Enhancement of Reduction Rate of Iron Ore by Utilizing Iron Ore/Carbon Composite Consisting of Fine Iron Ore Particles and Highly Thermoplastic Carbon Material

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Decreasing the thermal reserve zone temperature is believed to increase the energy efficiency of blast furnace iron-making. To do so, either the direct reduction reaction rate or the coke gasification reaction rate must be significantly increased below 1000°C in CO-lean atmosphere. An iron ore/carbon composite (IOC) has been proposed as a new raw material that can enhance the reduction rate of iron ore. In this paper the possibility of the reduction rate enhancement was examined by preparing a kind of ideal IOC sample consisting of nano-sized Fe₂O₃ particles (10–70 nm in diameter) and a carbon material prepared from a thermoplastic resin. The nano-sized Fe₂O₃ particles in the IOC sample were surprisingly reduced to Fe in a few minutes at as low as 650°C in an inert atmosphere. This was realized by increasing the interfacial area between the Fe₂O₃ particles and carbon and by establishing intimate contact between the two. The carbon in the IOC sample was also completely gasified in less than 10 minutes at as low as 750°C in a CO₂ atmosphere. The dramatic enhancement of the gasification rate was found to be realized by the enhancement of one of the direct reduction reactions, the reaction between Fe₃O₄ particles and carbon, by the aid of in-situ XRD measurement. This suggested that the enhancement of both the reduction reaction rate and the gasification reaction rate is realized by the same mechanism. These new findings will give a clue for designing IOC samples applicable to the blast furnace iron-making.

KEY WORDS: iron ore/carbon composite; ultrafine Fe₂O₃ particles; thermoplastic carbon; in situ XRD; rapid reduction of iron ore.

1. Introduction

In the blast furnace iron ore is reduced by the following reactions:

Direct Reductions: 
3Fe₂O₃ + C → 2Fe₃O₄ + CO .......(1a)
Fe₃O₄ + C → 3FeO + CO ........ (1b)
FeO + C → Fe + CO ................ (1c)

Indirect reductions: 
3Fe₂O₃ + CO → 2Fe₃O₄ + CO₂ .......(2a)
Fe₃O₄ + CO → 3FeO + CO₂ .......... (2b)
FeO + CO → Fe + CO₂ ............ (2c)

Gasification of coke: C + CO₂ → 2CO ............ (3)

Reactions (1a) to (1c) are the reduction reactions of Fe₂O₃ by carbon (direct reduction, endothermic), reactions (2a) to (2c) are the reduction reactions of FeO₂ by CO (indirect reduction, exothermic), and reaction (3) is the gasification of coke (solution loss reaction, endothermic). Since the rate of the indirect reduction reactions (2a) to (2c) are much faster than the direct reduction reactions in the presence of CO, the reduction of iron ore in the upper part of blast furnace proceeds by the indirect reductions (2a) and (2b) using CO produced by the coke gasification reaction. In the middle part of blast furnace the so called thermal reserve zone kept at a constant temperature of around 1000°C is formed due to the heat balance and equilibrium constraint. This is probably because the rate of solution loss reaction is slow below 1000°C. The solution loss reaction is enhanced in the lower part of blast furnace, and the direct reduction reaction (1c) becomes significant at the bottom of blast furnace where molten FeO can contact intimately with coke at temperatures over 1300°C. It is said that 60 to 70% of reduction of iron ore is accounted for by the indirect reactions and the rest of reduction is due to the direct reduction.

It is believed that the coke to iron ore ratio (C/Fe) can be reduced if the thermal reserve zone temperature can be lowered. The reduction of the C/Fe ratio directly contributes to a decrease in the CO₂ emission of blast furnace operation. Then a raw material forming fine iron ore particles and carbon material as briquette or pellet was proposed as a new feedstock of blast furnace. We call this new raw material “iron ore/carbon composite (IOC)” in this paper. Since the iron ore particles and the carbon material are in close contact in the IOC, the reduction rate of the iron ore particles is expected to be increased.

