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A novel method for producing hydrogen from water with Fe enhanced by HS^- under mild hydrothermal conditions

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ABSTRACT

In this paper, a novel method for producing hydrogen from water with Fe as a reductant promoted by HS^- under mild hydrothermal conditions was proposed. Results showed that hydrogen production significantly increased in the presence of HS^- compared to that in the absence of HS^- . The obvious hydrogen production was achieved in a low reaction temperature of 250 °C and a very short reaction time (less than 2 h). The maximum yield of hydrogen production, which was defined as the percentage of produced hydrogen amount to theoretical one according to complete oxidation of Fe to Fe_3O_4 to produce hydrogen from water, was 34% at 300 °C. HS^- may act as a catalyst and a possible HS^- -catalyzed mechanism was proposed. This process may provide a promising solution for biomass-driven hydrogen production from water combined with the process of reducing iron oxide into their zero-valent state by bio-driven chemicals, such as glycerin.

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1. Introduction

To solve the problem of the world's increasingly serious energy crisis and carbon emission, hydrogen is considered to be a promising alternative fuel [1]. The main advantages of hydrogen fuel are the lack of CO_2 and other pollutant emissions such as NO_x and SO_x . In addition, the amount of energy produced during hydrogen combustion is greater than that of other fuels on a mass basis. Moreover, the lower heating value (LHV) of hydrogen is 2.4, 2.8 and 4 times greater than that of methane, gasoline and coal, respectively. Technically speaking, there are three main resources for the production of hydrogen, namely fossil fuels, biomass and water. However, currently, 98% of hydrogen is derived from the reformation of fossil fuels [2]. Due to the non-renewability of fossil fuels,

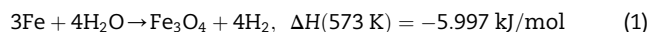
new methods for the production of hydrogen from water or renewable biomass must be developed. Methods for producing hydrogen from biomass can be divided into two main groups, (i) thermo-chemical processes (pyrolysis, aqueous phase reforming, gasification including supercritical water gasification) [3–11], and (ii) biological conversions (fermentative hydrogen production) [12]. Biomass materials might be derived from plant crops, agricultural residues, woody biomass, etc. For the hydrogen production from biomass, no net greenhouse gas emissions occur if the cycle of growth and harvest of biomass is sustained. However, more technical improvement and cost reduction is needed for them to take over the current fossil fuel reforming technology. Besides, the impurity of CO or CO_2 from biomass conversion is detrimental in the hydrogen fuel cells.

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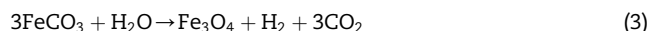
The second option is to explore hydrogen from water including water electrolysis, thermochemical water splitting and photocatalysis [13–15]. The “Steam-Iron” process is one of the oldest commercial methods for producing hydrogen from water. The process was practiced from the early 1900 s into 1930 s to supply small quantities of pure hydrogen (e.g., aerial navigation). Later, the technology was supplanted by the more efficient and economical fossil fuel reforming process. Recently, there has been an increasing interest in the “Steam-Iron” process [14,16–23] because of its simplicity, the high purity of hydrogen obtained, which is especially crucial for the use of hydrogen in fuel cells, the feedstock flexibility and the possibility to use renewable energy sources in this process [24]. This process has an advantage of decreasing a large volume of storage of hydrogen because the hydrogen produced could be seen as stored in Fe.

The “Steam-Iron” process for producing hydrogen contains two steps. The first step is the oxidation step based on the following reaction.



