Micro Pore Structure and Reaction Rate of Coke, Wood Charcoal and Graphite with CO$_2$

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The reaction rate of coke, wood charcoal and graphite with pure CO$_2$ were obtained at 1 173 and 1 373 K. The change in the reaction rate, specific surface area and micro pore size distribution with reaction degree were examined. The results are summarized as follows.

1. The specific surface area changes remarkably with reaction degree, while the reaction rate does not change so much.
2. The change in the specific surface area accords well to the change in the volume of smaller pores than $10^{-8}$ m in diameter.
3. The reaction occurs exclusively on the surface of pores between $10^{-8}$ to $10^{-6}$ m in diameter.
4. The effective surface area for the reaction is from 0.064 to 0.25 of the total surface area.

KEY WORD: coke; wood charcoal; graphite; reaction rate with CO$_2$; change in specific surface area; size distribution of micro pore; effective surface area for reaction.

1. Introduction

In order to operate the blast furnace at lower temperature than usual, the highly reactive carbonaceous materials at low temperature should be developed. For that purpose, the reaction kinetics of various carbonaceous materials should be clarified. In the previous work, wide variety of materials from the activated carbon to glassy carbon were examined with respect to the reaction with CO$_2$ in the low temperature range between 823 and 1 173 K. The reaction rates were two orders of magnitude different from each other. In order to explain the difference, the new reaction rate was defined by the reaction rate per unit surface area using the data of specific surface area. There have been many papers on the reaction kinetics of carbonaceous materials with CO$_2$. In their studies, the reaction rate was expressed by the change in reaction degree with time, regardless of the reaction surface area. In the present work, in order to discuss the reaction kinetics more precisely, the effective reaction site was examined by following the change in reaction rate, specific surface area and pore structure with the reaction degree.

2. Experimental

2.1. Apparatus

Figure 1 shows the experimental apparatus. The reaction tube was made of mullite and of 48 mm inner diameter and 1 m length. The alumina balls of 8 mm diameter were filled up to 30 mm beneath the setting position of samples in the reaction tube, in order to preheat the gas flow. The gas flow system was made of gas cylinder, silica gel column, flow meter and valve to control the gas flow rate. The CO$_2$ was...
used for the reaction. The N₂ gas was used for flashing the inside of the reaction tube before and after the experiment. The sample weight was measured with the electronic balance which was connected to a personal computer with the RS232C cable. The top of the reaction tube was equipped with blanch tube. The outlet gas was introduced to the infrared gas monitor to measure the CO and CO₂ contents.

2.2. Procedure
The sample was put in the basket and set at the center of the isothermal zone of reaction tube. The sample was heated to the experimental temperature under N₂ atmosphere. After the weight became constant at the temperature, the gas flow was changed to CO₂ to start the gasification reaction. The output from the electronic balance was continuously recorded with the computer. When the reaction reached the fixed reaction degree, the atmosphere was changed again to N₂. From the time of atmosphere change, the outlet gas was lead to the infrared gas monitor of CO and CO₂ in order to estimate RSA by the transient kinetic method. The sample was cooled in N₂ atmosphere to the room temperature and taken out from the reaction tube. Then the sample was subjected to the measurement of the specific surface area by BET method with N₂ as the operating gas. The pore size distribution of the sample was estimated by mercury porosimeter in the larger range than 10⁻⁸ m and by BET method in the smaller range than 10⁻⁸ m.

2.3. Experimental Condition
The carbonaceous materials used were coke, wood charcoal and graphite. The composition of the sample is shown in Table 1. The ash content was determined by the weight of residue after burning the ground sample in the air at 1273 K. The volatile matter V.M. was estimated by the weight loss during heating the sample in N₂ at the experimental temperature. The fixed carbon content, FC, was the rest of ash content and V.M. content. The samples were cut in the cubic form of 10×10×10 mm. The experimental temperature was 1173 and 1373 K. The gas flow rate was 50 cm³ (STP)/s each for N₂ and CO₂, respectively. The reaction degree was every 5% up to 25% at 1373 K and every 2.5% up to 10% at 1173 K.

