Reduction Mechanism of Iron Oxide–Carbon Composite with Polyethylene at Lower Temperature

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(Received on June 28, 2010; accepted on September 1, 2010)

Plastic wastes have a potential to play a significant role in the reduction of iron oxides by supplying reducing gases, e.g., H2 and CO, through pyrolysis. However, they are difficult to use as reducing agents because the thermal degradation temperatures of plastics are significantly lower than the reduction temperatures of iron oxides. In this study, the reduction mechanism of iron oxides by carbon and hydrogen obtained from polyethylene in the composite at lower temperature was studied in order to attain a high utilization ratio of polyethylene to the reduction. The reduction experiments were carried out under an Ar–5%N2 gas flow with a heating rate of 0.33 K/s, and the gases formed during reduction were continuously analyzed. The reduction degree of hematite was calculated using the concentration of these gases. The peak temperatures of gas generation rate for the polyethylene–graphite–hematite composite were obtained at 770, 1070, and 1370 K. The peaks at 770 and 1070 K originated from the reaction of polyethylene, and the peak at 1370 K originated from that of graphite. Larger specific surface area of the iron ore leads to fast reduction rate of the ore by polyethylene. Therefore, high utilization rate of carbon derived from polyethylene was obtained when using iron ore with a large specific surface area, such as goethite ore.

KEY WORDS: ironmaking; reduction; plastic wastes; composite; low-grade iron ore.
PE (3.5 mass%) and graphite (12.0 mass%) were added to hematite powder, and mixed well. This mixture ratio was based on the mass ratio of volatile matter to fixed carbon in non-coking coal. The powder mixture was kept in a die, and heated up to 423 K for 900 s. Then, it was press-shaped under a pressure of 98 MPa at the same temperature. A composite sample with weight, diameter, and height of 2 g, 10 mm, and approximately 10 mm, respectively, was obtained. A horizontal hole of diameter 0.5 mm was drilled at the center of the composite sample, and a Pt/Pt–13%Rh thermocouple was set in the hole to measure the temperature at the center of the composite. The experimental apparatus for the reduction of the composite is shown in Fig. 1; details of this apparatus have previously been reported. The prepared composite was heated in Ar–5% N₂ gas flow at a heating rate of 0.33 K/s. The concentrations of CO, CO₂, H₂, H₂O, CH₄, C₂H₄, and C₂H₆ gases generated from the composite were measured by gas chromatography.

Gasification tests were carried out at a heating rate of 0.33 K/s using thermal gravimetry-differential thermal analysis (TG-DTA) in a CO₂ gas atmosphere. The used carbonaceous materials were charcoal, coke, and graphite. The charcoal was prepared by heating at 1 073 K for 3.6 ks in an inert gas. The coke contained 86.0% of fixed carbon. These carbonaceous materials had particle size of <44 μm. PE, polypropylene (PP), and polystyrene (PS) were used for thermal decomposition tests in an inert gas atmosphere at a heating rate of 0.33 K/s using TG-DTA.

3. Results and Discussions

3.1. Reduction Behavior of the Composite at a Low Heating Rate

Figure 2 shows temperatures and generation rates of CO, CO₂, H₂, and H₂O gases from the composite using a Fe₂O₃ reagent with an average particle size of 0.6 μm. The temperatures were measured at 1 mm from the upper surface of the composite and below the Al₂O₃ ball layer (called as “control”) in the sample holder. The temperature differences between the center of the composite and the other measurement points are shown in Fig. 3. The temperature of the composite surface was measured to understand the temperature difference between the place on the surface and at 1 mm upper because the temperature at 1 mm upper was utilized for the following discussion. It shows that the temperatures of the composite center and of its surface do not increase in line with that of the control in the early stages of heating. The maximum temperature difference between the control and the center is 47 K when the temperature of the composite center is 393 K. It can be ascribed to the melting of polyethylene because the melting point of medium density polyethylene is about 383 K. This difference decreases with further increase in temperature.

