



Thermochemical reactivity of 5–15 mol% Fe, Co, Ni, Mn-doped cerium oxides in two-step water-splitting cycle for solar hydrogen production



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ABSTRACT

The thermochemical two-step water-splitting cycle using transition element-doped cerium oxide ($M\text{-CeO}_{2-\delta}$; $M = \text{Fe, Co, Ni, Mn}$) powders was studied for hydrogen production from water. The oxygen/hydrogen productivity and repeatability of $M\text{-CeO}_{2-\delta}$ materials with M doping contents in the 5–15 mol% range were examined using a thermal reduction (TR) temperature of 1500 °C and water decomposition (WD) temperatures in the 800–1150 °C range. The temperature, steam partial pressure, and steam flow rate in the WD step had an impact on the hydrogen productivity and production rate. 5 mol% Fe- and Co-doped $\text{CeO}_{2-\delta}$ enhances hydrogen productivity by up to 25% on average compared to undoped CeO_2 , and shows stable repeatability of stoichiometric oxygen and hydrogen production for the cyclic thermochemical two-step water-splitting reaction. In addition, 5 mol% Mn-doped $\text{CeO}_{2-\delta}$, 10 and 15 mol% Fe- and Mn-doped $\text{CeO}_{2-\delta}$ show near stoichiometric reactivities.

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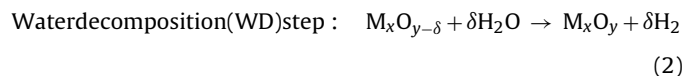
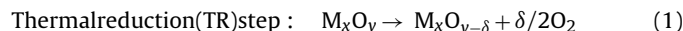
1. Introduction

Water-splitting thermochemical cycles are a promising means to produce hydrogen and oxygen by dissociation of water. The procedure can be rendered more attractive and environmentally friendly when combined with a renewable energy source such as solar energy [1]. Because of the incomparable magnitude and availability of solar energy, the solar-driven water-splitting thermochemical cycle is generally considered one of the few solutions for hydrogen production from water as it employs renewable technologies that are independent of fossil fuels [2]. Recent works on solar-driven water-splitting thermochemical cycles have focused on identifying materials that can reversibly participate in a lower-temperature redox cycle whose net output is $\text{H}_2 + \frac{1}{2}\text{O}_2$; an analogous process can be envisaged for the thermochemical splitting of CO_2 . In principle, such redox cycles can have an arbitrary number of steps; a larger number of steps lowers the temperature required for each, but reduces the maximum thermodynamic efficiency of the cycle [3].

From this perspective, the two-step (or, in some instances, three-step [4]) water-splitting cycle using a metal oxide as the

redox medium combines technically manageable temperatures with the simplicity and higher thermodynamic efficiency of a small number of steps [5,6]. Direct decomposition of water by solar heat requires impractical temperatures of above 2000 °C to obtain sufficient amounts of hydrogen [5,6] and a high-temperature gas separation mechanism to prevent the recombination of the gaseous products [7–9]. The two-step cycle can eliminate the need for *in situ* gaseous separation of oxygen and hydrogen. In addition, the material constraints for the solar chemical reactor operating at high temperatures can be alleviated.

A thermochemical two-step water-splitting cycle using a metal oxide as a redox pair is generally represented [5,6,9] as:



where M is a metal, M_xO_y is the corresponding metal oxide, and $M_xO_{y-\delta}$ is the reduced oxide. In the first step, oxygen is evolved when the metal oxide is thermally reduced at high temperature. Then, in the second step, further oxidation of the reduced oxide reacting with steam at a relatively low temperature generates hydrogen. The oxide is then recycled in the first step. According

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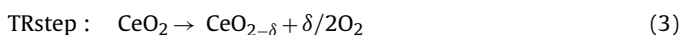
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to the redox mechanism, the oxygen productivity during the TR step is obviously dependent upon the extent of reduction of the metal oxide: the oxidized form of the redox material with the metal cation in its highest valence state can be either partially reduced to a lower-metal-valence oxide or fully reduced to the respective metal.

In principle, redox materials with high hydrogen and oxygen productivities are as desirable as those with lower operating temperatures, since the oxygen lost by the oxide during the reduction step is completely restored to the reduced oxide from water during the WD step, resulting in higher H_2/O_2 product yields per mass of redox material. Hence, the oxygen and hydrogen productions of both metal oxide/metal systems, such as ZnO/Zn and CdO/Cd, and metal oxide/metal oxide systems have been investigated. In the latter case, both single multivalent metal oxides, such as Fe_3O_4/FeO , Mn_3O_4/MnO , or the more recently tested CeO_2/Ce_2O_3 , and multivalent mixed metals, such as ferrites, doped-ceria, or the more recently tested perovskites, have been extensively explored as redox materials for the thermochemical two-step water-splitting cycle. Of these, the ferrite [5,6,8–14] and doped-ceria [15–18] systems have been the most thoroughly investigated.

Ferrites are attractive materials for thermochemical cycles, and have consequently been the subject of a number of experimental and modeling investigations [5,6,8–14]. The reduction of Ni-ferrite ($NiFe_2O_4$) is thermodynamically favorable relative to that of ceria at the same temperature and extent of reduction [14,19]. However, ferrites suffer from the problems of sintering and melting at high temperatures, and from slow kinetics.

