Redox characteristics of Cu-ferrite for thermochemical hydrogen production

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Abstract

As the redox pair for thermochemical hydrogen production, Cu-ferrite was examined. Thermochemical hydrogen production process using metal oxides consisted of thermal reduction step and oxidation step by a steam as an oxidant. It was confirmed that crystal structure of Cu-ferrite was changed to metal and cation excess metal oxide during the reduction step. The reduced metal oxide reacted with steam at $800^{o}C$. It was found that the weight of the reduced Cu-ferrite was increased during reaction time, and it means the hydrogen production by water decomposition and oxidation of the reduced Cu-ferrite.

Key words: *Thermochemical water-splitting, Hydrogen production, solar heat, Cu-Ferrite, Metal oxide*

1. INTRODUCTION

Hydrogen is an attractive fuel for the future because it is renewable as an energy resource and it is also flexible as an energy carrier. Specially, if hydrogen used as a fuel, it does not release the earth environmental pollution materials such as carbon dioxide (CO_2) and sulfur dioxide (SO_2). Therefore, if human beings desire to obtain the ultimately clean H_2 as an energy carrier, water is the only source of H_2 on the earth. However, it requires greatly high temperature (above 4000 K) to directly obtain the H_2 from the water under 1 atm. To solve this problem, the thermochemical water-splitting cycles have been proposed for the hydrogen production from the water at low temperature (Funk et al., 1966). The water-splitting method by a metal oxide using the heat energy of concentrated solar

radiation was investigated by Nakamura (Nakamura, 1977). He proposed the reactions:

$$MO_y \rightarrow M + (1/2) O_2 \qquad (1)$$

$$M + yH_2O \rightarrow MO_y + y H_2 \qquad (2)$$
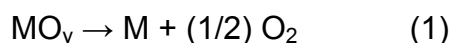
The thermal decomposition of Metal oxide in the reaction (1) endothermically proceeds in air at above 2300K and 1 atm and is called the solar reaction step. However, this proposed process has problems such as materials and process technologies at the high temperature (a loss of the concentrated solar radiation) (Tofighi et al., 1980, Steinfeld et al., 1993). The reaction (2) is an exothermic reaction and the metal is reoxidized to metal oxide by water to produce hydrogen and is called the water-splitting step.

Recently, Steinfeld (Steinfeld et al., 1999) proposed the combination of the decomposition of metal oxide with natural gas such as CH_4 to decrease the process operation temperature as shown in the following reaction and are called the solar methane reforming:

$$Fe_3O_4 + CH_4 \rightarrow 3 FeO + CO + 2H_2 \qquad (3)$$

$$H_2O + 3FeO \rightarrow Fe_3O_4 + H_2 \qquad (4)$$
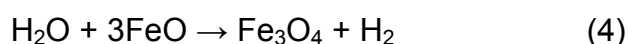
Here, CH_4 is used for the activation of the metal oxide and the produced CO and H_2, which are used for the synthetic gas. However, the operating temperature of thermal decomposition of metal oxide combined with CH_4 as shown in Eq.(3) is relatively low and it has merit for the two-step water-splitting cycle, but CO_2 formation is thermodynamically more favorable at a lower temperature in CH_4-reduction of metal oxide. The choice of metal oxide in reaction (3), which determines high selectivity and reactivity for CO formation, is very important to avoid CO_2 emission.

In the thermochemical water-splitting method using the heat energy of concentrated solar radiation, the development of the metal oxide is very important for the hydrogen production by only water decomposition and not uses a fossil fuel such as methane, at low temperature. In the previous research, the authors (Park et al., 2004) reported the characteristics of Cu-ferrites and the possibility of the 2-step water-splitting cycles for the hydrogen production by only water decomposition.

In this study, Cu-ferrite was prepared as a basic metal oxide and examined for the two-step water-splitting cycles consisting of solar reduction step and the water-splitting step at low temperature of below 1173K, and evaluated the redox characteristics of the prepared Cu-ferrite.

