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Chemical hydrogen storage and release properties using redox reaction over the Cu-added Fe/Ce/Zr mixed oxide medium

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ABSTRACT

The chemical hydrogen storage (hydrogen reduction) and release (water-splitting oxidation) properties of the Cu-added Fe/Ce/Zr mixed oxide medium were investigated. The media with Cu content ranging from 0 to 5 wt% were prepared by a co-precipitation method using urea as a precipitant. The hydrogen reduction and the water-splitting oxidation on the medium were tested by temperature programmed reduction/oxidation (TPR/TPO) and repeated isothermal redox cycles at 550 °C for reduction and 350 °C for oxidation. The initial reduction rates and oxidation rates of the media increased with increasing the amount of the Cu additive. In addition, the reactivity of the medium for water-splitting oxidation was enhanced as the CeO_2/ZrO_2 ratio increased. Especially, the Fe-based mixed oxide medium with Cu/CeO_2/ZrO_2 contents of 3/30/10 wt% (Cu(3%)-Fe-CeO_2/ZrO_2(3/1)) showed superior performance in chemical hydrogen storage and release. As the results of isothermal redox cycles using the medium, the total amount of hydrogen evolved in water-splitting oxidation was maintained at ca. 8.5 mmol g^{-1}-medium (ca. 1.8 wt% hydrogen storage amounts on the basis of the total medium) over 15 repeated redox cycles.

1. Introduction

Recently, hydrogen has been recognized as an environmentally benign and resourceful energy source alternative to the conventional systems based on fossil fuels. Many investigations into such fields as hydrogen production, storage, and utilization are being performed [1–3]. In the area of hydrogen storage, physical storage methods such as compressed hydrogen gas and liquid hydrogen, and chemical storage methods such as metal hydrides [4] and chemical hydrides [5] are well known. Compressed gas storage is dominant technology available in present, but the volumetric hydrogen content still remains a concern due to relatively low energy density and safety issues. On the other hand, liquid hydrogen storage at low temperature is compact, but this method has problems in the energy losses during liquefaction (about 33% of the overall energy content) and evaporation in off-operation periods [6]. Currently, a great deal of effort has been addressing to develop new hydrogen storage methods using materials such as metal hydrides [4], chemical hydrides [5] and carbon nanostructures [7].

On the other hand, a hydrogen storage method that utilizes a simple reversible redox reaction using iron oxides was proposed by Otsuka et al. [8–10]. This process is based on a traditional steam-iron reaction [11–13] and consists of the following two-step reactions: reduction of Fe_3O_4 with hydrogen and oxidation of Fe metal with water vapor.

Step 1: Chemical hydrogen storage (hydrogen reduction):

$$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(g)$$

Step 2: Hydrogen release (water-splitting oxidation):

$$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

Assuming that the hydrogen reduction and water-splitting oxidation reactions occur stoichiometrically, hydrogen can be theoretically stored 23.8 mmol (4.8 wt% hydrogen storage) on the basis of 1 g-Fe. This process is more efficient and economical than the other chemical storage methods since iron oxide is readily available. In addition, the hydrogen released in the water-splitting oxidation is pure, so it may be directly applied to a PEMFC (polymer electrolyte membrane fuel cell) [14].

However, this method has some drawbacks including the deactivation of iron oxide during repeated redox cycles and a higher required reaction temperature in the water-splitting step [8–10]. To solve these problems, many researchers have focused on

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modifying the iron oxide medium by adding a metal additive to the medium [15–19]. In our previous studies, the effects of several metal additives such as Pd, Pt, Rh, Ru, Al, Ce, Ti, and Zr were investigated in terms of the reactivity and thermal stability of the medium. As the results, we conclude that the co-addition of Ce/Zr mixed oxides to iron oxide was the favorable combination in improving the reactivity and thermal stability of the medium during repeated redox cycles. Additionally, the addition of Rh to Fe/Ce/Zr mixed oxides greatly promoted the re-oxidation rate at a relatively lower temperature [20,21]. It was previously reported that Rh on the surface of the particles of Fe_3O_4/Fe would activate H_2O molecules into H and OH or 2H + O, and hence the rate was enhanced [10]. Despite good performance of Rh, however, it is necessary to develop an inexpensive additive to replace Rh metal for industrial use.

In this work we have studied the behavior of Cu, as a good and inexpensive candidate for the replacement of Rh, added to Fe/Ce/Zr mixed oxide medium in the hydrogen reduction and water-splitting oxidation. For this purpose, the effects of Cu additive contents and CeO_2/ZrO_2 ratios on the reactivity of the Fe-based mixed oxide medium were investigated to find an optimized composition of the medium. On the selected medium, the isothermal redox reactions were carried out for up to 15 cycles to confirm its availability for chemical hydrogen storage and release.

