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Solar thermochemical process for hydrogen production via two-step water splitting cycle based on $Ce_{1-x}Pr_xO_{2-\delta}$ redox reaction

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ABSTRACT

$Ce_{1-x}Pr_xO_{2-\delta}$ (x = 0, 0.05, 0.1, 0.2 and 0.3), as reactive ceramics synthesized by combustion method for H_2 production via two-step water splitting reaction with concentrated solar energy, was investigated in present work. XRD analysis of the samples shows that Pr_6O_{11} underwent a phase transition into Pr_2O_3 and Pr_2O_3 cannot be oxidized by steam to yield H_2 in two-step water splitting reaction. The solid solutions of the samples containing Ce were formed with a single cubic CeO_2 fluorite structure after synthesis and even after two-step water splitting reaction. Although Pr cannot be oxidized by steam to generate H_2 in two-step water splitting reaction, the promotion effect is present with the introduction of 5 mol% and 10 mol% Pr into CeO_2 on the amounts of O_2 and H_2, but the volume of H_2 evolved is enhanced or not, strongly dependent on the H_2-generation temperature. The optimum H_2-generation temperature is 1023 K.

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1. Introduction

Hydrogen (so-called solar fuel) is not only environmentally friendly [1] but also a high-energy fuel [2] comparing with conventional fuels, and hence it is an ideal fuel to replace traditional fuel to solve energy shortage and environmental pollution problems [3]. Particularly, producing hydrogen driven by concentrated solar energy via thermal two-step water splitting reaction has been attracted much more attention in recent decades because there is no pollution both in production and utilization processes.

Cyclic two-step water splitting reaction with metal oxides driven by the concentrated solar energy can be expressed as following equations [4,5]:

O_2-releasing step:

$$MO_x \xrightarrow{\text{concentrated solar energy}} MO_{red} + O_2\,(g) \quad (1)$$

H_2-generation step:

$$MO_{red} + H_2O \rightarrow MO_{ox} + H_2\,(g) \quad (2)$$

where MO stands for metal oxides with variable valences, the subscripts red and ox represent reduction state and oxidation state of the metal oxide. Undoubtedly redox pairs formed by metal oxides with reversible valences play the most important role in this cyclic reaction system. Various materials for two-step water splitting reaction driven by concentrated solar energy have been extensively studied. The research mainly aiming at lowering O_2-releasing temperature and enhancing hydrogen yield has been conducted with different redox pairs of metal oxides or mixed oxides, including Fe_3O_4/Fe_2O_3 [6], ZnO/Zn [7–9], Mn_3O_4/MnO [10] $(Fe_{1-x}M_x)_3O_4$ (M = Mn, Mg, Co, Ni, Zn) [11–13] and YSZ–Fe_3O_4 [14], but they were restricted by the problems, such as ceramics sintering and thermal stability in O_2-releasing reaction at high temperature, reaction rate in H_2-generation reaction and amount of hydrogen generated.

The facile Ce^{4+}/Ce^{3+} repeatable redox process of CeO_2 under rich and lean oxygen conditions makes it possible to utilize CeO_2 as a reactive ceramic for hydrogen production via two-step water splitting reaction [15], however, the reduction reaction took place above 2000 K, which is too high to achieve for practical application driven by concentrated solar energy and causes serious sintering problem at so high temperature. Since the introduction of other rare earth or transition metals into CeO_2 lattice could enhance the chemical and physical properties by creating oxygen vacancies inside the host oxide [16–19], the CeO_2–MO_x (M = Mn, Fe, Ni, Cu, Zr) have been confirmed by our group as good reactive ceramics [20,21], in comparison with pure CeO_2, which not only lowers the reduction temperature down to approximately 1773 K but also promotes the amount of hydrogen generated. Additionally, it is applicable for rotary-type solar beam reactor devised by our group [22] to produce hydrogen with concentrated solar energy. So far, CeO_2-based ceramics have been the most promising material for hydrogen

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production using the rotary-type solar beam reactor driven by concentrated solar energy via two-step water splitting reaction.

Many studies have already reported that the introduction of appropriate content Pr into CeO_2, to a great extent, can enhance oxygen storage capacity and oxygen mobility [23–25]. So the promotion effect of Pr doped CeO_2 as a material on hydrogen production via two-step water splitting reaction is anticipated.

In this study, the $Ce_xPr_{1-x}O_{2-\delta}$ (x = 0, 0.05, 0.1, 0.2 and 0.3) for hydrogen production via two-step water splitting reaction was carried out, with a purpose of demonstrating the feasibility of $Ce_xPr_{1-x}O_{2-\delta}$ as promising reactive ceramics to convert the concentrated solar energy, especially using the rotary-type solar beam reactor, into chemical energy (hydrogen, solar fuel), and investigating the optimal H_2-generation temperature for hydrogen production.

2. Experimental

2.1. Sample synthesis

The rare-earth metal solid solutions, $Ce_{1-x}Pr_xO_{2-\delta}$ (x = 0, 0.05. 0.1, 0.2, 0.3 and 1) for two-step water splitting reaction, were synthesized by combustion method taking stoichiometric amounts of cerium nitrate hexahydrate $Ce(NO_3)_3{\cdot}6H_2O$ and oxalyldihydrazide ($C_2H_6N_4O_2$, OBH) and Pr_6O_{11}. The chemical reaction equation for the preparation has been reported somewhere else [26].

