



Feasibility study of the use of by-product iron oxide and industrial off-gas for application to chemical looping hydrogen production



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HIGHLIGHTS

- Industrial off-gas is upgraded to H₂ using iron oxide in chemical looping process.
- By-product iron oxide exhibits good fluidization behavior by addition of sand.
- Industrial off-gas is completely oxidized in 2-stage fluidized bed.
- Recycled by-product iron oxide shows good cyclibility by providing porous structure.
- H₂ and CO₂-rich gas can be produced in separate streams of 3-step cycle.

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ABSTRACT

The chemical looping strategy for hydrogen production (CLH₂) offers a potentially viable option for efficient fuel conversion to hydrogen with the simultaneous capture of CO₂. Typically, this process uses an iron-based composite as an oxygen carrier and syngas or methane as a fuel. The environmental and economic concerns motivate the use of abundant by-product iron oxide and the industrial off-gas for CLH₂. Here we showed that H₂ could be simply recovered from the industrial off-gas in a circulating fluidized bed with a mixture of the inexpensive raw material of by-product iron oxide and sand particle. The fluidization of the by-product iron oxide powder, which showed poor fluidization behavior, is improved by adding 60 vol% of sand particle. The industrial off-gas was completely converted to CO₂ and H₂O in a two-stage fluidized mode with a solid reactant of Fe₂O₃ of the binary particles, and then H₂ was produced by oxidizing the reduced by-product iron oxide powder with steam. The binary particles showed consistent catalytic activity under multiple redox cycles by providing macropores with a size of ~5 μm which facilitated gas diffusion. These findings provided valuable information for the future development of CLH₂ based on by-products.

1. Introduction

The chemical looping process for hydrogen production (CLH₂) can produce pure hydrogen by splitting water with simultaneous CO₂ capture. The CLH₂ mainly consists of the fuel reactor (FR) in which the oxidized iron oxide is reduced by carbon-based fuel to produce CO₂ and H₂O, and the steam reactor (SR) in which steam reacts with the reduced iron oxide (i.e., FeO or Fe) to produce pure hydrogen [1–7]. The air oxidation step is added depending on heat and mass balance. This process involves the use of Fe₂O₃ as an oxygen carrier due to the ability

to split water into hydrogen in a reversible manner, the low cost, and the abundance [8]. Many researches focused on the development of synthetic composites to improve reactivity and stability [9–17]. Several methods for preparing the synthesized oxygen carrier have been reported, such as ball milling, co-precipitation, and freeze granulation [18–23]. For example, the oxygen carriers that are prepared by freeze granulation are typically manufactured by slurry mixing, ball milling, freeze granulation, and annealing at high temperatures of 900–1300 °C, thereby affecting the production cost and environment.

The availability of feasible Fe-based ores and naturally occurring

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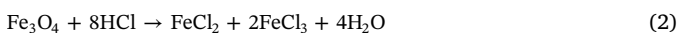
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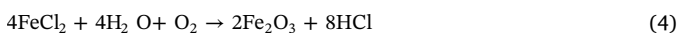
Nomenclature			
m	mass of the oxygen carrier in the reactor (g)	C_{i0}	concentration of species i initially present (mol L^{-1})
$m_{\text{Fe}_2\text{O}_3}$	mass of the oxygen carrier when fully oxidized (Fe_2O_3) (g)	F_{i0}	mole flow rate of species i initially present (mol s^{-1})
m_{Fe}	mass of the oxygen carrier when fully reduced (Fe) (g)	K_n	thermodynamic equilibrium constant at each reaction
\dot{n}_{in}	total inlet molar flow rate (mol min^{-1})	M_{H_2}	molecular weight of hydrogen (g mol^{-1})
n_o	moles of oxygen in the oxygen carrier that can be removed from the fully oxidized oxygen carrier (mol)	$M_{\text{Fe}_2\text{O}_3}$	molecular weight of the oxygen carrier when fully oxidized (Fe_2O_3) (g mol^{-1})
\dot{n}_{out}	total molar flow rate of non-condensate gas measured at the wet gas meter (mol min^{-1})	X	solid conversion of the oxygen carrier (dimensionless)
Δt	time interval for data acquisition (min)	Y	gas conversion (dimensionless)
Δz	a small cross position of reactor length	θ_c	ratio of flow rate of CO_2 to flow rate of CO initially present, $\frac{F_{\text{CO}_2 0}}{F_{\text{CO} 0}} = \frac{C_{\text{CO}_2 0}}{C_{\text{CO} 0}}$
$y_i^{j,\text{in}}$	mole fraction of inlet gas j	θ_s	ratio of flow rate of Fe_2O_3 to flow rate of CO initially present, $\frac{F_{\text{Fe}_2\text{O}_3 0}}{F_{\text{CO} 0}}$
$y_i^{j,\text{out}}$	mole fraction of outlet gas j		

