

Studies on Key Reactions in Iron-Making Process Mediated by Oxalic Acid

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Abstract

The iron- and steel-making is considered as one of the most important processes in industries because iron and steel are essential materials in modern society. Nevertheless, it is also recognized as one of the most energy-intensive process and CO₂ emitter. CO₂ is heavily generated from the conventional blast furnace (BF) that is a reactor of primary step in the iron-making process. The use of coke as the fuel and reductant in BF is the main cause of the huge CO₂ emission and high energy consumption. To cope with this environmental problem, there have been many efforts to technically improve energy efficiency of BF, and alternative processes such as direct reduction (DR) and smelting reduction have been introduced to the iron-making. However, there have been still no significant decreases of CO₂ emission and energy consumption in this industry due to its reliance on the fossil-fuel-based high temperature processes.

Therefore, the primary aim of this study is to propose a more sustainable iron-making process which has a potential to be free from fossil fuel and high temperature by employing unique chemical properties of oxalic acid including its affinity for complexation with iron ions. The proposed iron-making process, called iron-making process mediated by oxalic acid, consists of four key reactions: (1) dissolution of iron oxide with oxalic acid to prepare an aqueous solution of iron(III) oxalate, (2) photochemical reduction of iron(III) oxalate to iron(II) oxalate that is precipitated and recovered as solid from the solution, (3) pyrolytic reduction of iron(II) oxalate to produce metallic iron, and (4) synthesis of oxalic acid from CO₂ generated in the reactions of (1)-(3). The first three steps of the proposed process do not require a high temperature while enable the production of quality iron with chemical reaction selectivities caused by oxalic acid. When all CO₂ generated during the iron-making are used for the synthesis of oxalic acid at the last step, overall reaction of the process can be stoichiometrically described by $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$, which is carbon free. In this dissertation study, the

first three steps of the process have been experimentally investigated to demonstrate the proposed iron-making method and its performance as an iron-making process.

This thesis consists of six chapters. Brief summaries of each chapter are presented in the followings;

Chapter 1 of this thesis introduces the background, motivations, and objectives of this work. The current status of industrial iron-making processes including both conventional and alternative iron-making processes is briefly reviewed. Then, the concept of iron-making process mediated by oxalic acid is explained in detail.

Chapter 2 shows the study on the dissolution of iron oxides with oxalic acid, which is the first step of the proposed iron-making process. To be an iron-making method, reactions in the proposed method are required to occur at high reaction rates. The iron dissolution step, in particular, is required to prepare a high concentration of the iron oxalate aqueous solution. In this study, therefore, the dissolution of iron oxides highly loaded in the oxalic acid aqueous solution (up to 1.3 mol-Fe/L) is investigated. The dissolution is carried out in the absence of light and with no addition of other chemical reagents. Factors affecting the dissolution, such as iron oxide types, temperature, and the concentrations of oxalic acid and iron oxides, are varied in order to optimize the dissolution conditions and reveal chemistry of the dissolution. The results show that the rate of dissolution is affected by the type of iron oxides. Fe_3O_4 shows a distinguished fast dissolution due to the facile and fast release of catalytic iron(II) oxalate, followed by $\alpha\text{-Fe}_2\text{O}_3$ and FeOOH . Due to high acidity of the solution and high dissolution temperature, non-reductive dissolution is suggested to be a predominant dissolution mechanism, which is demonstrated by the presence of dissolved Fe^{3+} as major iron species in the leachate. Increasing temperature not only improves the dissolution efficiency but also enhances the rate of oxalic acid dissociation. The dissolution temperature around 90 °C is suggested to be an optimum temperature to provide the fast Fe dissolution without boiling the

solution. More importantly, the results reveal that iron concentration in the prepared iron oxalate solution can be well above 0.5 mol/L regardless of the iron oxide types. Furthermore, a required minimum ratio of oxalic acid to iron (OxA/Fe) to completely dissolve the loaded iron oxide at 92 °C is found to be 1.82.

Chapter 3 reports the study on the second step of the iron-making method, which is the photochemical reduction of iron (III) oxalate to recover iron as a solid form of iron(II) oxalate dihydrate. The results of experiments using simulated sunlight show that the rate of conversion is approximately proportional to the light intensity (photon flux density: PFD), whereas sources of iron in iron(III) oxalate solution and the depth of solution do not show significant influence on the rate of conversion. When the LED lights are used, it is confirmed that light in the wavelength of 365-550 nm can induce the photochemical reduction. Moreover, it reveals that, apart from the light intensity, the wavelength region of light also plays an important role in the rate of reaction: light near UV-region has a high impact on the conversion rate. Natural sunlight also reduces the iron(III) oxalate aqueous solution to iron(II) oxalate dihydrate precipitate, but it requires more time to complete the reaction due to the weather condition dependency. The iron(II) oxalate precipitates obtained from experiments under all conditions are indexed to be pure $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, but they are slightly different from each other in terms of their structures, crystallinities, and crystal sizes, which probably results from the rate of conversion.

Chapter 4 describes the pyrolytic reduction of the iron(II) oxalate dihydrate to produce metallic iron, which is the last step of the proposed iron-making. Various atmospheres, namely, N_2 , 50%- H_2/N_2 , 50%- CO_2/N_2 , 50%- CO/N_2 , and 50%-air/ N_2 , are used to investigate the thermal behaviors of iron(II) oxalate dihydrate. The results show that the gas composition influences the thermal decomposition of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Under 50% H_2/N_2 atmosphere, the metallic iron forms from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ even below 500 °C. Moreover, the iron(II) oxalate dihydrate precipitates obtained from the previous dissolution and photochemical reduction steps are used

as the precursor for metallic iron, and the results prove that all precipitates can be converted to α -Fe under this condition.

In chapter 5, the findings in chapters 2-4 are applied to the proof of iron-making from iron feedstocks containing other elements. The demonstration experiment of the proposed process achieves satisfactory results: three different iron sources were successfully converted into metallic iron at a low processing temperature of 500 °C. The conditions of iron dissolution step and the presence of impurity elements in the feedstock primarily determine the overall yield and purity of the produced iron. By using the proposed process, a major portion of impurities, such as Al, Si, P, and S were removed. Therefore, a recovery of metallic iron with high purity is achievable. On the other hand, the presence of Ca, Mg and Mn, affects the process performance as well as the quality of iron product by the consumption of oxalic acid during the dissolution.

Chapter 6 summarizes the findings described in the preceding chapters, and the future challenges of this process are also described.