Typically, synthesis for $Ce_{0.9}Pr_{0.1}O_{2-\delta}$, 0.18916 g Pr_6O_{11} was dissolved in hot dilute nitric acid and 4.322 g $Ce(NO_3)_3{\cdot}6H_2O$ and 1.771 g OBH were separately dissolved in minimum amount of deionized water, and then mixed the specified amounts of aqueous solutions together. The solution containing $Ce(NO_3)$, $Pr(NO)_3$ and OBH($C_2H_6N_4O_2$) was heated on a hot stirrer at 623 K inside fume hood, which underwent boiling frothing, foaming and ignited to a voluminous oxide powder. The resultant powder was, in turn, burnt with a burner flame and ground by agate mortar and pestle. In order to eliminate the undesirable impurities and/or organic components, the resulting powder, subsequently, was heated in an electric resistance furnace at 1273 K for an hour and then cooled down to 773 K to hold at 773 K for 30 min, finally, swiftly quenched with ice. The red powder was eventually formed, whose colour slightly varies with the mole ratio of cerium to praseodymium.

2.2. Experimental setup

A quartz tubular reactor system, where two-step water splitting reaction alternately took place, is schematically depicted in Fig. 1. The sample packed into a mesh platinum cup (gases could pass through the platinum cup) was mounted above a support composed of a platinum holder and a fine ceramic tube. Infrared image furnace was used to simulate the concentrated solar energy for heating sample in two-step water splitting reaction. In order to efficiently control the reaction temperature by temperature program controller (TPC), a thermocouple in close contact with the platinum cup was inserted in the ceramic tube. The gases evolved in two-step water splitting reaction were recorded online by direct gas mass spectrometer (DGMS).

2.3. Two-step water splitting reaction

Two-step water splitting reaction was consecutively carried out for several cycles, and O_2-releasing reaction and H_2-generation reaction were alternately performed in the reactor by swiftly switching the valves (Fig. 1). Heating-up and cooling rates were always the same, 200 K min^{-1} and 1000 K min^{-1}, respectively.

It has been reported that the optimal O_2-releasing reaction temperature of CeO_2-based materials is about 1773 K, but the optimum H_2-generation reaction temperature is different according to CeO_2 doped different metal oxides [20,21], so the same O_2-releasing temperature (1773 K) was used in present work. The O_2 releasing process was first performed in Ar (100 cm^3 min^{-1}) at 1773 K for 3 min, and subsequently H_2-generation process was conducted in steam (0.36 cm^3 min^{-1}) generated by vaporizing dropwise degassed deionized water (provided by a micropump) with electric resistance furnace at 673 K, along with Ar (100 cm^3 min^{-1}) gas. In order to determine the appropriate H_2-generation reaction temperature, the H_2-generation reaction was performed at 773 K, 1023 K and 1223 K, respectively and two-step water splitting reaction was repeated for five cycles at each H_2-generation temperature.

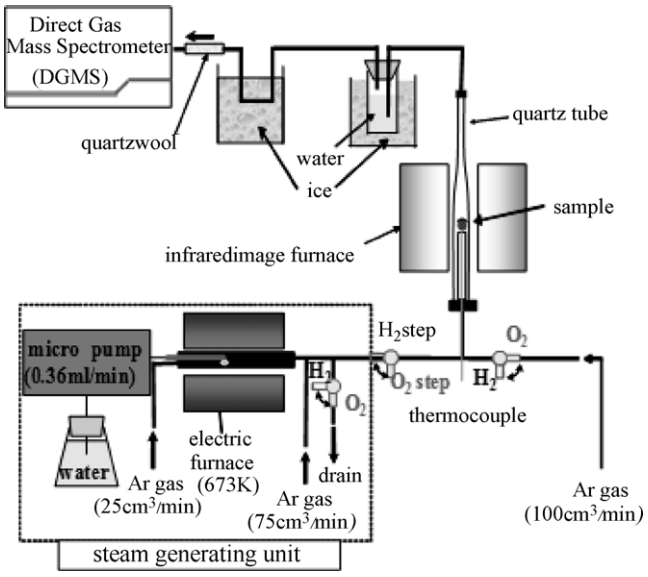

Fig. 1. Experimental set-up for two-step water splitting reaction.

2.4. Sample characterization

All the samples synthesized, as well as obtained from two-step water splitting reaction were subjected to X-ray diffraction (XRD), with Ni-filtered Cu-Kα radiation (Rigaku, RINT 2100) to identify the existing phase. The samples were scanned in the 2θ range from 20 to 100. The qualitative analysis, such as identification of crystalline phase and lattice constant was executed by PDXL software.

3. Results and discussion

3.1. Sample characterization

The sample of $Ce_{1-x}Pr_xO_{2-\delta}$ as-synthesized powder was characterized by XRD and the patterns are shown in Fig. 2. It can be observed that when x = 0 and 1, the diffraction peaks are attributed to cubic CeO_2 and Pr_6O_{11} fluorites, respectively. When x = 0.05, 0.1, 0.2 and 0.3, the diffraction patterns are indexed to CeO_2 cubic fluorite structure and no other impurity peak can be observed in XRD patterns. This indicates that CeO_2 solid solution was formed with a single phase after synthesis (Figs. 3 and 4).

From the XRD patterns of the samples after synthesis (Fig. 2) and two-step water splitting reaction (Fig. 3), it can be observed that the synthesized pure Pr_6O_{11} phase transferred into Pr_2O_3 phase in two-step water splitting reaction and always retained the Pr_2O_3 phase during two-step water splitting reaction, indi-

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