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# Kinetics of the reduction of wüstite by hydrogen and carbon monoxide for the chemical looping production of hydrogen



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## HIGHLIGHTS

- Kinetics of the reduction of porous particles of wüstite by H<sub>2</sub> and CO were studied using fluidised beds.
- The intrinsic rates are the first order with respect to the concentration driving force in the gas phase.
- Activation energies for the rate constants were estimated.
- The reduction was found to undergo three different stages.
- Models and rate expressions were proposed to describe the intrinsic kinetics.

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## ABSTRACT

Hydrogen of very high purity can be produced *via* the steam-iron process, in which steam oxidises metallic Fe in  $3/4\text{Fe} + \text{H}_2\text{O} \rightarrow 1/4\text{Fe}_3\text{O}_4 + \text{H}_2$ . It is then advantageous to oxidise Fe<sub>3</sub>O<sub>4</sub> in air to Fe<sub>2</sub>O<sub>3</sub>, an oxygen-carrier. This higher oxide of Fe is then reduced to regenerate metallic iron by reacting with synthesis gas, producing metallic Fe and possibly some wüstite (Fe<sub>x</sub>O,  $0 < x < 1$ ). In this three-stage process, the reduction of Fe<sub>x</sub>O to Fe is the slowest reaction. This paper is concerned with the kinetics of the reduction of wüstite (Fe<sub>x</sub>O) by reaction with CO, and, or, H<sub>2</sub>. Starting with pure (99 wt%) wüstite, the intrinsic kinetics of its reduction to metallic iron were measured in fluidised beds at different temperatures. The reaction was found to have 3 distinct stages, (i) the removal of lattice oxygen in wüstite, (ii) rate increasing with conversion of solid and (iii) rate decreasing with conversion of solid. A random pore model was used to simulate the latter stages of the reduction of wüstite by either H<sub>2</sub> or CO or a mixture of the two. It was found that the intrinsic rate of reduction in H<sub>2</sub> is substantially faster than with CO, whereas the resistances to diffusion of H<sub>2</sub> and CO through the product layer of Fe are comparable; these factors account for differences in the overall rates observed with these gases.

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## 1. Introduction

Hydrogen is an environmentally-benign energy vector, since the combustion of hydrogen produces water as the sole product. However, to fuel a hydrogen economy, hydrogen would probably need to be generated by the consumption of another energy source, such as a carbonaceous fuel, e.g. from methane by reforming with steam, followed by the water-gas shift reaction.

A significant contaminant of the hydrogen produced from reforming is CO, which restricts the use of the hydrogen in proton exchange membrane fuel cells, in which the Pt anodes are poisoned by CO with a volume fraction as low as  $5 \times 10^{-5}$  (Choudhary and Goodman, 2002). Alternatively, pure hydrogen can be produced by reacting steam with iron at high temperatures in the steam-iron process (Messerschmitt, 1910), employing:



Reed and Berg (1953) proposed three inter-connected fluidised beds to run the steam-iron process continuously, by successively reducing and oxidising iron oxides using:



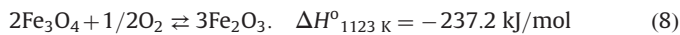
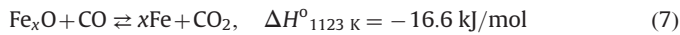
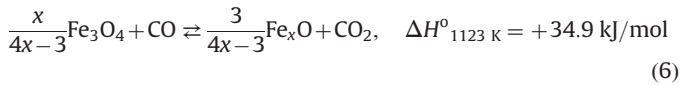
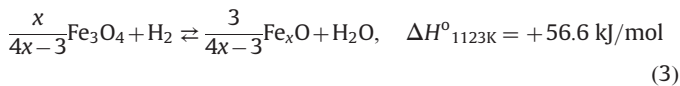
Abbreviations: b.c.c, body-centred cubic; BET, theory of Brunauer; Emmett and Teller; CCS, carbon capture storage; CSTR, continuous stirred tank reactor; I.D, internal diameter; PEMFC, proton exchange membrane fuel cell; PFR, plug flow reactor; SEM, scanning electron microscopy