The maximum temperature difference between the surface and the center of the composite is 30 K; this occurred at approximately 500 K, which is close to the temperature at which thermal decomposition of PE begins. From approximately 500 to 1300 K, the maximum temperature difference is not significant, only 7 K. At 1370 K, the increase in temperature at the center of composite slows temporarily, and therefore the temperature differences increase rapidly. The temperature difference between the places at 1 mm upper and the center of the composite shows similar behavior to those between the surface and the center. Hence, the
temperature at the 1 mm upper the composite is used in the rest of this discussion.

Figure 2 shows that gas generation occurred in three steps. The first step begins at 620 K and almost ends at 820 K. The main gases generated were CO₂ and H₂O. Small amounts of H₂, CH₄, C₂H₂, and C₂H₆ gases were also detected. Figure 4 shows the changes in the weight of olefinic plastics with increasing temperature under inert atmosphere. Weight losses due to thermal decomposition are observed for all plastics, including PE, at the temperature range 600–750 K. This temperature range is similar to that of the first step described above. Mastellone et al. reported the generation of gases like C₆H₆, C₅H₈, C₄H₄, and C₂H₆ gases were also detected. From PE by heating at 823 K. In the present experiment, iron oxide is the only source of oxygen in the composite. These facts indicate that in the first step, the iron oxide in the composite was reduced by H₂ and hydrocarbon gases generated from PE. However, the reaction process is very complicated because there are many possible elementary reactions. It is impossible to elucidate the elementary reduction reactions from the results obtained in this study alone. The overall reaction can be expressed by Eq. (1).

\[ 18\text{Fe}_2\text{O}_3 + (\text{C}_n\text{H}_m)_n = 12\text{Fe}_2\text{O}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O} + (\text{C}_n\text{H}_m)_{n-1}. \]  

The second step took place in the time period 1750–2300 s, beginning at 870 K and ending at 1090 K. CO and CO₂ gases were detected. The thermal decomposition of PE was completed as shown in Fig. 4. This temperature range is too low for the gasification of graphite. Therefore, heat treatment of Al₂O₃–3.5mass% PE composite to 923 K was obtained. The same treatment was also carried out using Fe₂O₃–3.5mass% PE composite. After heating, the composite surface was white, and the only residue obtained was Al₂O₃. The same treatment was also carried out using Fe₂O₃–3.5mass% PE composite. After the treatment, the composite was black and residual carbon was obtained. Chemical analysis of the residual carbon in the composite was carried out. It was clear that approximately 20% of the carbon originated from the PE initially added to the composite remained in the composite. Baker et al. reported that not only metallic iron but also magnetite and hematite acted as catalysts of carbon decomposition from C₆H₆ and CH₃COCH₃ at 973 K. It is predicted that these oxides would act as a catalyst for other hydrocarbon gases. It is therefore suggested that carbon remained in the composite because of the presence of iron oxide enabled decomposition of PE-derived hydrocarbons as shown in Eq. (2).

\[ \text{CH}_n = \text{C} + n/2\text{H}_2 \]  

The residual carbon from the Fe₂O₃–3.5mass% PE composite after heating at 923 K was obtained by treatment with hydrofluoric acid to elute the iron oxide. The gasification test on the residual carbon was carried out at a heating rate of 0.33 K/s in a CO₂ atmosphere. Figure 5 shows the weight changes of the residual carbon together with those of other carbonaceous materials. The temperature at which the weight of the residual carbon starts to decrease was lower than that for charcoal, which has a relatively low gasification temperature. The temperature range, in which a marked decrease in weight was obtained, was similar to the temperature for the second step, as shown in Fig. 2. On the other hand, the gasification of graphite does not proceed in this temperature range. Mastellone et al. reported that molten PE had good wettability with silica sand. It is expected that hematite particles would have good wettability with molten PE because it consists of oxide particles. It seems that there are few direct contact points between graphite and iron oxide. The direct reduction reaction by graphite expressed in Eq. (3) therefore only takes place to a very small extent.

\[ 3\text{Fe}_2\text{O}_3 + \text{C} = 2\text{Fe}_2\text{O}_4 + \text{CO} \]  

It can therefore be concluded that the gas generation at the second step is caused by PE-derived carbon. However, there is a possibility that gas generation from the residual carbon could be attributed not only to the gasification of carbon but also to direct reduction of iron oxide if PE-derived carbon formed on the iron oxide surface. Further investigation is required to evaluate the mechanism of this gas generation. A part of the generated CO gas spends for the indirect reduction of iron oxide, and CO₂ gas generates.