To increase the reduction rate of iron ore particles in the
thermal reserve zone where CO concentration is rather low, either the rates of the direct reduction reactions (1a) to (1c) or the rate of the gasification reaction (3) must be enhanced. The rates of the direct reactions for several IOC samples were examined by Iguchi et al.\(^8,9\) The reaction rates were, however, rather small below 1,000 °C. Kasai et al.\(^10\) examined the reactions involved in the reduction of IOC sample by preparing IOC samples through mixed-grinding of carbonaceous material and iron oxide. They found that the reduction rate was increased with the increase of milling time. They presumed that the increase was brought about by the catalytic effect and/or change of the rate limiting step from the gasification of carbon to the direct reduction reactions. However, the discussion was all for the reactions around 1,000 °C or over.

Kashiwaya et al. examined the effect of the mixed-grinding on the reduction rate in more detail using hematite-graphite mixture in a series of works.\(^11–14\) They have found that the milling in an Ar atmosphere for 1,000 h decreased the reduction reaction peak temperature to as low as 700 °C. This dramatic effect was realized by the changes in not only the particle size but in the crystalline sizes of both iron ore and carbon during the milling, enhancing the direct reactions between solid iron oxide and carbon. This is interesting finding, but 1,000 h milling will not be realistic for practical application. The occurrence of the direct reactions at around 700 °C was also confirmed by in-situ TEM observation between a wuestite and carbon deposited on it.\(^15\)

Adding catalyst is well known as one of the methods to increase the gasification rate of carbon. Alkaline metals, alkaline earth metals, and transition metal oxides are well known to act as such catalysts.\(^16\) It would be very natural to employ iron oxide as the catalyst when we intend to increase the rate of gasification reaction in the blast furnace. Then, several works have been presented to examine the effect of the addition of iron oxides on the gasification rate.\(^17–20\) The gasification rate was actually significantly increased by adding iron oxide. Meng et al.\(^18\) for example, reported that the gasification rates of a coal char and a graphite were increased by 1.5 to 4.9 times and 14.3 times, respectively, when the Fe to carbon weight ratio was 4. Even so, the gasification rate was not so high below 900 °C.

As briefly reviewed, it has been reported that the reduction rate can be increased significantly by using IOC as the raw material. Many works also have been performed to examine the rate enhancement mechanism of IOC. However, the mechanism of the rate enhancement is not completely clarified, and hence how low the thermal reserve zone temperature can be decreased by using IOC is unknown. Then the purpose of this paper is to examine the possibility of enhancing the reduction rate of iron ore at low temperatures by enhancing either the direct reduction reaction or the coke gasification reaction by using a kind of ideal IOC samples. To do so, IOC samples were prepared using nano-sized Fe\(_2\)O\(_3\) particles and a pure carbonaceous material. The IOC samples were heated in an inert atmosphere to estimate the direct reduction rate, and they were heated in a CO\(_2\) atmosphere to estimate the gasification rate of carbon. In-situ XRD analysis and TEM observation were also made to clarify the mechanisms of the reduction reaction and the gasification reaction.

## 2. Experimental

### 2.1. Sample Preparation

IOC samples were prepared from a reagent grade Fe\(_2\)O\(_3\) particles (Sigma-Aldrich Co.) of three different particle sizes of 10–70 nm, 150–300 nm, and 150–300 μm and an ion-exchange resin (Mitsubishi Chemicals Co. Ltd., DIAION WK11). The chemical formula of the ion-exchange resin, which is a co-polymer of styrene and methacrylic acid, is shown in Fig. 1. The resin was free from mineral components and was spherical particles of 0.7 mm in diameter. It was ground into powders less than 75 μm in diameter before use. The Fe\(_2\)O\(_3\) particles were mixed with the powdered ion exchange resin (abbreviated to Resin) by the weight ratio of 12 to 88 and kneaded for 3 min in a mortar at room temperature. The samples were abbreviated to “particle size of Fe\(_2\)O\(_3\)/Resin” as shown in Table 1. When the samples were heated to 500°C at the rate of 10°C/min in a He atmosphere, the resin softens, melts, and is carbonized to form an amorphous carbon. It is expected that an intimate contact of Fe\(_2\)O\(_3\) particles and the amorphous carbon is realized in the carbonized samples. The weight ratio of the Fe\(_2\)O\(_3\) particles to the carbonized resin was 58 to 42 when the IOC sample was heated up to 500°C. Then the C to O mol ratios in the mixed samples at 500°C were calculated from the carbon content of the carbonized resin and the amount of oxygen in the Fe\(_2\)O\(_3\) particles, and are listed in Table 1. The temperature of 500°C was chosen as a reference temperature to calculate the C to O ratio, because the rate of the reduction reaction is negligibly small below 500°C and because little carbon is lost by the pyrolysis reaction above 500°C. The amounts of carbon are in excess with regard to the stoichiometry of the reduction reaction. For comparison purpose, the Fe\(_2\)O\(_3\) particles mixed with the Resin pre-carbonized at 500°C (abbreviated to Coke) by the weight ratio of 58 to 42 were also prepared. They were abbreviated to “particle size

