Water Splitting Capacity Improvement of Mn-Fe Oxide Prepared by Ball Milling with ZrO_2

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Abstract

Mn-Fe oxide and Mn-Fe oxide/ZrO_2(50wt%/50wt%) were prepared by ball milling method. XRD data of the prepared samples revealed that hematite and ferrite phase coexisted. Water splitting at 1273K, after thermal reduction at 1573K, was performed 4 times for the samples. Hydrogen production amount was analyzed by GC with TCD detector. Water splitting capacity of Mn-Fe oxide was improved by ball milling with ZrO_2.

Keywords : hydrogen, ferrite, thermochemical water splittng

1. Introduction

There have been many efforts on producing hydrogen from water in the field of solar thermochemical production of hydrogen that uses concentrated solar radiation as the energy source. Several 2-step, muti- step thermochemical water splitting methods are reported at various temperatures. Among them, the most simplest and promising thermochemical water splitting is 2-step thermochemical cycle using metal oxide redox pairs.

$$\text{Reduction step: } MO_{ox} \xrightarrow{\textit{Thermal Energy}} MO_{red} + O_2 \quad (1)$$

$$\text{Water splitting step: } MO_{red} + H_2O \rightarrow MO_{ox} + H_2 \quad (2)$$

Nakamura originally proposed the thermochemical 2-step water splitting using redox pair of FeO/Fe_3O_4. But the thermal reduction temperature of the process is above 2000K.

To decrease the reduction temperature, some researchers combined the Mn, Ni, Co oxides with Fe_3O_4. It has shown the decreased reduction temperature and good hydrogen yields.

But the thermal sintering deactivates the metal oxide for repeated cyclic reaction. For ferrite systems, passive oxide layer formation at the surface blocks diffusion channels for gaseous species. To prevent these phenomena, Kodama et al. have prepared Mn-ferrite, Co-ferrite by aerial oxidation method on the ZrO_2 powder. It showed good thermal stability and hydrogen production capacity.

In the present work, we prepared Mn-Fe oxide by ball milling method which is easier and suit for mass production. And we improved the hydrogen production amounts by mixing the Mn-Fe oxide with ZrO_2 by the same method.

2. Experimental and Results

10g MnO (Aldrich 99%) was mixed with Fe_2O_3 (Aldrich 98%) to form Mn-Fe oxide with atomic ratio Mn/Fe=1/5 in a zirconia container (500ml) containing zirconia balls (diameter=5.3mm) corresponding to ball to powder ratio 10/1. Ethanol and oleic acid were used as a solvent and a dispersion agent, respectively. Milling was performed for 24hrs at 300rpm. The slurry was filtered, dried, and calcined for 10hrs at 1373K in air. Mn-Fe oxide/ZrO_2 (50wt%/50wt%) was prepared by the same procedure after mixing ZrO_2 (Aldrich 99.9%) with the prepared Mn-Fe oxide.

As can be seen in Fig. 1, Ar(99.999 vol%) was used as a carrier gas and mass flow controllers were used to control the Ar flow rate (20ml/min). Quartz tube (OD 20mm, L 500mm) was used as the reactor and the prepared samples were placed in the reactor by mounting on the packed quartz wool and then carefully located in the center of the furnace vertically. To rise and control the temperature, Mo-Si furnace and S-type thermocouple were used. The thermal reduction maintained for 30min at 1573K, water splitting was conducted at 1273K for 1hr. Peristaltic pump supplied water to vaporizer at the flow rate 10cc/hr and carrier gas (Ar 20cc/min) swept the vaporized water vapor to reactor.

To determine the total amount of gas products evolved during water splitting reaction, the effluent gas was collected in a bottle by water displacement. The volume of the collected effluent gas was measured and the concentration of hydrogen was determined by GC (HP6890 TCD). For the repetition test, thermal reduction and water splitting reaction were alternately repeated 4 times. The prepared samples and the repetition test samples were

subjected to XRD with CuK α radiation (Model D-8 advance, Bruker) for the structural characterization. The morphology of the samples was examined with a FE-SEM (S-4700, Hitachi) for analysis.

