

Solar hydrogen production via thermochemical iron oxide—iron sulfate water splitting cycle



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ARTICLE INFO

Article history: Received 18 September 2014 Received in revised form 19 November 2014 Accepted 25 November 2014 Available online 20 December 2014

Keywords: Solar fuel Iron oxide—iron sulfate water splitting cycle Thermodynamics Hydrogen production

ABSTRACT

This paper reports the thermodynamic analysis of solar H₂ production via two-step thermochemical iron oxide—iron sulfate (IO—IS) water splitting cycle. The first step belongs to the exothermic oxidation of FeO via SO₂ and H₂O producing FeSO₄ and H₂ and second step corresponds to the endothermic reduction of FeSO₄ into FeO, SO₂, and O₂. The products, FeO and SO₂ can be recycled to step 1 and hence, reutilized for the production of H₂ via water splitting reaction. Thermodynamic equilibrium compositions and variations in enthalpy, entropy and Gibbs free energy of the thermal reduction and water splitting reactions were computed as a function of reaction temperatures. Furthermore, the effect of molar flow rate of inert Ar (n_{Ar}) on thermal reduction temperature (T_R) and equilibrium compositions during the thermal reduction of FeSO₄ was also examined. Second law thermodynamic analysis was performed to determine the cycle efficiency (η_{cycle}) and solar to fuel energy conversion efficiency ($\eta_{solar-to-fuel}$) attainable with and without heat recuperation for varying n_{Ar} (0–30 mol/s) and T_R (1280–1510 K). Results obtained indicate $\eta_{cycle} = 39.56\%$ and $\eta_{solar-to-fuel} = 47.74\%$ (without heat recuperation) and $\eta_{cycle} = 51.77\%$ and $\eta_{solar-to-fuel} = 62.43\%$ (by applying 50% heat recuperation) at $T_R = 1510$ K.

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Introduction

 H_2 is considered as one of the potential energy carriers due to its capacity of producing 143 MJ/kg of energy (higher in comparison with the oil, gas, and coal individually) and its environmentally friendly nature (burning of H_2 produces water with no other polluting gases). Water splitting reaction is considered as one of the most promising ways for the production of H_2 . However, direct water thermolysis is not favored thermodynamically as it requires process heat at temperatures above 2723 K for obtaining a significant degree of dissociation of water [1]. Furthermore, to avoid the formation of an explosive mixture comprised of H₂ and O₂, a gas separator unit (for the separation of H₂ and O₂ at high temperatures) needs to be equipped near to the water dissociation reactor which further enhances the overall cost of the H₂ production process.

As the direct dissociation of water is not practical due to the high operating temperature and gas separation problem,

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attempts are currently underway to achieve H_2 production via water-splitting reaction at lower operating temperatures and via bypassing the formation of H_2 and O_2 explosive mixture. Several thermochemical cycles such as iron oxide cycle [2–6], zinc/zinc oxide cycle [7–10], tin/tin oxide cycle [8,11–13], mixed ferrite cycle [14–21], ceria cycle [22–24], sulfur–iodine cycle [25–27], and hybrid sulfur cycle [28,29] were investigated towards H_2 production via water-splitting reaction. Among these, the sulfur–iodine cycle (reaction set I) and its variation the hybrid sulfur cycle (reaction set II) are more appealing as the required operating temperatures are lower as compared to other thermochemical cycles.

Reaction set I: sulfur-iodine cycle

$$H_2SO_4 \rightarrow SO_3 + H_2O$$
 (673 K) (1)

 $SO_3 \leftrightarrow SO_2 + 1/2O_2$ (1123 - 1273 K) (2)

 $SO_2 + 2H_2O + I_2 \rightarrow H_2SO_4 + 2HI$ (393 K) (3)

 $2HI \rightarrow H_2 + I_2 \quad (573 - 723 \text{ K})$ (4)

Reaction set II: hybrid sulfur cycle

 $H_2SO_4 \rightarrow SO_3 + H_2O$ (673 K) (5)

 $SO_3 \leftrightarrow SO_2 + 1/2O_2$ (1123 - 1273 K) (6)

$$SO_2 + 2H_2O \rightarrow H_2SO_4$$
 (353 - 393 K) (7)

For both sulfur-iodine cycle and hybrid sulfur cycle, the most energy consuming step is the dissociation of SO_3 into SO_2 and O_2 . The reduction of SO_3 into SO_2 and O_2 is possible only under catalytic conditions and takes place at high temperature due to its endothermic nature. Several metal based catalytic systems have been investigated previously towards the decomposition of the gaseous SO_3 [30]. As sulfation poisoning is a major concern related to such reactions, the

investigated metal catalysts were loaded either on nonsulfating substrates or substrates forming very stable sulfates. At high reaction temperatures, most of the transition metal catalysts (such as nickel, manganese based) undergo formation of stable sulfates and resulted as inefficient in terms of their catalytic activity towards the reduction of SO₃ into SO₂ and O₂ [31]. In contrast, the noble metal catalysts (e.g., platinum based) supported on BaSO₄-TiO₂, ZrO₂, or SiO₂ were observed to be active towards the endothermic dissociation of SO₃. Although, the noble metal catalysts are attractive for such reactions, they are less preferable due to the limited availability and high cost.

Utilization of metal oxides as the catalytic materials (instead of noble metal catalysts) and converting the sulfur-iodine and hybrid sulfur cycle into a 'metal oxide-metal sulfate' cycle operated using concentrated solar energy is one of the alternative to achieve H_2 production at moderate temperatures. Solar 'metal oxide-metal sulfate' thermochemical cycle utilizes solar energy, metal oxide (MO), SO₂ and H_2O for the production of H_2 and O_2 . It is a two-step process in which the first non-solar step belongs to the exothermic oxidation of MO by SO₂ and H_2O producing metal sulfate (MSO₄) and H_2 (reaction 8). The endothermic step two corresponds to the solar thermal reduction of MSO₄ into MO, SO₂, and O_2 . The MO and SO₂ produced in step 2 are recycled back to step 1 and hence can be used in multiple cycles.

 $MO + SO_2(g) + H_2O(g) \rightarrow MSO_4 + H_2(g) \quad (Non - solar)$ (8)

$$MSO_4 \rightarrow MO + SO_2(g) + 1/2O_2(g) \quad (Solar)$$
(9)

According to the previous investigations [2-24], among the several MO systems examined for the solar thermochemical water splitting application, iron oxide based redox materials are considered as one of the most favorable materials. In this viewpoint, this paper proposes the utilization of the 'iron oxide—iron sulfate' (IO–IS) cycle for the production of solar H₂



Fig. 1 – Typical two-step solar thermochemical IO-IS water splitting cycle.

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