![Fig. 1. Chemical structure of the ion exchange used as carbon precursor.](image)

### Table 1. Iron-ore/carbon composite samples prepared.

| Sample        | D\(_0\) of Fe\(_2\)O\(_3\) | Fe\(_2\)O\(_3\)/Coke wt. ratio | C/O mol ratio at 500°C |
|---------------|-------------------------|-------------------------------|-----------------------|
| Nano-Fe\(_2\)O\(_3\)/Resin | 10–70 nm | 12/88 | 2.9 |
| Submicron-Fe\(_2\)O\(_3\)/Resin | 100–300 nm | 12/88 | 2.9 |
| Micro-Fe\(_2\)O\(_3\)/Resin | 150–300 μm | 12/88 | 2.9 |
| Nano-Fe\(_2\)O\(_3\)/Coke | 10–70 nm | 58/42\(^a\) | 2.9 |
| Micro-Fe\(_2\)O\(_3\)/Coke | 150–300 μm | 58/42\(^a\) | 2.9 |

\(^a\) Fe\(_2\)O\(_3\)/Coke wt. ratio
of Fe₂O₃/Coke" as shown in Table 1. The C to O mol ratios of these samples were set equal to those of Fe₂O₃/Resin samples.

For the gasification experiment, a typical metallurgical coke, a char prepared from an Australian brown coal (Loy Yang) at 900°C, and Coke itself were served as carbon materials. However, the gasification rates of these carbon materials are expected not to be high enough. Adding iron oxide as catalyst is one of the methods to increase the gasification rate of carbon in practical operation as stated earlier. Iron oxides used as catalysts must be well dispersed in the carbon materials so as to act as good gasification catalysts. Then the Nano-Fe₂O₃/Resin and the Submicron-Fe₂O₃/Resin prepared for the reduction experiment were used as the samples of the gasification experiment, because iron oxides are expected to be highly dispersed in these samples. It is also very advantageous if we can use IOC samples for increasing the gasification rate. The two IOC samples were heated to 500°C at the rate of 10°C/min in a He atmosphere before being served to the gasification experiment.

2.2. Reduction and Gasification Experiments

Figure 2 shows the experimental setup used for the reduction and gasification experiments of the IOC samples. For the reduction experiment, about 20 mg of the IOC sample was heated at the rate of 10°C/min up to 1350°C in a helium stream flowing at 150 mL/min using a thermobalance (Shimadzu, TGA-50H). The resin is carbonized below 500°C and an intimate contact of Fe₂O₃ particles and the amorphous carbon formed is expected. The weight change was continuously measured by the thermobalance, and the product gas formed after 500°C was analyzed for CO, CO₂, H₂ and H₂O using a micro gas chromatograph (GL Science Co. Ltd., Micro GC CP 4900). Since H₂O was not detected in the product gas, and since the amount of CO formed from the coke itself at the temperature region where the reduction reaction proceeds was much smaller than the amount of CO formed by the reduction reaction, the fractional reduction rate of Fe₂O₃ (RR) was approximately calculated from the amounts of CO and CO₂ formed by

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RR = \frac{\text{Amount of oxygen in the produced CO and CO}_2 [\text{mol}]}{\text{Amount of oxygen in Fe}_2\text{O}_3 \text{ particles} [\text{mol}]} \] (4)

For the gasification experiment, about 1 mg of sample was heated at the rate of 10°C/min up to 1200°C in a CO₂ flowing at 300 mL/min using the thermostbance. The weight change above 500°C was judged to be due to gasification, and the fractional gasification conversion of the carbon in the sample, Xc, was calculated from the weight change of the sample above 500°C.