3. Results and Discussion
3.1. Reaction Rate
Figure 2 shows the weight change with time after the gas was changed to CO₂. The curve was not strictly linear. Therefore, the reaction rate was obtained from the slope of the line at the end of reaction. Figures 3 and 4 show the change in reaction rate with reaction degree, respectively at 1173 and 1373 K. The reaction rate of wood charcoal was about 5 times larger than that of coke. That of graphite was about a half of that of coke. The reaction rate of coke and graphite did not change so much with reaction degree at both temperatures. That of wood charcoal seems to change more than those of coke and graphite. But, the amount of change does not seem so much for example 1.5 times at most. Figure 5 shows the Arrhenius plot of the reaction rate. The slopes of lines are similar to each other. The activation energy was estimated as 189, 178 and 191 kJ/mol, respectively for coke, wood charcoal and graphite. These activation energy data accorded well to those in the previous work₁ which were obtained at lower temperature than 1173 K.

3.2. Specific Surface Area
Figure 6 show the change in the specific surface area with reaction degree at 1373 K. The specific surface area
increased remarkably about 5 times with the reaction degree up to 20% and decreased slightly at 25% both in the case of coke and wood charcoal. That of graphite increased continuously but not so much. The increase in specific surface area of coke with reaction degree was also reported by Tate.13) Figure 7 shows the change in the specific surface area with reaction degree at 1 173 K. The abnormal increase can be seen at 2.5%. At 5%, however, the specific surface area dropped and at larger reaction degree, increased again, in the case of wood charcoal. In the case of coke, it increased at 2.5% but seemed to be constant at larger reaction degree. These changes in the specific surface area with reaction degree do not accord with the change in reaction rate. Thus, it can be seen that the reaction should not occur on the entire surface area determined by BET method.

3.3. Pore Size Distribution by Mercury Porosimeter

Figure 8 shows the pore size distribution of coke, wood charcoal and graphite before the reaction. The volume of smaller pores than $10^{-6}$ m was larger in the order of wood charcoal, coke and graphite. This order accorded well with that of the reaction rate shown in Figs. 3 and 4. Figure 9 shows the change in pore size distribution with reaction degree at 1 373 K. In the figure, the result of 0% shows the datum of raw material sample. At the reaction degree of 5%, the volume of smaller pores than $10^{-6}$ m decreased and that of larger pores than $10^{-6}$ m increased. It can be seen that the reaction occurred on the surface of smaller pores than $10^{-6}$ m and the pore size increased by the reaction during the reaction to the reaction degree of 5%. After the 25% reaction, the volume of all pore sizes increased. The similar results were obtained for other materials. It can be seen from Figs. 8 and 9 that the reaction should occur exclusively on the surface of smaller pores than $10^{-6}$ m in all materials.

3.4. Pore Size Distribution by BET Method

The pore size distribution in the smaller range than $10^{-8}$ m cannot be estimated by the mercury porosimeter. The distribution was obtained by BET method. Figure 10 shows the change in pore size distribution in the smaller
range with reaction degree. The sample was coke and the experimental temperature was 1373 K. The volume of pores in this range increased with reaction degree up to 20% but decreased from 20 to 25% reaction. This trend accorded well with the change in the specific surface area with reaction degree shown in Fig. 6.

Figure 11 shows the change in micro pore size distribution of wood charcoal at 1173 K. The volume at 2.5% reaction was the largest. The volume dropped once at 5.0% and increased thereafter. This trend again accorded well with the change in the specific surface area with reaction degree shown in Fig. 7. It can be seen from Figs. 10 and 11 that the change in specific surface area should indicate the change in the volume of smaller pores than 10^{-8} m. But the surface of these small pores did not contribute so much to the reaction. In these small pores, the gaseous diffusion should be Knudsen type and slow, because the mean free path of CO molecule should be calculated as ca. 10^{-6} m. Thus, the reaction should be controlled by the slow diffusion process.