The third step was gas generation above 1090 K. CO and CO₂ gases were detected. A rapid increase in the generation rate of CO gas was obtained at 1370 K. This corresponded to the temperature at which the increase in temperature was temporarily retarded. This resulted from the large endothermic energy caused by an abrupt increase in the rate of the solution loss reaction shown in Eq. (4) together with that of the iron oxide reduction reaction expressed by Eq. (5).

\[ \text{C} + \text{CO}_2 = 2\text{CO} \]
coexistence line of Fe$_3$O$_4$/FeO at 940 K. The reduction degree at 940 K is approximately 11%, which corresponds to the beginning of FeO formation. The gas ratio then followed the coexistence line with increasing temperature by 1090 K. This indicates that the reaction, which controls the gas ratio, is reduction of Fe$_3$O$_4$ because the reaction rate for the reduction shown in Eq. (6) is higher than that of the gasification described by Eq. (4).

$$\text{Fe}_3\text{O}_4 + CO = 3\text{FeO} + CO_2 \quad \text{.........(6)}$$

The gas ratio moves to the FeO single-phase region with further increasing temperature, and the ratio increases slightly. However, the reduction degree hardly increases because there was little generation of reducing gases in this temperature range. Above 1270 K, the reduction degree starts to increase because direct reduction by CO gas generated by the gasification of graphite begins to occur. The gas ratio exceeds the coexistence line of FeO and metallic iron at 1370 K. The reduction degree was 39% at this temperature. This shows that metallic iron formed in the composite because a reduction degree of 30% indicates the beginning of metallic iron formation. The reason for the stagnation in reduction at 1370 K, and the rapid generation of CO gas from the composite, as shown in Fig. 2, is the catalytic effect of metallic iron on the gasification of graphite.

A large amount of tar was obtained in the tube at the outlet side after the reduction experiments. The utilization ratio of PE-derived carbon in the reduction reaction was calculated from the volume of gas generated from the composite. The calculated value was only 33%. The reasons for the low value are that the reduction reaction rate is very low in the temperature range at which the reducing agent is formed from PE, the small temperature distribution in the composite because of the low heating rate, and so on.

### 3.2. Effect of Specific Surface Area of Iron Oxide on Reduction Behavior

An increase in the utilization ratio of PE-derived carbon is very important since the reduction reaction can be driven at lower temperature. In the previous study, the effect of the temperature distribution under high heating rates, and use of the composite with a double-layer structure, in which the inner and outer layers had different compositions, were discussed. The reactive area for reduction of iron oxide and decomposition of hydrocarbons strongly affects the reaction rates because the rates are low at low temperature. In this study, therefore, the effects of the specific surface area of the iron oxide on the reaction rate of reduction and on the utilization ratio of PE-derived carbon were evaluated.