2. Experimental

2.1. Synthesis of Cu-ferrite

The Cu-ferrite was prepared as follows. Appropriate portions of ferric nitrate solution $(Fe(NO_3)_3 \cdot 9H_2O)$ and copper nitrate solution $(Cu(NO_3)_2 \cdot 3H_2O)$ were dissolved in distilled water, respectively, and then mixed. The molar ratio Cu/Fe_{total} in the starting solution was 2. 0.5mol KOH aq. solution was added to the mixed solution adjusting to pH 10 for co-precipitation. The co-precipitation formed was aged for 24h at the room temperature, and then the precipitation was obtained by filtering through washing with the distilled water. The products were dried at $100^{\circ}C$ for 24h. The obtained products were sintered at $950^{\circ}C$ in Air gas. The prepared Cu-ferrite crushed to 200 mesh size particles (75μm).

The prepared Cu-ferrite was identified by X-ray diffractometry (XRD) with CuKα radiation (Rigaku, RAD-rA diffractometer).
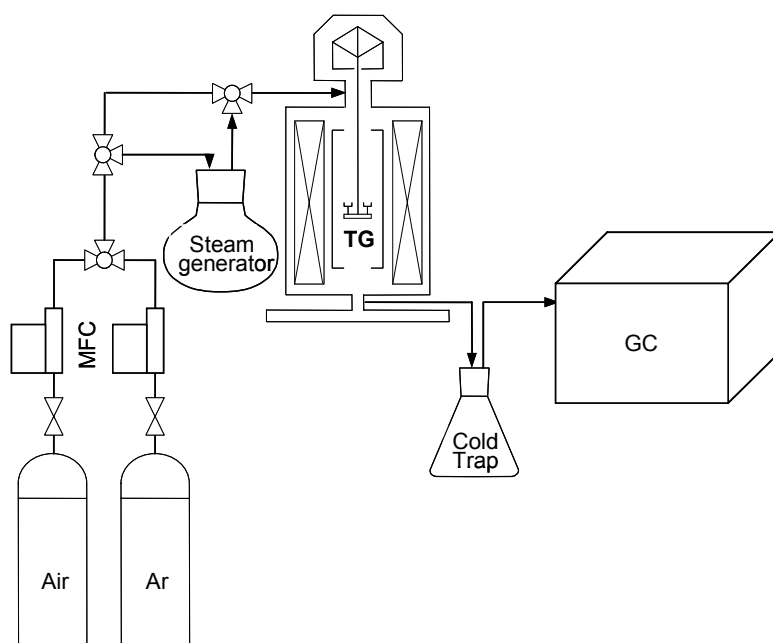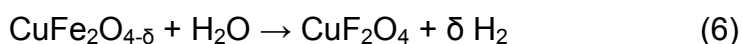

Fig.1 schematic diagram of experimental apparatus (TG reactor).

2.2. Two-step water-splitting cycles using Cu-ferrite

Fig. 1 shows a schematic diagram of experimental apparatus (TG reactor).

The prepared Cu-ferrite of 20 mg was set in an alumina sampler and placed in a furnace. The following reactions were examined for the Cu-ferrite:

$$CuF_2O_4 + thermal \rightarrow CuFe_2O_{4-\delta} + (\delta/2) O_\delta \qquad (5)$$

$$CuFe_2O_{4-\delta} + H_2O \rightarrow CuF_2O_4 + \delta H_2 \qquad (6)$$

Eq. (5) is referred to as solar reduction step, and Eq. (6) is referred to as the water-splitting step. The solar reduction step of Cu-ferrite was first performed. Ar gas was introduced in the reactor with flow rates of 60 ml/min. The reactor with Cu-ferrite was

heated to 900°C. After reaching to 900°C, the temperature was kept constant during each time. In this step, oxygen was released. The water-splitting step was then performed. The reactor was heated to 800°C. The steam was produced by steam generator at 250°C and mixed it with Ar gas of 60 ml/min. The reduced Cu-ferrite reacted with H_2O when passing mixed Ar/H_2O gas through the reactor, and hydrogen was produced. To determine the total weight change of metal oxide, the weight change was continuously recorded.

3. Results and discussion

3.1. Synthesis of Cu-ferrite

    Fig. 2 shows the XRD pattern of the prepared Cu-ferrite.

    As shown in Fig. 2, it was identified by XRD analyzer that the prepared Cu-ferrite at 950°C was crystallized as spinel-type ferrites ($CuFe_2O_4$) and also synthesized CuO.