2.3. In-situ XRD and TEM Observation

To directly observe the iron oxidation state of the iron oxide during the reduction and gasification experiments of the IOC sample, in situ XRD measurement was performed using an X-ray diffractometer (RIGAKU Co. Ltd., Ultima IV) which can scan at the rate of 10°/min. About 50 mg of IOC sample placed on a sample holder made of Pt was heated at the rate of 10°C/min up to 1300°C during which XRD profiles were acquired at predetermined temperatures by halting the heating for 5 min at the temperatures. XRD profiles were also measured at room temperature after the experiment by resetting the sample on the sample holder to confirm the final iron oxidation state. An inert and a CO₂ atmospheres were employed for the reduction experiment and the gasification experiment, respectively. XRD measurement was also performed in a CO atmosphere for the Nano-Fe₂O₃/Resin to estimate the rate of the indirect reduction reaction.

TEM observations were also made for the IOC samples heated to several pre-determined temperatures and cooled immediately to room temperature by a TEM spectrometer (JEOL, JEM-1010).

3. Results and Discussion

3.1. Reduction Behavior of IOC in an Inert Atmosphere

Figure 3 shows the RR profiles estimated by the reduction experiments for the five IOC samples prepared. Figure 4 shows the gas formation profiles during the reduction experiment of Nano-Fe₂O₃/Resin and Nano-Fe₂O₃/Coke.

![Fig. 2. Schematic of experimental setup for the reduction and gasification experiments.](image-url)

![Fig. 3. Reduction profiles of Fe₂O₃ particles in the five IOC composite samples prepared (Data by Kasai et al.) was obtained in the atmosphere simulating blast furnace.](image-url)
The total amounts of oxygen evolved as either CO or CO$_2$ coincided with the amount of oxygen in the Fe$_2$O$_3$ particles within experimental errors. The oxygen content of the Coke was 5.9%. Even if all the oxygen of the Coke evolved as CO and all the CO produced was utilized for the reduction at the temperature region where a large amount of CO is produced by the reduction reaction, the CO contribute to only 0.18 of RR. Based on the discussion it is well acceptable to calculate the RR profile from the formation rates of CO and CO$_2$. The RR profiles were significantly different among the samples. The reduction of Fe$_2$O$_3$ particles in the Nano-Fe$_2$O$_3$/Resin started at as low as 550°C and was completed at as low as 650°C in a single step. This reduction temperature range is 400–500°C lower than the reduction temperature range in conventional blast furnace. The formation rates of CO and CO$_2$ in Fig. 4 shows that the CO formation rate was much larger than the CO$_2$ formation rate, and the CO formation rate reached a maximum at 600°C at which the reduction rate reached a maximum. The reduction of Fe$_2$O$_3$ particles in the Submicron-Fe$_2$O$_3$/Resin also started at as low as 600°C and was completed at as low as 800°C in a single step. The Fe$_2$O$_3$ particles in the Nano-Fe$_2$O$_3$/Coke and the Micro-Fe$_2$O$_3$/Resin were reduced in three steps (Fe$_2$O$_3$→Fe$_3$O$_4$→FeO→Fe) at similar temperature ranges as reported by Kasai et al. for the reduction of an IOC in the atmosphere simulating blast furnace. The RR profile of the Micro-Fe$_2$O$_3$/Coke shifted to higher temperature range than the other three IOC samples. The reduction of the Fe$_2$O$_3$ particles in the Nano-Fe$_2$O$_3$/Coke is judged to proceed by the direct reduction reactions from the gas formation rate shown in Fig. 4. These results indicate that the RR profiles are affected by both the particle size of Fe$_2$O$_3$ and the contact state of Fe$_2$O$_3$ particles and carbon. It was clarified that the reduction temperature of iron ore can be decreased to as low as 650°C in the inert atmosphere by minimizing the particle size of iron ore and by realizing intimate contact between iron ore particles and carbon.

