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Phase distribution and stepwise kinetics of iron oxides reduction during chemical looping hydrogen generation in a packed bed reactor

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ABSTRACT

The reduction performance greatly impacts the efficiency of chemical looping hydrogen generation (CLHG) using iron oxides. This work studied the feature of packed bed technology for CLHG. First, a prevention strategy of fuel breakthrough was applied to simulate an industrial process. 25% solid conversion and 2000 μmol H_2/g Fe_2O_3 hydrogen production were achieved. Then, a novel idea to directly investigate the reduced particle bed using sub-layers was performed to characterize the reactor. Fe, FeO and Fe_3O_4 distributed in an orderly manner due to the plug flow gas–solid contact pattern in the reactor. The quantitative calculation showed that the area of Fe_3O_4 → FeO took up 80% space of the bed. The kinetic reason for this phenomenon was explored by means of a thermodynamically controlled method. The continuous reduction of iron oxides was successfully decoupled into three independent reactions and the step of Fe_3O_4 → FeO was found as the limiting step with a maximum reaction rate of 0.0008 s^{-1}.

Introduction

Hydrogen is one of the most important feedstocks in the modern chemical industry [1] and also well accepted as an environmentally benign energy carrier to reduce emissions of greenhouse gases in the future [2,3]. Current worldwide annual production of hydrogen is about 600 billion Nm^3 with a consumption growth rate at 5–10% per year [4–6]. Chemical looping hydrogen generation (CLHG) is a promising technology that converts fossil fuels to produce pure hydrogen and enables the inherent CO_2 capture using iron oxides as oxygen carriers [7–9]. The species of iron phases involved are Fe_2O_3, Fe_3O_4, FeO, and Fe. The fossil fuels are usually natural gas, syngas and coal, but can also be the gas products derived from biomass wastes gasification process. Therefore, CLHG also has the potential to convert biomass wastes based pyrolysis gas and even these wastes themselves into clean energy. Considering CO as the fuel, a CLHG cycle includes three main periods [10–12].

First, iron oxides are reduced by CO to generate CO_2 in the reducer reactor according to Eqs. (1)–(3) when the temperature is usually above 850 K in the chemical looping field. When CO is fully converted to CO_2, a pure stream of CO_2 is gained and can be captured downstream without any energy penalties.

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$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2 \quad (1)$$

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2 \quad (2)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (3)$$

When using pure CO as the fuel, a small amount of CO will also convert to the deposited carbon through a side reaction named Boudouard reaction (Eq. (4)).

$$2CO \rightarrow C + CO_2 \quad (4)$$

Then, the reduced species of Fe or FeO react with steam to produce pure H_2 and Fe_3O_4 in the steam reactor according to Eq. (5) and Eq. (6). After the condensation of remaining steam, pure H_2 can be obtained. It should be mentioned that only Fe or FeO can react with steam to H_2 due to the reaction Gibbs free energy. Fe with the deeper reduction degree favors to produce more hydrogen.

$$Fe + H_2O \rightarrow FeO + H_2 \quad (5)$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \quad (6)$$

Finally, air is needed for complete regeneration from Fe_3O_4 to Fe_2O_3 in the combustion reactor in accordance with Eq. (7).

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad (7)$$

The challenge of this technology lies in the complicated thermodynamics of the reduction of iron oxides in Eqs. (1)–(3) [14]. The reduction thermodynamics have been well established as shown in Fig. 1 [13]. When temperature is above 850 K, from the gas conversion point, CO can be almost fully oxidized to CO_2 with the presence of Fe_2O_3 while lower CO conversion will achieve when only Fe_3O_4 and FeO are present. From the solid conversion point, the phases of FeO and Fe for H_2 generation will not be produced unless CO concentration is beyond 38% and 70% at 1200 K according to the values of K_p, respectively. Therefore, a reducer that maximizes fuel conversion and solid conversion for simultaneous CO_2 capture and H_2 generation is preferred in an industrial CLHG process.

