Research article

Reduction of mild-dehydrated, low-grade iron ore by ethanol

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ABSTRACT

Low-grade iron ore with high combined water (CW) content (e.g., goethite) has been first dehydrated at low temperatures *mildly* to be slit-shaped nano-order pore, then has been reduced by ethanol (C_2H_5OH) charging under the heating conditions. *Bioethanol* as derived from biomass, regarded as a renewable and carbon-neutral resource, is a promising candidate as a reducing agent for ironmaking. In the experiments, ethanol was dropwise added to the mild-dehydrated, porous iron ore beds at heating conditions using the temperature-program. As a result, the ethanol was soon decomposed to CO and H_2, which then reduced the iron oxides. Porous iron ore acts as a good catalyst for ethanol decomposition as it simultaneously reduces to metallic iron. Interestingly, iron oxides were reduced at a lower temperature, compared to conventional coal-based ironmaking in the blast furnace. Metallic Fe was obtained at only 750 °C, showing a reduction degree of 81%, due to the contribution of hydrogen reduction. The longer charging time of ethanol promotes the higher reduction degree as well as sufficient compositions of reducing gas (H_2-CO) for the reduction process. The results of experiments using different iron ores revealed the general rule that the higher CW content in ore makes the larger surface area of the iron ore by mild-dehydration, causing higher reactivity in the reduction process. The results appealed that mild-dehydrated iron ore is good raw materials of bioethanol ironmaking, due to its nanopores.

1. Introduction

Recently, numerous methods have been proposed to reduce carbon dioxide emissions in the ironmaking process. The *Paris Agreement* (2015) requires the implementation of several actions on climate change mitigation by reducing greenhouse gas emissions [1]. One of the most challenging problems for reducing carbon dioxide emissions is to replace non-renewable carbonaceous materials such as coke as the reducing agent in ironmaking. Another difficult challenge is to improve the reactivity of iron ore and the reducing agent, resulting in the opportunity to perform faster and lower-temperature reduction processes. In the case of blast furnaces, the temperature of the thermal reserve zone, where the temperature is 1000 °C, is determined by the reaction rate of coke gasification by carbon dioxide; this prevents the effective use of the reducing agent [2]. Thus, one of the most effective solutions to improve reactivity is to place composites of the iron ore and carbon in close contact with each other [3–6].

On the other hand, to overcome the abundance trend of low-grade iron ore (i.e., goethite) over hematite/magnetite ore, an innovative solution is required. A new ironmaking method known as *chemical vapor infiltration* (CVI) ironmaking using a renewable carbonaceous material such as biomass together with nanoporous hematite ore was proposed [7]. This process requires three steps to reduce the iron ore.

The first step is the *dehydration* process of the combined water (CW) contained in the goethite in high amounts, e.g., 8.8 mass% in lower temperature (so-called mildly-dehydration), to change the goethite ore structure to nanoporous hematite ore [8]. The second step is the *carbonization* process of the porous iron ore to invoke the simultaneous mechanisms of pyrolysis, catalytic tar decomposition, and carbon deposition through CVI in one integrated process [9–13]. The deposited carbon structure, detected as amorphous carbon, provides higher reactivity for the reduction process [14]. Infiltration of carbon into the ore pores improves not only the reactivity of the iron ore but also its mechanical strength [15]. During tar decomposition and carbon deposition in iron ore, the iron ore structure changes from hematite to magnetite (or even wüstite), meaning the reduction occurs; that is called pre-reduction processes [16]. However, because pre-reduction produces mainly the magnetite structure, the reduction degree (RD) is only approximately 11% [17]. Thus, it requires a third step, which is the *reduction* process to reach metallic Fe (RD 100%) [18]. Narrowing the large gap of RD from 11% to 100% by increasing the RD from the pre-reduction process has aroused much research interest. By focusing on the improvement of the pre-reduction mechanism, CVI technology might become more attractively applicable.

One approach is to introduce a small-molecule carbonaceous material such as ethanol as the reducing agent in porous hematite ore. As a

biomass derivative considered carbon-neutral in contributing to CO_2 emission, bioethanol is widely applicable as a fuel with a simple production process. It might be attractive as a reducing agent in ironmaking to solve the depletion of carbonaceous reducing agents in ironmaking as well [19]. Yet, few researchers have tried to explore the merits of ethanol use in ironmaking, because the ethanol availability is bound by the limitation of land use for ethanol crops and the lower yield of ethanol fermentation technologies [20]. However, ethanol yield technologies are still emerging, and gas fermentation has become attractive [21]. Recently, some projects have started to utilize the tail gas consisting of H_2-CO-CO_2 and waste heat from the steelmaking process to produce ethanol via gas fermentation by microorganisms [22,23]. Those emerging technologies are promising approaches to ensure the availability of ethanol. Therefore, ethanol-assisted ironmaking might become an attractive option in the future.

This study aimed to investigate the simultaneous decomposition of ethanol over porous iron ore along with the reduction of the porous iron ore, in which the effects of decomposition temperatures, ethanol flowrates, and charging temperatures on the reduction were mainly investigated by temperature-programmed reaction experiments. Different iron ores with different CW content were also investigated. Combined with the utilization of nanoporous iron ore, this approach would enhance the merits of co-utilization of low-grade iron ore with a renewable reducing agent.