2. Experimental

2.1. Preparation of the metal oxides media

The media were prepared by a co-precipitation method using urea as the precipitant. Iron (III) nitrate enneahydrate (99%, Kanto), ammonium cerium (IV) nitrate (99.99%, Aldrich), and zirconium (IV) propoxide (70 wt%, Aldrich) were used as the precursors for the Fe/Ce/Zr mixed oxides. Copper (II) nitrate hydrate (99%, Junsei) and rhodium (III) chloride hydrate (99.98%, Aldrich) were used as the precursors for the Cu and Rh additives in the medium, respectively. The mixing ratios of each metal additive were determined depending on the crystal structure (Fe_3O_4, Rh, Cu, CeO_2 and ZrO_2) of the final oxide media. The amount of CeO_2/ZrO_2 as binder was fixed at 40 wt%. The final media obtained are hereafter designated as M(*X*%)-Fe-CeO_2/ZrO_2(*Y*/*Z*), where M can be Rh or Cu, X represents the M weight content in the mixed oxide and *Y*/*Z* the CeO_2/ZrO_2 loading ratio. The nomenclature of the prepared media and their compositions are listed in Table 1.

A 0.5 M aqueous solution containing Fe, Ce, Zr, Cu, and Rh ions was stirred strongly at 90 °C for 2 h while 8 M urea solution was added as a precipitant, until the pH of the solution was ca. 9. The resulting precipitant was washed three times with deionized water, dried at 100 °C for 24 h, and then calcined in air at 300 °C for 5 h and at 500 °C for 10 h. The media with particle sizes that ranged from 180 to 425 μm were used in the redox reaction.

Table 1
Nomenclature and composition for each mixed oxide medium.

Nomenclature	Composition (wt%)				
	Fe_3O_4	Rh	Cu	CeO_2	ZrO_2
Fe-none	100				
Fe-CeO_2/ZrO_2(1/3)	60			10	30
Rh(1%)-Fe-CeO_2/ZrO_2(1/3)	59	1		10	30
Cu(1%)-Fe-CeO_2/ZrO_2(1/3)	59		1	10	30
Cu(3%)-Fe-CeO_2/ZrO_2(1/3)	57		3	10	30
Cu(5%)-Fe-CeO_2/ZrO_2(1/3)	55		5	10	30
Cu(3%)-Fe-CeO_2/ZrO_2(2/2)	57		3	20	20
Cu(3%)-Fe-CeO_2/ZrO_2(3/1)	57		3	30	10
Cu(10%)-Fe-CeO_2/ZrO_2(1/3)	50		10	10	30

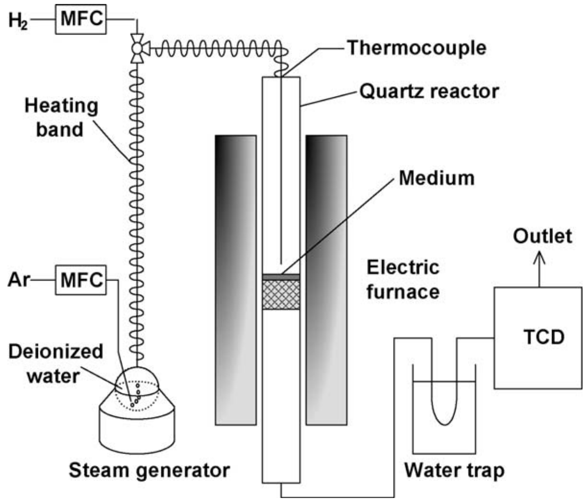

Fig. 1. Schematic diagram of the experimental apparatus for the redox reaction.

2.2. Apparatus and procedure

The experimental apparatus used for the redox reactions of the media is shown in Fig. 1. The redox reactions were performed in a conventional gas-flow system with a fixed-bed quartz reactor of 8 mm inner diameter. The amount of medium loaded in the reactor was 50 mg. The H_2–Ar mixture (10% H_2 in Ar balance) was introduced at a flow rate of 40 ml min^{-1} for the reduction. The water vapor was supplied with argon as a carrier gas at a total flow rate of 40 ml min^{-1} with partial pressure of ca. 32 kPa for the oxidation.

The redox behavior of the medium was investigated with temperature programmed reduction/oxidation (TPR/TPO). The medium was reduced while the temperature increased from room temperature to 550 °C at a heating rate of 10 °C min^{-1}. After the temperature reached 550 °C, it was maintained at that temperature until no consumption of hydrogen was detected. After cooling to room temperature, the reduced medium was oxidized with water vapor for oxidation. The temperature was increased from room temperature to 600 °C at a heating rate of 10 °C min^{-1} and then was maintained at 600 °C until no hydrogen formation was observed. For the isothermal redox reaction, a test used to determine the durability of the media, the reduction and oxidation temperatures were fixed at 550 and 350 °C, respectively, based on the TPR/TPO results.

During the redox reaction, the effluent gas from the reactor was analyzed using gas chromatography (Donam DS-6200) equipped with a thermal conductivity detector (TCD). The composition of the media was analyzed using the X-ray diffraction (XRD) technique (Rigaku DMAX 2500). Microphotographs on the surface of the medium were measured using field emission scanning electron microscopy (FE-SEM, Hitachi S-4700).

3. Results and discussion

3.1. Effects of the Cu additives in the medium

3.1.1. TPR/TPO

The effects of the amount of Cu additive in the medium on the redox properties were investigated using TPR/TPO tests, and the TPR results are shown in Fig. 2. For Fe-none (a), two peaks resulting from the consumption of hydrogen were observed, which indicates that the reduction of Fe_2O_3 to Fe_3O_4 and that of Fe_3O_4 to Fe occurred at under and over 400 °C, respectively. This result suggests that the reduction of Fe_2O_3 first progressed to Fe_3O_4 and