minerals have been investigated to find suitable low-cost and reactive materials in chemical looping combustion (CLC) [24–28]. The advantage of using such materials is their low cost compared to synthetic materials as well as their reduced environmental impact. There have also been several studies on using raw iron oxide as an oxygen carrier for the CLH_2 application. Bleeker et al. [29] have conducted the reactivity test in a fluidized bed, and modeled the deactivation of iron oxide obtained from catalytic oxides or grinded sintered pellets. Hacker et al. [30–32] evaluated the efficiency of hydrogen production system in a 2-step redox cycle and determine the reaction characteristics of iron ore pellets. Bohn et al. [33] found that iron oxide particle could show stable redox activity with a redox pair of Fe_2O_3 -FeO in a fixed bed. Müller et al. [34] also demonstrated pure H_2 could be produced by redox reactions of 100 wt% Fe_2O_3 prepared by commercial product in a packed bed from crude syngas produced by the gasification of low-rank coals. Liu et al. [35] reported that an iron ore impregnated by potassium salt improved the rate of reduction and hydrogen generation by keeping the porous structure. The reduction reaction (i.e., $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$ or $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$) showed slower kinetics and it was limited by the thermodynamic equilibrium as the reduction reaction proceeded. The synthetic oxygen carrier is able to facilitate the kinetics by either maintaining pores for gas diffusion or employing a mixed ionic-electronic conductor as a support [36]. Meanwhile, lattice oxygen in raw iron oxide can be exchanged by introducing the pores which allowed the intra-particle diffusion. Thus, the use of the porous iron oxide as the oxygen carrier will enhance the redox kinetics due to the reduced diffusion length.

Currently, a large amount of fine and porous iron oxide powder is produced as a by-product of the acid-pickling process, where chemical oxide films and other impurities from hot-rolled steel are removed. Washing the rusted surface (Fe_2O_3 , Fe_3O_4 , and FeO in reaction (1)–(3)) with hydrochloric acid (HCl) elicits the following reactions



Hydrochloric acid is recovered through pyrohydrolysis



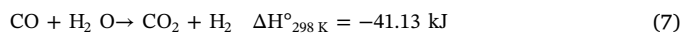
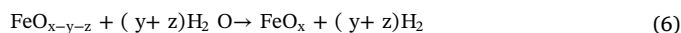
The by-product Fe_2O_3 in reaction (4) has been utilized in pigments, inductors, AC/DC motors, magnets, and catalysts, among others, because of the fine powder and its porous structure with high purity. Recent decreases in the demand for magnets have prompted research into new applications of inexpensive by-product Fe_2O_3 . In addition, plenty of low caloric gas is also produced as a by-product in the Finex, which is the name for an iron making technology that produces molten iron directly using iron ore fines and non-coking coal. The off-gas, commonly referred to as Finex off-gas (FOG), consists of 38 vol% CO , 16 vol% H_2 , 35 vol% CO_2 , and 11 vol% N_2 . The FOG is typically

recycled back into the process after purification and separation of CO_2 or used as a fuel for generating electricity. There are increasing demands to convert the FOG into H_2 for more valuable utilization [37]. Highly pure hydrogen can be used as a fuel in fuel cells vehicle, a reducing agent for vapor growth of silicon, and a feedstock in the petrochemical industries. The water gas shift (WGS) reaction followed by CO_2 separation step (Pressure Swing Adsorption, PSA) was applied to produce H_2 from the FOG. However, the intensive energy input in PSA units to purify H_2 from the product gas of WGS reaction (~ 40 vol% H_2 , ~ 50 vol% CO_2 , and ~ 10 vol% N_2 with a trace of CO) could be detrimental to process efficiency. Thus, it is required to find a new method to convert the FOG into H_2 with a significantly lower energy penalty.

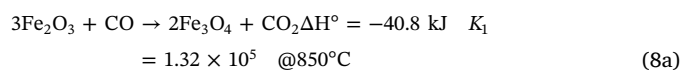
In this work, we first propose a CLH_2 system which converts the FOG into pure H_2 reusing the by-product iron oxide by addressing several key issues including thermodynamic relationship, fluidization properties, redox reactivity, and process schematic. The thermodynamic relation between by-product iron oxide and FOG was analyzed and the reactor performance was estimated using Aspen Plus simulator. The fluidization characteristics of the mixture of by-product iron oxide powder with sands were investigated in a cold flow bed. Then, the cyclic redox performance was evaluated in a batch fluidized bed reactor using a simulated FOG-varying gas-solid contacting mode (i.e., single- and multi-stage fluidized beds), the inlet solid reactant (i.e., Fe_2O_3 and Fe_3O_4), and operating temperature (650–850 °C). The reacted and fresh samples were characterized to study the correlation between the morphology and performance of the by-product iron oxide powder. Finally, the process schematic of the by-product CLH_2 was proposed based on the experimental and thermodynamic results.

2. Thermodynamic analysis and Aspen Plus simulation

The CLH_2 using the FOG involves alternative reduction and oxidation of iron oxide where it undergoes the following reactions



Reaction (5) is responsible for the reduction of iron oxides in the FR. Reaction (6) produce hydrogen in the SR by splitting water. Reaction (7) is the net reaction, which corresponds to the water-gas shift reaction. This indicates that the overall reaction of CLH_2 using the FOG is exothermic. The reduction of the oxidized iron oxide (Fe_2O_3 or Fe_3O_4), by the FOG, consisting of CO and H_2 , occurs in a stage-wise process, described as



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