2. Experimental methods

2.1. Preparation of porous ore samples

Different iron ores: Australian goethite (GE) ore, Western Australian (WA) ore, and Brazilian Riodoce (RC) ore with different CW contents were employed. Porous hematite (Fe_2O_3) reagent produced from goethite (FeOOH) reagent was also used as a reference. Table 1 shows the compositions and pore structure of the iron oxide and ores used in the experiments. The original ore was sieved so that a particle size ranged from 1 to 2 mm. The original reagent and ores were mildly dehydrated at only 300 °C with a heating rate of 3 °C min^{-1} and kept for 24 h under air atmosphere by a method similar to that in [8]. The detailed heating profile of mild-dehydration of the materials is shown in Fig. 1(a). This heat treatment makes the ore porous because CW is removed from the ore producing hematite structure with many nanopores. In order to confirm this effect, the surface area and pore volume of the ores were analyzed using N_2 adsorption equipment (Autosorb 6AG, Yuasa Ionics) before and after, as shown in Table 2.

2.2. Ethanol decomposition over porous iron ores

Fig. 1(b) shows the experimental apparatus scheme for the temperature programmed reaction (TPR) of the ethanol decomposition process. Approximately 0.3 g of iron ore was placed as a packed bed (7 mm of bed length) in a quartz tube reactor (6 mm of ID, 554 mm of length). Quartz wool of approximately 0.04 g was also put as bed support (8 mm of support length). The detailed information of the reactor set was reported in a similar study [24]. Argon at 100 Nml min^{-1}

was introduced to keep the atmosphere in an inert condition. The reactor was heated in a vertical infrared (IR) furnace from room temperature to different final temperatures (400–900 °C) at a heating rate of 10 °C min^{-1}. A thermocouple for the programmed temperature was placed inside the quartz tube below the bed support. A preliminary experiment had already conducted to confirm that there is no temperature disparity at the different axial position in the reaction. Ethanol (C_2H_5OH) reagent (99.5 vol%) at a liquid flow rate of 0.04 ml min^{-1} was introduced using a peristaltic injection pump into the ore bed in a quartz tube starting from 100 °C until the final temperature was reached. The starting temperature was chosen to ensure that the ethanol was vaporized (the boiling point of ethanol is 78 °C) before contacting the iron ore surface. The upper quartz wool was placed as an impingement baffle to prevent unvaporized ethanol liquid drops from propagating through the iron ore bed. The gas concentrations of the outlet gases, such as C_2H_5OH, H_2, CH_4, CO, CO_2, and H_2O were analyzed online using quadruple mass spectroscopy (QMS200, Pfeiffer). The evolution of total outlet gas flowrate was also monitored by a gas flowmeter. The molar flowrates of each gas were calculated using

$$\dot{n}_i = f_T \frac{C_i}{100} \frac{10^6}{24.0548} \tag{1}$$

where $\dot{n}_i$ is the calculated molar flowrate of each components i (i.e., C_2H_5OH, H_2, CH_4, CO, CO_2, H_2O) [µmol min^{-1}]. C_i is the gas concentration of each component i measured by QMS200 [mol%]. f_T is the total volumetric flowrate in the reactor outlet gas [Nml min^{-1}]. The factor of $\left(\frac{10^6}{24.0548}\right)$ is the conversion factor of gas volumetric flowrate to molar flowrates at NTP - Normal Temperature and Pressure - condition [µmol Nml^{-1}]. The NTP condition is defined as air at 20 °C (293.15 K) and 1 atm. Fig. 1(c) shows a schematic of the heating and ethanol charging scenarios during the reaction.

2.3. Sample characterizations

Characteristics of the ore structures and compositions before and after the reactions were analyzed using X-ray diffractometry (XRD; Miniflex, Rigaku). The carbon content in the iron ore was calculated by the weight change of the iron ore after reduction in ethanol decomposition and after combustion at 1000 °C for 30 min under 500 ml min^{-1} of air flow. Considering the reoxidation of reduced iron ore to hematite, the carbon content calculation as expressed

$$X_C = \left(1 - \frac{w_{sb}}{w_{sa}}\left(1 - \frac{23.99}{55.85}\frac{X_{Fe0}\,X_{RDa}}{(1-X_{CW})}\right)\right) \times 100\% \tag{2}$$

where X_C is the fraction of carbon content in the sample after reduction in ethanol decomposition [mass%]. w_{sa} and w_{sb} are the sample weight after reduction in ethanol decomposition and after combustion in air flow, respectively [mg]. The factor of $\left(\frac{23.99}{55.85}\right)$ corresponds to the ratio of the stoichiometric mass equivalent of oxygen to Fe in Fe_2O_3 structure (calculated as $FeO_{1.5}$). X_{Fe0} and X_{CW} are the mass fraction of total Fe and the combined water (CW) content in raw material, respectively [−]. X_{RDa} is the mass fraction of the reduction degree (RD) of the sample after reduction in ethanol decomposition [−]. The reduction degree (RD) of each sample was then calculated using

$$RD = \frac{mass\ of\ removed\ oxygen}{mass\ of\ removable\ oxygen} \times 100\% \tag{3}$$

However, it was difficult to evaluate the exact amount of removed and removable oxygen because the presence of gangue materials such as SiO_2, Al_2O_3, and other oxides might be different within the ore samples. The RD of each sample was then calculated on the basis of the composition of iron oxides in the sample using

$$RD = \sum x_i RD_i \tag{4}$$

Table 1
Properties of iron ore samples.

Sample	Particle size	Total Fe [mass%]	Combined water [mass%]
FeOOH reagent	1 µm	62	9.7
GE ore (Australian iron ore)	1–2 mm	57	8.6
WA ore (Australian iron ore)	1–2 mm	61	5.1
RC ore (Brazilian iron ore)	1–2 mm	65	0.77