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Here  $\text{Fe}_x\text{O}$  represents the oxide of Fe(II), viz. wüstite, which contains metal-deficient sites in its crystalline lattice, so that the ratio of Fe to O is variable within limits (Giddings and Gordon, 1973), discussed below. The first step in the above process is the reduction of  $\text{Fe}_2\text{O}_3$  (haematite), a so-called “oxygen-carrier”, to a mixture of wüstite and Fe by synthesis gas; this occurs in reactions (2)–(4) with  $\text{H}_2$  and (5)–(7), when the gaseous reductant is CO. Reducing almost 100% of the oxygen-carrier to metallic Fe is undesirable, because iron then catalyses the Boudouard reaction, causing the oxygen-carrier to coke. The result is that the hydrogen produced from the subsequent oxidation of the reduced carrier to  $\text{Fe}_3\text{O}_4$  (magnetite) by steam (i.e. the reverse reactions of (3) and (4)) will be contaminated with CO. In the final step,  $\text{Fe}_3\text{O}_4$  is oxidised in air to  $\text{Fe}_2\text{O}_3$  in reaction (8), which supplies a considerable amount of heat for use within the plant or for export. Accordingly, the reduction of  $\text{Fe}_2\text{O}_3$  by synthesis gas, the oxidation of  $\text{Fe}_x\text{O}$  and metallic Fe by steam and the oxidation of  $\text{Fe}_3\text{O}_4$  in air are undertaken in the “fuel reactor”, “steam reactor” and “air reactor”, respectively. This can be achieved by either (i) having three different operating conditions in a single reactor, e.g. a packed bed with concentration gradients (Bohn et al., 2008), or (ii) three interconnected fluidised beds, allowing oxygen-carriers to circulate between them. Ideally, with an optimised design, the gaseous products leaving the fuel reactor will contain only  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . After condensation of steam, the  $\text{CO}_2$  produced could be stored, e.g. by geological sequestration, making the overall process “carbon-neutral”, or “carbon-negative” when biomass is used as fuel. In addition, the hydrogen produced during the oxidation of  $\text{Fe}_x\text{O}$  and metallic Fe in steam can be kept free from contaminants such as CO, provided coking does not occur; this avoids additional steps purifying hydrogen.

To completely convert the fuel to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the fuel reactor, the solid at the exit of the gas stream must be an equilibrium mixture of magnetite and haematite (Cleeton et al., 2009) at e.g. 1123 K. Therefore, a fluidised bed cannot be used as the fuel reactor for this process. Li et al. (2010) have proposed an improved design, which replaces fluidised beds with moving beds for both the reduction of  $\text{Fe}_2\text{O}_3$  and the oxidation in steam to minimise axial mixing and allow the conversion of  $\text{Fe}_2\text{O}_3$  to Fe to reach up to 50 %, (giving 46% of the stoichiometric yield of hydrogen after oxidising the reduced bed using steam), while maintaining effectively 100% conversion of  $\text{H}_2$  and CO to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at the exit of the fuel reactor. Alternatively, Bohn et al. (2008) proposed using a fixed bed to run the cyclic reactions in a semi-continuous fashion, allowing some iron oxide to be reduced to a stage where it can be used for producing  $\text{H}_2$ , whilst maintaining effectively 100% conversion of fuel at the outlet of the “fuel reactor”.