Reduction experiments with composites using Fe$_2$O$_3$ reagents with an average particle size of 2.6 μm and 150.0 μm, and dehydrated pisolitic ore with an average particle size of 215.5 μm were carried out. Figure 7 shows the changes in the ratios of gases generated from the composite with temperature drawn on the Fe–O phase diagram. The changes in reduction degree are shown in Fig. 8. When Fe$_2$O$_3$ with an average particle size of 2.6 μm was selected, an increase in the gas ratio above 870 K is observed. This behavior is similar to that of Fe$_3$O$_4$ with an average particle size of 0.6 μm. However, when Fe$_3$O$_4$ with an average particle size of 150.0 μm was used, no increase is observed. The gas ratio starts to increase at 1270 K, and it increases abruptly at 1270 K. This result indicates that PE-derived carbon and hydrogen were little used in the reduction of iron oxide. The reduction degree also starts to increase at 1070 K. This behavior is similar to that observed with the addition of graphite. The reason is that the reactive area for the reduction of iron oxide is small. In the case of pisolitic ore, which has a larger particle size than the Fe$_2$O$_3$, the gas ratio starts to increase at 800 K. It is well known...
that dehydrated pisolithic ore has many nanosized pores and that its specific surface area is very large.\(^\text{51}\) It was, therefore, concluded that the reduction reaction proceeded well at low temperature.

**Figure 9** shows the effect of the specific surface area of iron oxide and pisolithic ore on the temperature at which the reduction degree of the composites reached 11.1% and 30%, and the utilization ratio of PE-derived carbon for the reduction. These reduction degrees indicate the beginning of FeO and metallic iron formations, respectively, in the composite. The temperature at which the reduction degree reached 11.1% decreases with increasing specific surface area. The formation of FeO was observed at the lowest temperature for the largest specific surface area, namely 44 m\(^2\)/g. The utilization ratio of PE-derived carbon increases with increasing specific surface area. The amount of deposited carbon originating from PE that has a strong effect on the amount of reducing agent increases with increasing specific surface area. These results indicate that an increase in the specific surface area of the iron oxide increases the reaction in the first step because of the contribution of PE-derived reducing agents, and also increases reduction in the second step because the amount of PE-derived carbon increases. Accordingly, iron ore with a high concentration of combined water, such as pisolithic ore, is suitable as a source of iron oxide for the effective utilization of PE-derived carbon because the high specific surface area enables the utilization ratio of PE-derived carbon to increase.

On the other hand, the temperature at which metallic iron starts to form decreases with increasing specific surface area. However, this effect is very small compared with the effect on the FeO formation temperature. The reason is that the indirect reduction reaction with CO gas generated by the gasification of graphite, which is activated above 1300 K, is dominant. The reactive area is not affected because the reaction rate of the reduction is high at this temperature. The temperature at which metallic iron starts to form in the composite using pisolithic ore is higher than that using Fe\(_2\)O\(_3\) with an average particle size of 150.0 \(\mu\)m, though the specific surface area of the pisolithic ore was larger than that of the Fe\(_2\)O\(_3\) reagent. This is because the rapid decrease in specific surface area and the formation of an FeO–SiO\(_2\) slag with low reducibility lead to the decrease in the reduction rate of composites containing pisolithic ore.\(^\text{51}\) Therefore, the utilization of carbonaceous materials with low gasification temperature is important for the promotion of reduction reactions at lower temperatures since the reduction reactions can proceed before a beginning of a decrease in specific surface area of iron oxide.

**4. Conclusions**

The reduction behaviors of composites prepared by using polyethylene, graphite, hematite reagents and pisolithic ore was evaluated under a heating rate of 0.33 K/s, in order to find an effective method of using waste plastics. The following results were obtained:

1. The reduction of iron oxide in the iron oxide–polyethylene–graphite composite proceeds by polyethylene-derived reducing agents below 1090 K when the composite is heated at a low heating rate which only small temperature differences between the inside and the outside of the composite. Above this temperature, the reduction proceeds by graphite.

2. Peaks in the rates of gas generation in the reduction reaction with polyethylene-derived reducing agents were obtained at 770 K and 1070 K. It is estimated that the peak at 770 K is attributable to H\(_2\) and hydrocarbon gases generated from polyethylene, and that the peak at 1070 K is attributable to carbon originating from polyethylene.

3. An increase in the specific surface area of the iron oxide in the composite increases the reduction rate. Since dehydrated pisolithic ore shows high specific surface area, it promotes the reduction when using polyethylene as a reducing agent. Therefore, it leads to lower reduction temperatures.

**REFERENCES**