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Thermochemical two-step water splitting cycles by monoclinic ZrO_2-supported $NiFe_2O_4$ and Fe_3O_4 powders and ceramic foam devices

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Abstract

A thermochemical two-step water splitting cycle is examined for $NiFe_2O_4$ and Fe_3O_4 supported on monoclinic ZrO_2 ($NiFe_2O_4$/*m*-ZrO_2 and Fe_3O_4/*m*-ZrO_2) in order to produce hydrogen from water at a high-temperature. The evolution of oxygen and hydrogen by *m*-ZrO_2-supported ferrite powders was studied, and reproducible and stoichiometric oxygen/hydrogen productions were demonstrated through a repeatable two-step reaction. Subsequently, a ceramic foam device coated with $NiFe_2O_4$/*m*-ZrO_2 powder was made and examined as a water splitting device by the direct irradiation of concentrated Xe-light in order to simulate solar radiation. The reaction mechanism of the two-step water splitting cycle is associated with the redox transition of ferrite/wustite on the surface of *m*-ZrO_2. A hydrogen/oxygen ratio for these redox powder systems exhibited good reproducibility of approximately two throughout the repeated cycles. The foam device loaded $NiFe_2O_4$/*m*-ZrO_2 powder was also successful with respect to hydrogen production through 10 repeated cycles. A ferrite conversion of 24–76% was obtained over an irradiation period of 30 min.

Keywords: Solar heat; Hydrogen production; Ferrite; Thermochemical cycle; Zirconia; Water splitting

1. Introduction

The conversion of solar high-temperature heat to chemical fuels has the advantage of producing long-term storable and transportable energy carriers from solar energy (Kodama, 2003). In sunbelt regions, where direct solar insolation frequently reaches up to 1 kW m^{-2}, modern solar concentrating systems of the central-tower-type and dish-type systems that reach a concentration factor of 1500–5000 can provide high-temperature solar thermal energy of up to hundreds of megawatts and a few hundred kilowatts, respectively (Johnston et al., 2003; Kalogirou, 2004; Mills, 2004). In the solar concentrating system of central-tower-type, the direct insolation is reflected with heliostats which are mirrors placed on the ground and are capable of tracking the movement of the sun, and the concentrated solar radiation is focused on a solar receiver/reactor. The solar receivers or reactors attain temperatures of above 1500 °C. The heat generated at such high-temperatures makes it thermochemically possible to produce hydrogen from water via a thermochemical cycle.

One of the promising solar thermochemical cycles is a two-step water splitting cycle using an iron oxide redox pair. This process, originally proposed by (Nakamura, 1977), is as follows:

$$Fe_3O_4 = 3FeO + 1/2O_2 \qquad (1)$$

$$3FeO + H_2O = Fe_3O_4 + H_2 \qquad (2)$$

This first thermal-reduction (T-R) step is highly endothermic and thermodynamically desirable at temperatures above 2200 °C under a pressure of 1 bar Eq. (1). The second water-decomposition (W-D) step is slightly

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exothermic and possible at temperatures below 700 °C Eq. (2).

The temperature of thermal-reduction varies with a partial pressure of oxygen (p_{O2}) in the atmosphere. The relation diagram between $\log p_{O2}$ and 1/T for the three-phase (liquid oxide, Fe_3O_4, and FeO) equilibrium (Darken and Gurry, 1946) shows that a phase transformation of Fe_3O_4 into FeO can occur at temperatures of 1300–1400 °C and in oxygen partial pressures of 10^{-6}–10^{-8} bar since the melting point of FeO is around 1400 °C. This indicates that the Fe_3O_4-to-FeO thermal-reduction can proceed to some extent at around 1400 °C if it is performed under an oxygen partial pressure lower than 10^{-6} bar. Moreover, mixed iron oxides, or $M_xFe_{3-x}O_4$ (M denotes Mn, Co, Mg, Ni or Zn), have been examined in order to lower the T-R step temperature and enhance the hydrogen productivity of the redox material (Lundberg, 1993; Ehrensberger et al., 1995, 1996; Tamaura et al., 1995).