### 3.2. In-situ XRD Measurement and TEM Observation during the Reduction Experiments of Nano-Fe$_2$O$_3$/Resin

To examine directly that the Fe$_2$O$_3$ particles in the Nano-Fe$_2$O$_3$/Resin was completely reduced to Fe below 650°C, in-situ XRD profiles were measured during the reduction experiment of the Nano-Fe$_2$O$_3$/Resin in an inert atmosphere. Figure 5 shows the in-situ XRD profiles measured. The profile at 630°C shows the existence of only Fe$_2$O$_3$, and the profile of 640°C shows existence of only FeO. However, the profile at 650°C clearly and directly shows that the Fe$_2$O$_3$ particles in the composite were completely reduced to Fe at this temperature. The in-situ XRD measurement did not exactly correspond to the RR vs. temperature relationship shown in Fig. 3. This is probably because the actual temperature of the sample during the in-situ XRD measurement was slightly lower than the controlled temperature shown as the abscissa in Fig. 5. Direct temperature measurement of the sample was difficult due to the configuration of the sample holder. Even so, the in-situ XRD profiles confirm that the Fe$_2$O$_3$ particles in the composite were completely reduced to Fe below 650°C.

Figure 6 shows the TEM images of the nano-sized Fe$_2$O$_3$ particles (Nano-Fe$_2$O$_3$) and the Nano-Fe$_2$O$_3$/Resin at different stages of reduction of Fe$_2$O$_3$ particles. The nano-sized Fe$_2$O$_3$ particles were confirmed to be particles of 10 to 70 nm in diameter. At 500°C Fe$_2$O$_3$ particles are completely reduced to Fe below 650°C.
and evenly covered by amorphous carbon layers of about 2 nm thick, suggesting intimate contact between the Fe₂O₃ particles and the carbon layers. At 580°C at which the RR value was about 0.4, most of the nano-sized particles are still covered by the amorphous carbon layers but iron oxide particles larger than the original Fe₂O₃ particles and spherical hollow spaces that were presumed to be occupied by the nano-sized Fe₂O₃ particles also existed. At 900°C at which the reduction was completed, only large Fe particles formed by the reduction and agglomeration of the nano-sized particles existed. Existence of ordered carbons such as carbon nano fiber and graphite like carbon was also confirmed.

3.3. Mechanism of Rapid Reduction of Fe₂O₃ Particles in Nano-Fe₂O₃/Resin

The reduction experiment and the in-situ XRD measurement showed that the nano-sized Fe₂O₃ particles in the Nano-Fe₂O₃/Resin were completely reduced to Fe at as low as 550–650°C in a single step. The CO formation rate was much larger than the CO₂ formation rate during the reduction experiment of the Nano-Fe₂O₃/Resin as shown in Fig. 4, and the CO formation rate reached a maximum at 600°C at which the reduction rate reached a maximum. TEM observation showed that the Fe₂O₃ particles in Nano-Fe₂O₃/Resin are completely and evenly covered by amorphous carbon layers of about 2 nm thick, suggesting an intimate contact between the Fe₂O₃ particles and the amorphous carbon. It was also shown that the nano-sized iron oxide particles are well mobile during the reduction. These results well suggest that the rapid reduction of the nano-sized Fe₂O₃ particles in the Nano-Fe₂O₃/Resin was realized mainly by the enhancement of the direct reduction reactions (1a) to (1c). We can now conclude that the direct reduction reaction of iron ore can be enhanced dramatically when nano-sized iron ore particles are in intimate contact with carbon.