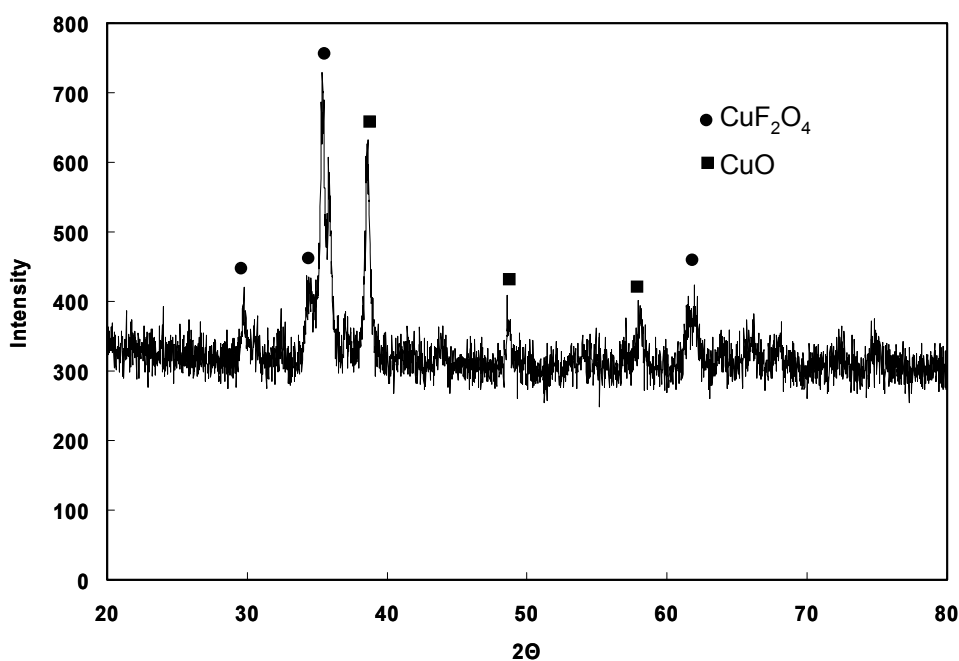Fig.2 XRD pattern of the prepared Cu-ferrite.

    The median particle size of Cu-ferrite analyzed by Particle Size Analyzer 22 (Fritsch Co.) was 25 µm.

3.2 Two-step water-splitting cycles using Cu-ferrite

3.2.1. Solar reduction step

    Fig. 3 shows the relationship between the weight change and the time.

With an increase of reaction time, the weight of Cu-ferrite decreased, and then that above 16 minutes was constant. The released gas might be oxygen which confirmed the previous work (Park et al., 2004).

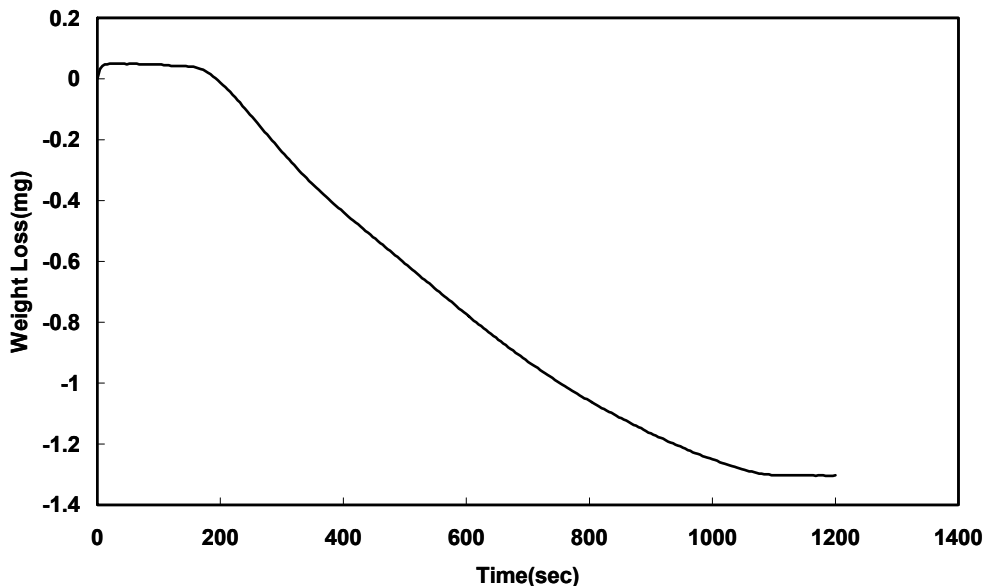The δ value shown in Eq. (5) was 0.91.　This value was the almost same 1/2 O_2.