However, the Fe_3O_4/FeO and mixed iron oxide redox pairs cause coagulation and sintering of the iron oxide particles during the cyclic reaction, resulting in rapid deactivation. Thus, the iron oxides are supported with monoclinic ZrO_2 (*m*-ZrO_2) particles that have a good coagulation or sintering resistance at temperatures of 1000–1400 °C because *m*-ZrO_2 has a higher melting point than ferrite and is chemically inert to ferrite at high-temperatures. As a result, repeatable two-step water splitting cycles were demonstrated by using highly active ZrO_2-supported ferrite particles since the unsupported ferrite particles caused the coagulation and sintering of iron oxide (Kodama et al., 2003, 2005, 2006). In addition, the present authors propose partially stabilized tetragonal zirconia (*t*-PSZ) and yttria-stabilized cubic zirconia (*c*-YSZ or YSZ) as a support of the redox material for use in the repeatable thermochemical two-step water splitting (Gokon et al., 2006a, 2008b). In particular, the YSZ support reacts with ferrite particles at temperatures above 1400 °C and in an inert atmosphere, and as a result, an iron-containing YSZ or Fe-YSZ is formed. Thermochemical cycles using Fe-YSZ particles can prevent the sintering or melting of iron oxides at high-temperatures due to the incorporation of active iron ions into the YSZ lattice, resulting in improved reproducibility of the cyclic reaction.

The abovementioned redox working materials are combined with a solar chemical receiver/absorber/reactor for producing solar hydrogen via a thermochemical two-step water splitting cycle by using concentrated solar radiation as the energy source. Diver et al. (2006) proposed the concept of a counter-rotating ring receiver/reactor/recuperator (CR5) enabling efficient recovery of sensible heat during a cyclic reaction. The predicted conversion efficiency of solar power into hydrogen for a Fe_3O_4/ZrO_2 system was theoretically estimated to reach approximately 30% upon 1 kW of solar input. Miller et al. (2006) performed material screening and characterization of various ferrite/YSZ systems in order to test the CR5 reactor. Kaneko et al. (2006) developed a rotary-type solar furnace by using Ni–Mn ferrite loaded on a YSZ support. A rotary-type solar furnace was experimentally tested in order to produce hydrogen and oxygen alternatively. The present authors have proposed and developed a new solar water splitting reactor with *m*-ZrO_2-supported $NiFe_2O_4$ particles in an internally circulating fluidized bed (Gokon et al., 2006b, 2008c). The conversion of ferrite reached approximately 45% upon 1 kW of input power by Xe-beam irradiation. The proposed solar reactor is assumed to be combined with newly developed beam-down optics of a solar concentrating system (Segal and Epstein, 2000, 2003).

A volumetric solar chemical reactor equipped with a multichanneled ceramic honeycomb receiver/absorber coated with an active ferrite powder has been proposed and demonstrated (Roeb et al., 2006). The ferrite loaded ceramic honeycomb, which is utilized as a solar receiver/absorber, is installed in the volumetric solar reactor and subjected directly to concentrated solar irradiation. The solar reactor is quite attractive for realizing a repeatable production of hydrogen and oxygen separately by passing steam or inert gas through the honeycomb. The present authors have proposed and tested ceramic foam devices, whose foam matrix is made of MgO-partially stabilized Zirconia (MPSZ); the foam is coated with *c*-YSZ and Fe_3O_4 particles (Fe_3O_4/YSZ/MPSZ foam device) that act as solar receivers/absorbers for multicycling the two-step water splitting process (Gokon et al., 2008a,b; Kodama et al., 2008, in press). The advantage of using a ceramic foam device is that it makes it possible to effectively absorb solar irradiation due to a large specific surface area. The hydrogen production by Fe_3O_4/YSZ/MPSZ foam devices is associated with the redox transition of Fe^{2+}–Fe^{3+} ions in the YSZ lattice (Gokon et al., 2008a,b). The deactivation of the Fe_3O_4 due to sintering at a high-temperature can be alleviated because of active Fe^{2+} ions that remain in the YSZ lattice. Recently, the authors reported that $NiFe_2O_4$/*m*-ZrO_2 powder exhibits its best reactivity at T-R temperature of 1400 °C and in an inert atmosphere among many ferrite/zirconia systems and subsequently provides great hydrogen productivity by W-D step at 1000 °C (Kodama and Gokon, 2007). Thus, the superior reactivity of the $NiFe_2O_4$/*m*-ZrO_2 will be exercised on ceramic foam if $NiFe_2O_4$/*m*-ZrO_2 powder is used as the redox material.

In the present study, reproducible and stoichiometric oxygen/hydrogen production is demonstrated through a repeatable two-step water splitting reaction by using *m*-ZrO_2-suported $NiFe_2O_4$ and Fe_3O_4 powders. A water splitting device in which the $NiFe_2O_4$/*m*-ZrO_2 particles are loaded on a ceramic foam is prepared and tested for hydrogen productivities through a repeatable two-step reaction upon direct irradiation with a Xe-beam in order to simulate solar irradiation.

2. Experimental

2.1. Synthesis of ZrO_2-supported ferrite powders

ZrO_2 particles with a monoclinic crystal structure (*m*-ZrO_2) were used to support ferrites ($NiFe_2O_4$ and