underestimated the experimental value at 1300–1500 K. In this temperature range, the difference between the calculated and experimental values for H₂O gasification was larger than that for CO₂ gasification. This is because the slope of the measured reaction rate in H₂O gasification changed around 1300 K, similar to CO₂ gasification, and this change was larger than that of the CO₂ gasification reaction. Thus, the accuracy of fitting in H₂O gasification was lower than that in CO₂ gasification. However, the calculated values of H₂O gasification and CO₂ gasification were similar to the experimental values obtained at reaction temperatures below 1300 K or over 1500 K. Therefore, the reaction rate calculated from the DAEM expressed the experimental value, suggesting that the analysis performed in this study is almost valid.

4. CONCLUSIONS

Gasification experiments of CO₂ gas or H₂O gas for coke pulverized to the micrometer scale were conducted, and kinetic parameters were determined based on the distributed activation energy model (DAEM).

To select the reaction model, the surface of the coke sample was evaluated by scanning electron microscopy (SEM) and gas adsorption. The SEM images showed that there were hardly any micrometer-scale pores on the sample surface. In contrast, the gas adsorption results showed that Coke S and Coke L have pores of size <1.4 nm. However, the cumulative volume of the small pores was approximately 0.001 vol %. Moreover, the specific surface area was larger with a decrease in the particle size. The reaction time decreased with the particle size for each reactant gas as well. These results suggest that the reaction occurs on the surface, and thus, the grain model was employed as a reaction model.

For the kinetic parameters, the activation energy of each gasification changed with the reaction and was hardly dependent on the particle size. The activation energy was 200–260 kJ/mol for CO₂ gasification and 220–290 kJ/mol for H₂O gasification. At the same activation energy, the frequency factor increased with the particle size, suggesting that the gasification of coke pulverized to a microscale size occurs on the particle surface.

In the comparison of the value predicted by the DAEM with the experimental one, the calculated and the experimental values corresponded well, and thus, it was confirmed that the analysis in this study is almost valid. As a future work, the kinetic parameters will be applied to large-scale simulation of coke degradation based on computational fluid dynamics and contribute to improve the prediction accuracy of the numerical simulation.

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ABBREVIATIONS

BET, Brunauer–Emmett–Teller; COG, coke oven gas; CRI, coke reactivity index; CSR, coke strength after reaction; DAEM, distributed activation energy model; DFT, density functional theory; SEM, scanning electron microscopy; TG, thermogravimetry; XRD, X-ray diffraction

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