Fig.3 The relationship between the weight change and the time.

From those results, it is supposed that the reaction time of solar reduction step was suitable within 20 minutes to release the oxygen from Cu-ferrite.
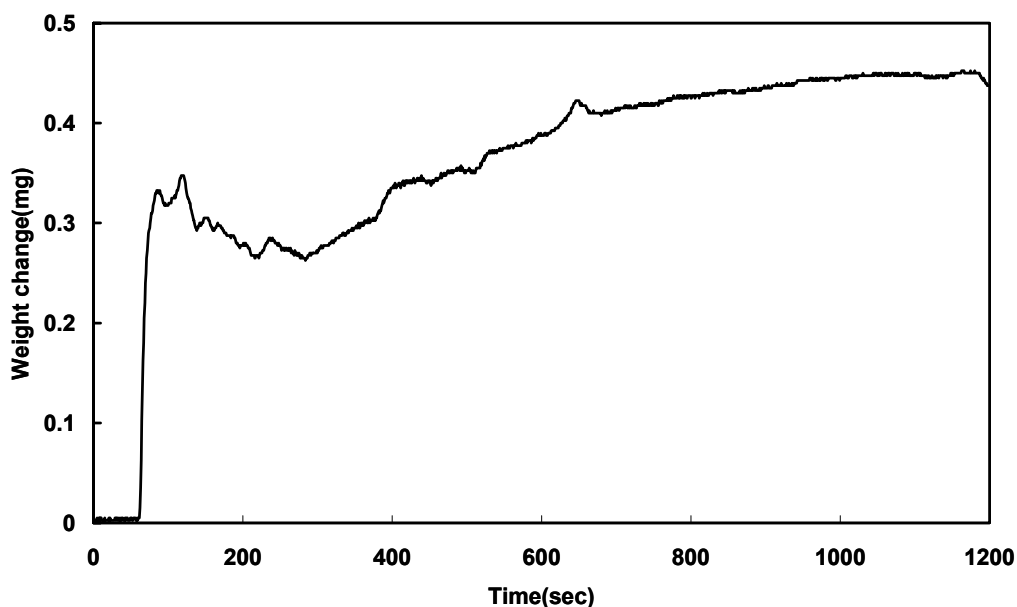

Fig.4 The relationship between the weight change and the time.

3.2.2. Water-splitting step

Fig. 4 shows the relationship between the weight change and the time.

With an increase of reaction time, the weight of the reduced Cu-ferrite increased, and then that above 20 minutes was constant. The released gas might be hydrogen which confirmed the previous work (Park et al., 2004).

The δ value shown in Eq. (6) was 0.32.　This value was the almost same 0.32 H_2.

From those results, it is supposed that the reaction time of water-splitting step was suitable about 20 minutes to produce the hydrogen from the reduced Cu-ferrite.

It is expected from above results that the 2-step water-splitting cycles for the hydrogen production using Cu-ferrite might be possible as shown in Eq.(5) and (6).

For the further study, it is necessary to clarify the stability of the prepared Cu-ferrite by the repetition experiments of two-step water-splitting cycles for a long life time and evaluate the thermal efficiency.

4. Conclusions

(1) The Cu-ferrite was prepared as a basic metal oxide for the two-step water-splitting cycles consisting of solar reduction step and water-splitting step using the solar heat.

(2) All steps were carried out at relatively low temperature below 1173K.　In the solar reduction step, it was confirmed that oxygen release from the prepared Cu-ferrite thermally progressed within reaction time of 20 minutes.　The δ value shown in Eq. (5) was 0.91.

(3) The water-splitting step was carried out after the solar reduction step.　The δ value shown in Eq. (6) was 0.32.

(4) The 2-step water-splitting cycles for the hydrogen production using Cu-ferrite might be possible as shown in Eq.(5) and (6).

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