Combining the results of the present and previous section, it can be seen that the reaction should occur exclusively on the surface of pores of 10^{-8} and 10^{-6} m in diameter. Kashiwaya et al. suggested that the reaction should not occur on the surface of smaller pores than 10^{-3} m which are found in the highly graphitized area. The area becomes inactive because of the graphitization by heated up to higher temperature than 1773 K. On the other hand, one of the present authors reported in the previous work that the reaction of coke occurred just in the surface layer and no reaction occurred in the bulk at higher temperature than 1373 K. In this case, the CO_{2} molecules are consumed in the surface layer and cannot penetrate into the bulk. Thus, apparently, the small pores in the bulk cannot contribute to the reaction. At lower temperature than 1373 K, however, the CO_{2} molecules can penetrate into the bulk to contribute the reaction. Thus, the reaction occurs on the surface of small pores between 10^{-8} to 10^{-6} m in diameter in the present work.

### 3.5. Total Surface Area and Reactive Surface Area

The total surface area TSA (m\(^2\)) can be obtained by the product of specific surface area and the weight of sample after reaction. The reactive surface area can be obtained by the transient kinetic method. When the gas was changed to N\(_2\) after reaction, the outlet gas contained CO\(_2\) and CO. The CO\(_2\) and CO contents in the outlet gas decreased gradually. The reactive surface area is estimated by counting the amount of CO adsorbed on the reactive site. The adsorbed CO is considered to be flashed by the N\(_2\) gas stream. Therefore, the CO content after CO\(_2\) content dropped to zero must be counted. But the change in CO content continued for long time, because the outlet gas flow must not be plug flow. In the present experiment, the CO content after the CO\(_2\) content dropped less than 10 vol% was integrated to obtained the reactive surface area RSA which was expressed in terms of mol CO/g. In practice, the CO content was multiplied by gas flow rate of N\(_2\) to obtained the CO evolution rate. Figure 12 shows an example of the evolution rate change with time. Integrating the curve of hatched part, the amount of CO adsorption was obtained. In the previous work, the amount was divided by the sample weight to estimate the RSA. In the present work, however, the actual area for active site RSA\(_2\) (m\(^2\)) was estimated by using the cross sectional area of CO molecule of 16.3 \times 10^{-20} m\(^2\). Figure 13 shows the change in TSA and RSA\(_2\) with reaction degree at 1373 K. The change in TSA was similar to that shown in Fig. 6. On the contrary, the RSA\(_2\) increased until the reaction degree of 5% and was kept almost constant at larger reaction degree. The RSA\(_2\) was smaller than TSA in all materials. Table 2 shows the ratio of RSA\(_2\) to TSA. The ratio of graphite was almost constant at 0.25. The ratio of wood charcoal decreased from 0.135 to 0.064. The ratio of coke also decreased from 0.183 to 0.064, but in...
creased to 0.114 at the reaction degree of 25%. It can be seen that the effective reaction site should be from 0.064 to 0.25 of the TSA depending on the kind of materials.

3.6 Relation between RSA and Reaction Rate

As shown above, the specific surface area has no meaning to consider the reaction area. Figure 14 shows the relation between RSA and reaction at 1173 K. In the figure, the reaction rate was converted to mole CO per second. The proportional relation was obtained between them. Thus, the RSA can be used as the measure to evaluate the reaction area. If the relation is examined more precisely, the slope of connecting line for each material’s plot differs each other to some extent depending on the materials. This will be the next problem in a future. At 1373 K, however, no clear proportional relation was obtained. This might be due to the influence of gaseous diffusion on the reaction mechanism, which can be neglected at 1173 K.

4. Conclusion

(1) The specific surface area changes remarkably with reaction degree, while the reaction rate does not change so much.

(2) The change in the specific surface area accords well to the change in the volume of smaller pores than 10^{-8} m in diameter.

(3) The reaction occurs exclusively on the surface of pores between 10^{-8} to 10^{-6} m in diameter.

(4) The effective surface area for the reaction is from 0.064 to 0.25 of the total surface area.

(5) The RSA can be used as the measure to evaluate the reaction area so far as the diffusion can be neglected in the reaction mechanism.

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REFERENCES