The reduction experiment was performed using a very small sample (20 mg) under a flowing He atmosphere to minimize the occurrences of the indirect reduction reactions (2a) to (2c) and the gasification reaction (3). However, Fig. 4 shows that a small amount of CO₂ was formed when a large amount of CO was formed by the direct reduction reactions. This suggests that the indirect reduction reactions (2a) to (2c) occurred by using CO produced by the direct reduction reactions even in a small thin sample layer from which the produced CO will escape very rapidly. This, in other words, suggests that the rates of indirect reduction reactions are very rapid for the Nano-Fe₂O₃/Resin. Then the rates of the indirect reduction reactions of Nano-Fe₂O₃ in a CO atmosphere were estimated by using the in-situ XRD apparatus. Figure 7 shows XRD profiles of the nano-sized Fe₂O₃ particles heated up to 1 200°C in a CO atmosphere. It was found that nano-sized Fe₂O₃ particles were completely reduced to the form of Fe in at as low as 500°C. This result indicates that the rates of the indirect reductions (2a) to (2c) are very rapid when nano-sized Fe₂O₃ particles are in contact with sufficient amount of CO, and it confirms that the indirect reactions can well proceed during the reduction experiment using a small amount of Nano-Fe₂O₃/Resin.

Above results in summary suggest that the Nano-Fe₂O₃/Resin placed in a blast furnace will enhance the reduction rate of iron ore particles by accelerating not only the direct reduction reactions but the indirect reduction reactions, which will surely decrease the temperature of the thermal heat reserve zone.

3.4. Gasification of IOC Samples in CO₂ Atmosphere

Next, the possibility of enhancing the reduction rate of iron ore at low temperatures by enhancing the coke gasification reaction was examined. To do so, the gasification experiments of the Nano-Fe₂O₃/Resin, the Submicron-Fe₂O₃/Resin, Coke, the metallurgical coke, and the char prepared from Loy Yang coal (Brown coal char) were gasified in a CO₂ atmosphere using the experimental setup shown in Fig. 2. The Nano-Fe₂O₃/Resin and the Submicron-Fe₂O₃/Resin were carbonized in a He atmosphere at 500°C before being served to the gasification experiment.

Figure 8 shows the relationship between the gasification conversion Xc and temperature for the 5 samples. The RR profiles of the Nano-Fe₂O₃/Resin and the Submicron-Fe₂O₃/Resin obtained above are also shown by the broken lines in the figure. The metallurgical coke started to be gasified over 900°C and temperature as high as 1100°C is necessary to obtain appreciable gasification rate. The gasification of the brown coal char started over 900°C and around 950°C was high enough to obtain appreciable gasification rate. The gasification of the Coke started at as low as 650°C, but around 950°C was necessary to obtain appreciable gasification rate. The gasification rates of both the brown coal char and the Coke are much larger than the metallurgical coke, but may still not be large enough to significantly enhance the reduction rate of iron ore. On the other hand, the gasification of the carbon in the Nano-Fe₂O₃/Resin started at as low as 500°C and was completed at around 750°C. The gasification of the carbon in the Submicron-Fe₂O₃/Resin also started at around 550°C and was completed below 800°C. Since the mol ratios of C/Fe and C/O of these samples are 4.3 and 2.8, respectively, as shown above, the consumption of carbon in these samples is not totally due to the oxygen involved in Fe₂O₃. These results show that either the Nano-Fe₂O₃ and
the Submicron-Fe$_2$O$_3$ themselves or their transformed forms of iron oxides acted as highly effective gasification catalysts.

It is also very interesting to note that the temperature ranges of the gasification reaction and the reduction reaction overlap to each other for the Submicron-Fe$_2$O$_3$/Resin. For the Nano-Fe$_2$O$_3$/Resin, however, the temperature range of the gasification reaction is a little higher than the reduction reaction. In other words, the temperature ranges of gasification reaction for the Submicron-Fe$_2$O$_3$/Resin and the Nano-Fe$_2$O$_3$/Resin seem to be so close.