Since the intrinsic rate of reduction of  $\text{Fe}_2\text{O}_3$  by syngas is much slower than the rate of oxidation of the reduced oxides, or metal, by steam or air, the residence time of the oxygen-carriers in the

fuel reactor (i.e. where their reduction takes place) is the longest. This sets constraints on parameters such as the circulation rate and the overall inventory of carrier particles, when designing a system of continuous fluidised beds. Similarly, in a system of fixed or moving beds, slow kinetics leads to low utilisation of the beds. As noted above, iron oxide undergoes three phase transitions during reduction, of which the slowest is the reduction of wüstite to iron (Liu et al., 2012a). However, the oxidation of Fe by steam produces about four times as much hydrogen as the oxidation of wüstite by steam, so that reducing the iron oxide fully to metallic iron is important for achieving the maximum yield of hydrogen per unit mass of oxygen-carrier.

There have been extensive studies of the reduction of wüstite in the fields of metallurgy and metal corrosion. Experimental work has mainly focused on two extreme cases: (i) the reduction of finely-powdered wüstite (Coombs and Munir, 1990; Mondal et al., 2004; Ryzhonkov and Sorin, 1999) and (ii) the reduction of dense slabs of wüstite of millimetre thickness (Hayes, 1979; John and Hayes, 1982; John et al., 1984; Turkdogan and Vinters, 1972). In both cases, the intrinsic rates of reaction are generally considered to be first order with respect to the chemical driving force in the gas phase, being  $\{[\text{CO}]-[\text{CO}_2]/K_{p7}\}$  for reaction (7), where  $K_{p7}$  is its equilibrium constant, equal to the ratio of  $[\text{CO}_2]$  to  $[\text{CO}]$  in the gas phase in equilibrium with the solid reactant and product. Typically, when the overall rate is controlled by intrinsic chemical reaction, the specific rate of reaction per unit mass of solid reactant can be expressed as:

$$r' = \frac{1}{\rho_{\text{Solid}}} \times A' \exp\left(-\frac{E}{RT}\right) \times \text{chemical driving force in gas phase} \times f(X) \quad (9)$$

Here  $\rho_{\text{Solid}}$  is the mass density of the solid reactant;  $A'$  is a pre-exponential factor for the intrinsic rate constant;  $k_i = A' \exp(-E/RT)$ ;  $E$  is the activation energy and  $X$  is the fractional conversion of the initial oxide. For fine powders, the rate is often considered to be the first order with respect to the fraction of solid reactant present, so that in Eq. (9)  $f(X) = (1-X)$  (Ryzhonkov and Sorin, 1999).

Where the reduction of dense slabs of wüstite has been measured, it has been generally found that the reduction can be divided into three stages with different time-scales, namely (i) a reduction of the stoichiometric ratio of O:Fe prior to the nucleation of iron (John et al., 1984), (ii) nucleation and growth of iron on the surface of the solid (Moujahid and Rist, 1988), and (iii) a slow growth of layers of Fe as product (John and Hayes, 1982). These layers of Fe affect significantly the diffusion of oxygen ions from the underlying wüstite to the outer surface of the Fe, where they react with gaseous reductant (Farren et al., 1990).

For chemical looping applications, oxygen-carriers are usually sub-millimetre porous particles, composed of sub-micron solid grains. They are thus different from the particles mentioned in the above studies. Accordingly, the aim of this research was to measure the rate of reduction of unsupported wüstite by hydrogen and also carbon monoxide in reactions (4) and (7), and to derive their rate expressions and kinetic parameters. Of course, in a practical chemical looping process, one would never perform reactions (4) and (7) on pure, unsupported wüstite, but instead, it would be supported on a ceramic oxide, such as alumina or zirconia. This is because pure wüstite sinters, particularly when reduced to Fe metal, giving a substantial fall in reactivity after a single redox cycle. In fact, stable reactivity of wüstite can be usually achieved by supporting it on e.g.  $\text{Al}_2\text{O}_3$  (Kierzkowska et al., 2010) or  $\text{ZrO}_2$  (Liu et al., 2012a). Nevertheless, by studying the kinetics of unsupported wüstite, the complicating effects of supporting materials on the kinetics can be excluded.

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