Kinetic modeling of the reduction of pure iron oxide monolayer with hydrogen

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Highlights

- In-depth iron oxide reduction modeling study using the SCM in a packed bed system.
- Novelty evaluation of experimental data.
- Kinetic parameter estimation.

1. Introduction

The aim of reducing greenhouse gas emissions is driving all manufacturing and industrial sectors to seek alternative solutions that are viable in the short term and offer excellent margins for improvement in the years ahead. With around 30% of global direct industrial emissions (2.6 Gt/year), iron production represents one of the largest CO_2 emitting sectors [1]. The classical production process involves the use of iron ores (i.e., iron oxides) which are reduced to metallic iron using carbon monoxide (CO). CO, produced during the partial oxidation of coal, reacts by removing oxygen from the ore to produce iron and CO_2. The most feasible alternative to using carbon is to replace it by hydrogen, but this requires considerable modifications of the current production plants, replacing the blast furnace with a suspension or direct reduction unit producing direct reduced iron (DRI) [2]. To investigate the kinetic dependence of the reduction on the main operating conditions, several works examine in depth the effect of temperature or the composition of the reducing gas on the system [3]. Many authors focused their efforts on the determination of the rate-limiting step of the heterogeneous process and on the importance of diffusion phenomena. For this reason, the study of morphology, geometry, and other properties of the solid is crucial. The main mathematical models used to describe the process and evaluate the kinetic parameters are the Shrinking Core Model (SCM) or the Porous Model [4]. Given this enormous variety of experimental conditions and modelling assumptions, a wide range of activation energies (E_a), are reported in the literature. The E_a for individual intermediate reactions or for the whole process can vary between 11 and 246 kJ/mol [5]. To accurately describe the chemical kinetics and mass transfer phenomena of the reduction process, an intensive kinetic study is required. This work focuses on the description of iron oxide reduction, which will be useful in the future for the development and design of hydrogen DRI processes.

2. Methods

To support the development of a mathematical model capable of correctly describing the reduction process, several experimental tests have been conducted using the Autochem2910. This device, which is normally used for the characterization of catalysts (e.g., TPR, TPO etc.), permitted the dissimulation of results that would be obtained for the reduction of iron ores in a small packed bed reactor. The reactive bed (diameter 8.5 mm, height approx. 0.5 mm) consisted of hematite or magnetite powder (Sigma-Aldrich, purity 97% and 96% respectively), with a particle diameter of less than 5 μm. The reduction was carried out using a gas mixture containing the reducing species (H_2 purity 99.9%) and an inert (Argon, Ar purity 99.9%). The composition of the gas leaving the bed was analyzed using a thermal conductivity detector (TCD) and a mass spectrometer. The tests were conducted isothermally at a specific H_2/Ar ratio and total volumetric gas flow rate.

Starting from an in-depth study of the key assumptions behind the shrinking core model and the characteristics of the experimental setup, a mathematical model was developed in MATLAB 2023a to simulate the (partially overlapping) three different reduction steps, where hematite (Fe_2O_3), magnetite (Fe_3O_4) and wüstite (FeO) are reduced by hydrogen. Molar balances for H_2 and H_2O were expressed as

partial differential equations in space and time, while ordinary differential equations were developed for the degree of conversion of the three different iron oxides.

3. Results and discussion

The signal obtained from the TCD is a function of the composition of the gas mixture leaving the reactor and the thermal conductivity of the chemical species involved. Since the thermal conductivity of H_2 is much higher than that of H_2O and Ar, the TCD signal roughly reflects the share of hydrogen in the gas leaving the reactive system. As an example, Figure 1a shows experimental results of the reduction of a monolayer of 0.01 g of fine hematite, carried out at different temperatures but at the same gas volume flow rate (20 mL/min) and molar ratio (H_2:Ar = 1:4), where the normalized signal of TCD is plotted over time. The signals show very different trends and changes in slope, which clearly depend on the number of reactions involved and their rate as the temperature changes. In general, the reaction can be said to be complete when the signal stabilizes at a value of 1, which means that no H_2 is consumed. The forms of the signals obtained show a faster reaction with the increasing temperature. To better understand the observed phenomenological dynamics, a profound experimental study supported by a well-characterized mathematical model is required. In order to indicate the potential of the model to quantitatively explain the results of iron oxide reduction experiments undertaken, a preliminary attempt was made to mimic the conditions in a reduction experiment of a 0.1 g bed of fine hematite at a temperature of 873 K at 20 mL/min and with a molar ratio of H_2:Ar of 1:4. As can be seen, manipulating the pre-exponential constant of the model, the simulation describes the experimental data qualitatively well, including the changes in the slope of the signal reflecting the transition from one reduction step to the next.

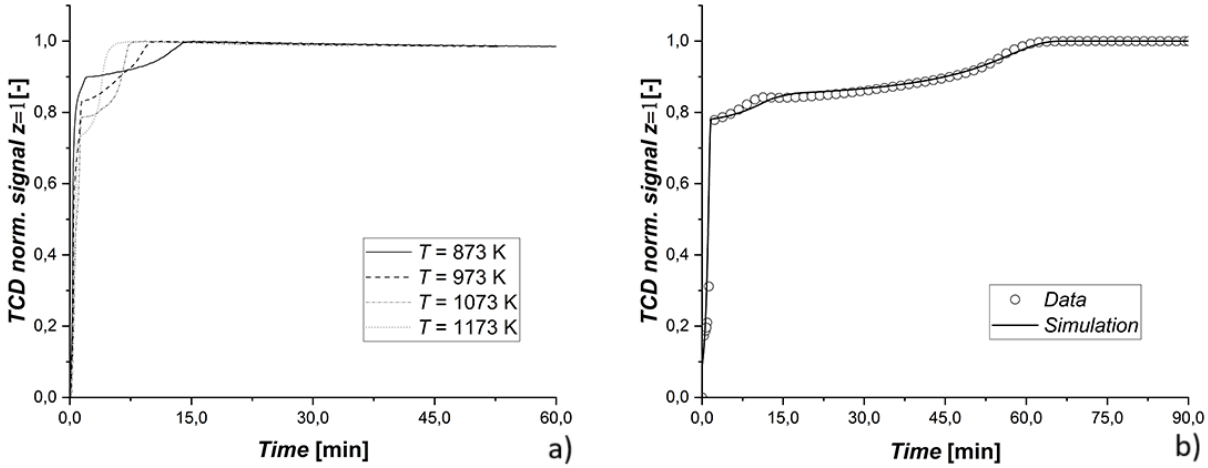

Figure 1. a) Examples of experimental results on the reduction of a monolayer of hematite powder at different operating temperatures, b) Preliminary comparison between bed experimental data and simulation.

4. Conclusions

In this work, an in-depth experimental and modeling study was conducted to describe the entire reductive process of a monolayer bed of iron oxides exposed to hydrogen-containing gas. For this purpose, the acquisition of accurate experimental data of a monolayer of iron oxides is crucial for estimating the kinetic parameters of the individual reaction steps.

References

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