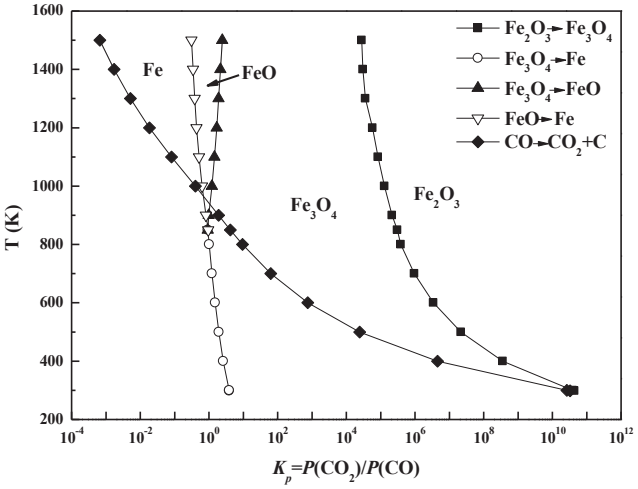

Fig. 1 – Baur–Glaessner diagram showing K_p versus temperature for Fe–CO–CO_2 system [13].

Some results concerning different types of reactors acting as reducers have been issued. Sridhar et al. [15] designed and conducted a 25 kW_{th} unit by using a countercurrent moving bed reactor. Syngas conversion of 99.96% and average H_2 purity of 94.4% were achieved. CH_4 conversion of 99% and H_2 purity of 99.99% were also obtained by Tong et al. [16] with this 25 kW_{th} unit. In addition, Hong et al. [17] demonstrated the characteristics of solid movement in a multistage circulating moving bed reactor. Cho et al. [18] proposed a 300 W_{th} countercurrent moving bed reactor with CH_4 conversion of 94% and H_2 purity of 99.9%. Further, dynamic modeling study of moving bed reactors have been carried out to reveal the inert characteristics of the reactors [19–21]. Meanwhile, fluidized bed reactors commonly used in chemical looping combustion (CLC) showed some limitations for deep reduction of iron oxides when fuel conversion was high [10,22,23]. Xiang and Xue et al. [24,25] suggested a compact fluidized bed reactor system as the reducer which was consisting of a bubble fluidized bed, a riser, a cyclone and a dipleg to solve this disadvantage. In this system, Fe_2O_3 was reduced to Fe_3O_4 by the unburned fuel gas to generate CO_2 and H_2O in the riser. Then Fe_3O_4 fell into the bubble fluidized bed and was further reduced to FeO or Fe by the fresh fuel gas again for hydrogen generation. The process efficiency and fluid dynamics of the compact fluidized bed reactor in cold models have just been carried out.

Recently, packed bed reactors have been proposed by Noorman et al. [26–31] for CLC. Packed bed reactors and moving bed reactors both have a plug flow gas–solid contact pattern. Compared with fluidized bed reactors and moving bed reactors, packed bed reactors also have some significant advantages, including the intrinsic avoidance of the separation between gas and particles, and no need to control hot particles movement and a more compact system. Therefore, some preliminary tests have been implemented using packed bed technology for CLHG.

Bohn et al. [32] proposed Fe_2O_3/FeO as the proper redox couple for stable H_2 production in a packed bed reactor because reduction reactivity was lost when Fe_2O_3 was reduced to Fe. Then, Kierzkowska et al. [33] suggested that the addition of 40 wt. % Al_2O_3 using sol–gel method gave stable reduction conversion of Fe_2O_3 → Fe near 75% over 40 cycles and thus enhanced the stability of H_2 generation. Solunke et al. [34] presented a proof-of-concept study for hydrogen generation in a simulated syngas fueled packed bed reactor and applied the energy balance model to discuss the temperature turbulence during the process of H_2 generation. Meanwhile, Müller et al. [35] integrated coal gasification system with the CLHG unit to investigate the reaction between crude syngas and iron oxides for H_2 production in a packed bed reactor.

However, in most current studies, packed bed reactors were generally used as experiment methods to investigate the material reactivity. The fuel breakthrough that the unconverted fuel gas escaped from the reactor in the reduction stage was observed in these studies. As a result, low fuel conversion and downstream CO_2 separation are still issues. Therefore, the application to the industrial processes has not yet been well investigated. In our previous work on the reduction period [36], the conversion of Fe_2O_3 was beyond 11% when CO was fully converted in a packed bed reactor. The solid