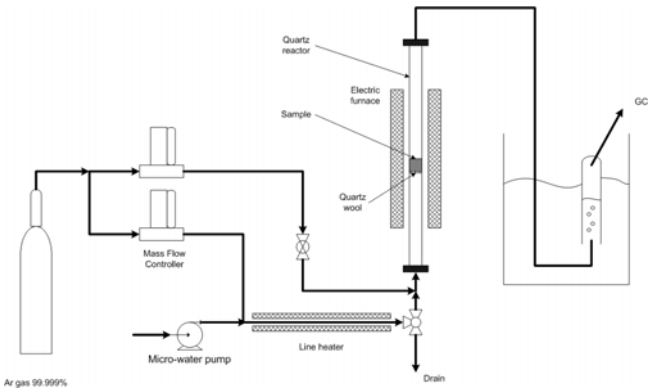

Fig. 1. Schematic of the experimental set-up

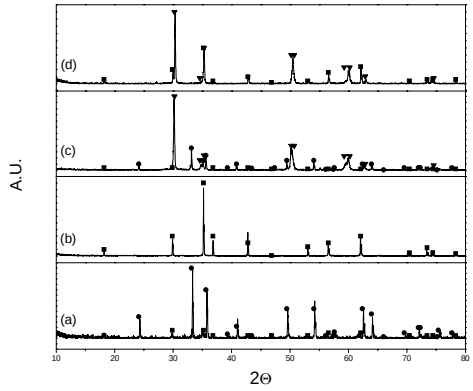

Fig. 2. XRD patterns of (a) the prepared Mn-Fe oxide, (b) that after 4 cycle repetition test, (c) Mn-Fe oxide/ZrO_2 (50wt%/50wt%), (d) that after 4cycle repetition test. (●:hematite, JCPDS card 89-2810 ■:$Mn_{0.43}Fe_{2.57}O_4$, JCPDS card 89-2807 ▼: tetragonal ZrO_2, JCPDS card 79-1766)

Fig. 2. shows the XRD patterns of the samples. The prepared samples showed hematite and Mn substituted ferrite phases. After 4 cycle repetition test, they showed only Mn substituted ferrite phase. ZrO_2 was originally monoclinic phase but they transformed to tetragonal phase. It is deduced that Mn, Fe stabilized ZrO_2 during thermal treatment during preparation.

Fig. 3. shows improvement of hydrogen production amounts by using ZrO_2. Mn-Fe oxide evolved maximum H_2, 15.178μmol/g-Mn-Fe oxide in 2nd cycle. Mn-Fe oxide/ZrO_2 (50wt%/50wt%) evolved maximum 29.196 μmol/g-Mn-Fe oxide in 4th cycle.

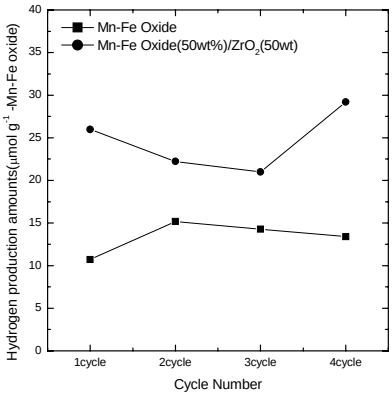

Fig. 3. Hydrogen production amounts in the 4 cycle repeated water splitting reactions using Mn-Fe oxide, Mn-Fe oxide/ZrO_2(50wt%/50wt%) based on the reaction involved Mn-Fe oxide.

3. Summary

Mn-Fe oxide showed water splitting ability after thermal reduction at 1573K. When Mn-Fe oxide mixed with ZrO_2, hydrogen production capacity was improved. Mn-Fe oxide and Mn-Fe oxide/ZrO_2 (50wt%/50wt%) formed Mn-ferrite phase after 4 cycle repetition test.

4. Acknowlegement

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5. References

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