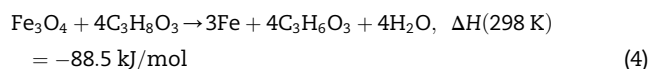
This step assures the high purity produced hydrogen free of CO and CO₂. The hydrogen production is a mildly exothermic reaction, which can produce hydrogen with a very high yield. According to this reaction, the theoretical amount of hydrogen being stored as Fe is calculated to be 4.8 wt% of Fe, which corresponds to ca. 534 L hydrogen to be stored on 1 kg of Fe. This value is very near to meet the US Department of Energy (DOE) and International Energy Agency (IEA) cost and performance targets for use in transportation vehicles that is hydrogen storage capacity of 6.5 wt% or 5 wt% [25]. The second step is the reduction step of Fe₃O₄. Reducing gas, such as CH₄, CO or mixture of them, is often employed to reduce Fe₃O₄ to metallic iron or FeO [14,19,22,23,26]. The main problems to be solved in this redox cycle, however, are (1) to decrease operational temperatures (often higher than 800 °C) for the oxidation of iron (the decomposition of water) as well as for the reduction of iron oxides and (2) to prevent the decrease in the reactivity of Fe due to sintering of Fe and Fe₃O₄ powders or pellets by repeated redox cycles [20]. Various metal additives to iron oxides were found to be effective to decrease operational temperatures and increase redox cycles [21]. But it is complicated and expensive due to consideration of costs and benefits.

Recently, some researchers, including us, have demonstrated that Fe can be easily oxidized and produce H₂ for reducing CO₂ at 200–300 °C under hydrothermal conditions [13,27–30]. Our researches also demonstrated that the presence of CO₂ can enhance the hydrogen production and the possible mechanism may be according to the following reactions [29].



Thus, Fe may also react with HS[−] to form iron sulfide (FeS) which then releases HS[−] with the product of hydrogen. That is, HS[−] may catalyze the hydrogen production from water with Fe as a reductant. It is known that millions of tons of H₂S are produced as a by-product around the world from

oil-refinery plants or natural-gas extraction every year. Sulfur oxyanion, S_xO_y^{2−}, would be reduced into HS[−] in a glucose solution at 105 °C [31]. Also, our previous researches [29,32] demonstrated that Fe₃O₄ can be easily reduced into zero-valent under a mild condition, such as at 250 °C for 30 min with a bio-chemicals such as glycerine according to the following reaction.



Thus, a novel hydrogen production process could be achieved combined with our previous results as shown in Fig. 1. The metallic Fe is first oxidized to Fe₃O₄ to produce hydrogen gas in the presence of HS[−] under mild hydrothermal conditions. Then, the oxidized iron is reduced into zero-valent Fe by glycerine [29]. The operation temperature at around 300 °C of this process is much lower than the conventional “Steam-Iron” methods. The aim of this study is to examine the availability of this novel cycle and discuss the hydrogen production in the first step.

2. Materials and methods

2.1. Materials

Na₂S·9H₂O (Sigma–Aldrich, ≥98%) was used as a source of HS[−] to simplify handling. The pH of the reaction solution at room temperature and 101 kPa is between 12 and 13, and thus HS[−] is the primary species in the solution. Iron powder (200 mesh, 96%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Iron wire (0.25 mm diameter, 99.995%) was purchased from Alfa Aesar. Iron (II) sulfide (100 mesh, 99.9%) was purchased from Sigma–Aldrich.

2.2. Experimental procedure

The experiments were conducted in three types of batch reactor. Most of experiments were conducted in a bomb-type reactor (hereafter referred as Type A reactor) connected to

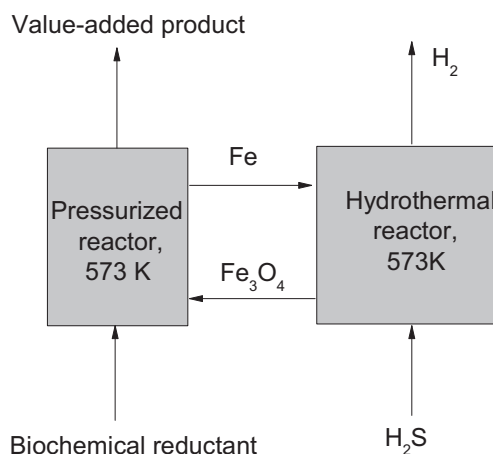


Fig. 1 – Proposed mechanism for hydrogen production in the presence of HS[−] via Fe/Fe₃O₄ redox cycle.

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