3.5. Mechanism of the Gasification of Nano-Fe$_2$O$_3$/Resin and Submicron-Fe$_2$O$_3$/Resin

The gasification mechanism of carbon in the Nano-Fe$_2$O$_3$/Resin and the Submicron-Fe$_2$O$_3$/Resin was examined by the *in-situ* XRD measurement and the TEM observation. *Figure 9* shows *in-situ* XRD patterns measured during the heating up of the Nano-Fe$_2$O$_3$/Resin in a CO$_2$ atmosphere. The Nano-Fe$_2$O$_3$/Resin was pre-heated to 500°C in a He atmosphere before the XRD measurement as for the gasification experiment. The XRD patterns showed no appreciable changes during the experiment, and the iron oxide in the Nano-Fe$_2$O$_3$/Resin sample is the form of Fe$_3$O$_4$ at all of the temperatures. Ohtsuka *et al.* also showed that the chemical form of iron catalyst during the gasification in a CO$_2$ atmosphere was Fe$_3$O$_4$ at all of the temperatures. Following this mechanism, the overall gasification rate is proportional to the interfacial area of Fe$_3$O$_4$ particles and carbon, which means that the rate is directly proportional to the amount and reciprocally proportional to the diameter of Fe$_3$O$_4$ particles. This is also the case for the direct reduction reactions. Since the amount of Fe$_2$O$_3$ added to the Nano-Fe$_2$O$_3$/Resin and the Submicron-Fe$_2$O$_3$/Resin are same, both the reduction reaction rate and the gasification reaction rate are reciprocally proportional to solely the diameter of iron ore particles at a same temperature. Then if we assume that the RR profiles for the Nano-Fe$_2$O$_3$/Resin and the Submicron-Fe$_2$O$_3$/Resin well reflect the effect of particle size difference of the two samples, the gasification profiles of the two samples look too close to each other as stated above.

Then it was examined how the interfacial area of Fe$_3$O$_4$ particles and carbon changes with the progress of gasification. *Figure 10* shows the TEM images of the Nano-Fe$_2$O$_3$/Resin and Submicron-Fe$_2$O$_3$/Resin at the carbon conversion of 0.5 ($X_c = 0.5$).
means that the size of iron ore particles is expected to be unchanged during the gasification for the Submicron-Fe2O3/Resin. Next, the TEM image of the Nano-Fe2O3/Resin sample at Xc = 0.5 (Panel a in Fig. 10) was compared with that at Xc = 0 (Panel b in Fig. 6). Smaller Fe2O3 particles less than 20 nm in diameter that were found in the sample at Xc = 0 are found to be missing in the sample at Xc = 0.5. This shows that the smaller Fe2O3 particles are easily sintered to form larger particles when temperature exceeds 600°C. This is probably the reason why the gasification profiles of the Nano-Fe2O3/Resin and the Submicron-Fe2O3/Resin look too close to each other.

By referring to these findings we can now conclude that the gasification reaction rate can be significantly enhanced by using the Nano-Fe2O3/Resin or the Submicron-Fe2O3/Resin. The gasification of carbon in these samples are catalyzed by FeO particles by the redox cycle shown by reactions (1b) and (5), and the rate controlling step of the gasification reaction is the direct reduction reaction (1b). In this sense, the mechanism of the rate enhancement of the direct reduction and the gasification is the same. The dramatic rate enhancement was realized by realizing intimate contact between iron ore particles and carbon. The gasification rate is expected to be reciprocally proportional to the contact between iron ore particles and carbon. The gasification is the same. The dramatic rate enhancement was realized by realizing intimate contact between iron ore particles and carbon. The gasification rate is expected to be reciprocally proportional to the contact between iron ore particles and carbon. The gasification is the same.

The possibility of the reduction rate enhancement was examined by preparing an ideal IOC sample consisting of nano-sized Fe2O3 particles (10-70 nm in diameter) and a thermoplastic resin. The Fe2O3 particles in the IOC sample were surprisingly reduced to Fe in a few minutes at as low as 650°C in an inert atmosphere. The carbon in the IOC sample was also completely gasified in less than 10 minutes at as low as 750°C in a CO2 atmosphere. The dramatic enhancement of the gasification rate was found to be realized by the enhancement of one of the direct reduction reactions, the reaction between Fe2O3 particles and carbon, by the aid of in-situ XRD measurement. This clarified that the enhancement of both the reduction reaction rate and the gasification reaction rate is realized by the same mechanism. Thus it was shown that the reduction rate can be enhanced dramatically if IOC is designed so as to maximize the interfacial area between iron ore particles and carbon and to realize intimate contact between the two.

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