Thermal reduction of ceria is quite different from that of ferrites. Ceria basically remains in the solid state during the two-step reaction, and the fluorite phase maintains its structure across a wide range of oxygen stoichiometries, δ [19]. This leads to the formation of oxygen vacancies that promote the transport of oxygen atoms through the material. However, ceria actually causes a partial sublimation of ceria and sintering at high temperatures (2000 °C) although in lower degree than Co- and Ni-ferrites [15]. The thermochemical water-splitting cycle based on the non-stoichiometry of ceria can be expressed as:



where $CeO_{2-\delta}$ represents a non-stoichiometric state of ceria (CeO_2) that is formed during the TR step when oxygen is released from CeO_2 . In the WD step, the $CeO_{2-\delta}$ can react with steam to produce hydrogen at temperatures of less than 1000 °C [20–27]. Recently, research on the thermochemical ceria-based cycle has shifted toward performing the reduction step at temperatures below the melting point of ceria, and improving oxygen and hydrogen productivities by doping ceria with other elements. The doping of a cationic metal into the fluorite structure of ceria has been implemented to enhance oxygen productivity during the TR step of the thermochemical two-step water-splitting cycle [9]. In earlier studies of doped-ceria cycles, alkaline earths (e.g. Ca or Sr), other elements (e.g. Zr or Al), transition elements (e.g. Mn, Fe, Co, Ni, or Cu) [26], and lanthanides (e.g. La, Pr, Sm, Gd, or Tb) [27–29] have been tested for their thermochemical cycles [18,30–32].

Hydrogen and oxygen productivity and cyclic reactivity of thermochemical two-step water splitting based on doped-ceria cycles has been investigated and reported in many of the studies mentioned above. However, in general, the production rates and amounts of oxygen evolved during the TR step depend on the reduction temperatures, while the productivity and stable cyclability of hydrogen generated during the subsequent WD step is associated with WD reaction conditions including the temperature, partial pressure, and flow rate of steam supplied to the reactor.

In this study, we examined the oxygen and hydrogen productivity of the respective steps and the repeatability of the two-step water-splitting cycle based on transition element (M = Fe, Co, Ni, Mn) doped ceria (M-doped $CeO_{2-\delta}$) over a wide range of WD step temperatures. In addition, we elucidated the reaction contribution of doped-ceria with different doping contents to oxygen evolution and hydrogen production in the TR and WD steps, respectively.

The objective of this work is to examine the oxygen and hydrogen productivity and repeatability of thermochemical two-step water splitting, based on $CeO_{2-\delta}$ doped with 5–15 mol% M as a reactive redox material. The thermochemical two-step water-splitting cycle is repeated at a temperature of 1500 °C for the TR step and in the relatively low temperature range of 800–1150 °C for the WD step. The effects of different temperatures and doping contents on the rate and amount of oxygen production from M-doped $CeO_{2-\delta}$, and the cyclability and reactivity with steam of the reduced phase of M-doped $CeO_{2-\delta}$ after the TR step are compared and discussed.

2. Experimental

2.1. Preparation of redox materials

M-doped $CeO_{2-\delta}$ powders were synthesized by a wet process using a method involving the co-precipitation of the precursor from an aqueous mixed solution of $Ce(NO_3)_3 \cdot 6H_2O$ (purity 98.0%) with $Mn(NO_3)_2 \cdot 6H_2O$ (purity 98.0%), $Fe(NO_3)_3 \cdot 9H_2O$ (purity 99.0%), $NiSO_4 \cdot 6H_2O$ (purity 99.0%), or $CoSO_4 \cdot 7H_2O$ (purity 99.0%). These reagents were purchased from Wako Pure Chemical Industries (<http://www.wako-chem.co.jp/english/>), Ltd., and used without further purification. Distilled water free of oxygen and CO_2 was prepared by passing N_2 through the distilled water for a few hours. The reagents above were dissolved in the distilled water at appropriate concentrations. The pH of each solution was adjusted to 8.5 by adding 0.15 mol dm^{-3} NaOH solution, thus resulting in the formation of the precursor. After heating the solution to 65 °C, air was bubbled into the suspension for 2 h while the pH was maintained at 8.5 by continuous addition of NaOH solution. The solid product was collected by centrifugation at 3000 rpm (KS-4000, Kubota), washed with distilled water and then acetone, and dried in vacuo at 100 °C for 1 day. The co-precipitate powders were then calcined at 900 °C for 2 h in air, before performing the high-temperature cyclic reactions.

Photographs of the synthesized Fe-, Co-, Ni- and Mn-doped $CeO_{2-\delta}$ powder materials are shown in Fig. 1. The amounts of transition element dopant were set to 5, 10, and 15 mol% of the total (dopant + cerium) metal content when the M-doped $CeO_{2-\delta}$ was synthesized. For comparison, undoped CeO_2 powders were also prepared as redox materials.

The synthesized powdered M-doped $CeO_{2-\delta}$ materials were characterized by X-Ray Powder Diffraction (XRD) (MX-Labo, MAC Science) using $CuK\alpha$ radiation for identification of the phases formed.

2.2. Activity test of M-doped $CeO_{2-\delta}$ powder

The powdered materials of M-doped $CeO_{2-\delta}$, and undoped CeO_2 were tested for activity in the two-step water-splitting thermochemical cycle under the same reaction conditions. Approximately 1 g of the powder material was packed into a platinum crucible (10 mm in diameter and 7 mm in depth) and mounted on the ceramic bar in a quartz reaction chamber (SSA-E45, Ulvac-Rico) with an inner diameter of 45 mm (Fig. 2(a)). In the TR step, the powder materials were heated to 1500 °C within 1 min using an infrared furnace (RHL-VHT-E44, Ulvac-Rico) while passing N_2 gas (purity 99.999%) through the reactor at a flow rate of $1.0 \text{ dm}^3 \text{ min}^{-1}$ at

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