Preparation of (Mn,Cu) Ferrite and Preliminary Study on Its Application in Two-step Water-splitting Hydrogen Production

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ABSTRACT

A novel thermochemical water splitting cycles based on metal oxides were developed, the ferrite, MnxCuyFe2O4 (in which x + y = 1), was prepared by co-precipitation method and following calcination, and its crystal structure was identified by XRD. The thermal characteristic of Mn0.1Cu0.9Fe2O4 was studied by TG-DTA. The ferrite was thermo-chemically activated to form oxygen deficient ferrite, MnxCuyFe2O4-δ at above 1073K in an activation step, and in the following water splitting step, the activated ferrite was reacted with water below 1073K to form hydrogen and the oxygen deficient ferrite was restored to the original status. By these steps, the feasibility of the thermochemical cycle based on (Mn, Cu) ferrite was confirmed and hydrogen could be generated by water splitting with solar or nuclear energy at above 1073K.

KEYWORDS: (Mn,Cu) ferrite, thermochemical cycle, hydrogen production

1. INTRODUCTION

Hydrogen production by thermochemical water-splitting can achieve the objective of decomposition of water into hydrogen and oxygen using only heat with the temperature much lower than that of direct water splitting [1]. If the high temperature heat is supplied by nuclear energy or concentrated solar energy, the whole hydrogen production process could meet the goal of low or no CO2 emission. Direct or one-step water-splitting reaction is the simplest concept, however, it requires high temperature (>3000K) to split water and bring about materials problem, in addition, the H2/O2/H2O mixture is difficult to separate in practice[2]. To lower the water-splitting temperature, the concept thermochemical cycle consists of two-step or multi-step water-splitting was suggested.

The two-step water splitting cycle using metal oxide for hydrogen production has been extensively studied [3,4]. The process consists of two steps: in the decomposition step, oxidized metal oxide (MOox) is thermally reduced with oxygen releasing, forming the reduced metal oxide (MOred); in the hydrogen production step, MOred reacts with H2O to generate hydrogen and restore the original MOred. By repeating the two steps, oxygen and hydrogen were produced alternatively. The cycle could be represented with following formulas:

\[ \text{MO}_{\text{ox}} \rightarrow \text{MO}_{\text{red}}(M) + \frac{1}{2}O_2 \]
\[ \text{MO}_{\text{red}}(M) + H_2O \rightarrow \text{MO}_{\text{ox}} + H_2 \]

The two-step water splitting cycle using Fe3O4/FeO, ZnO/Zn redox systems have been reported [5,6]. The decomposition temperatures are above 2300K when the process was operated in air or at P02 = 0.1 MPa. The Mn3O4/MnO and Co3O4/CoO systems were studied [7] and they can be reduced in air at 1810K and 1175K respectively. However, the hydrogen production yield was too low for economical production. Recently, the ferrite systems were paid much attention, as the O2 releasing step can be implemented at around lower temperature than natural metal oxides. Tamaura et al [8] demonstrated the two-step water splitting with (Ni, Mn)-ferrite using a solar furnace. The oxygen-deficient (Ni, Mn)-ferrite was formed in the oxygen releasing step at > 1173K in argon gas and the water-splitting step was implemented at < 1173K. In that case, the water splitting was caused by stripping of O from water molecule by active oxygen deficient ferrite, therefore, the reactivity and H2 production rate depend on the oxygen deficient degree.

In this work, we prepared a novel material, MnxCuyFe2O4 (x + y = 1), which could began to decomposition at about 1023K, and the oxygen deficient ferrite could react with water to...
generate H₂ at about 1023K and restore to the original status. In addition, the two-step cycle using Mn₀.₁Cu₀.₉Fe₂O₄ was validated.

2. EXPERIMENTAL

Preparation of ferrite

MnₓCu₀.₁Fe₂O₄ sample was prepared by a co-precipitation method. The requisite quantities of Mn(NO₃)₃, Cu(NO₃)₂, Fe(NO₃)₃ (analytical grade) were dissolved in de-ionized water. An aqueous solution of 0.5mol/L KOH was added dropwise by a peristalsis pump at the mixing condition until the pH value of the solution maintained in the range of 10 to 11. The solution was stirred at ambient temperature for 8 hours. The precipitate was filtrated and washed with de-ionized water for several times and dried at 378K for 12h. The dried product was grinded to powder and calcinated at 1073K for 4h. The ferrites were analyzed by X-ray diffraction (XRD, Rigaku D/max-RB) to analyze the structures.

Preparation of oxygen-deficient ferrite MnₓCu₀.₁Fe₂O₄ and the determination of δ

The oxygen-deficient ferrite was prepared by calcinations of the stoichiometric ferrite in nitrogen atmosphere at different temperatures for desired time. The obtained oxygen-deficient products were covered with liquid paraffin for XRD analysis and chemical determination.

The δ value was determined as follows: samples were resolved in concentrated HCl solution, Fe²⁺ was determined by chlorimetry using 2,2’-bipyridyl (Perkin Elmer L800) FeTotal and Cu were measured by AAS (Hitachi 180-80). The chemical composition and δ value was calculated by the ratio of n(Cu²⁺):n(Fe²⁺):n(Fe³⁺).

Oxygen releasing and water-splitting experiment

Oxygen releasing and water-splitting was studied using an experimental setup shown in Figure 1. Ferrite sample was placed in quartz reactor and nitrogen was passed through. The sample was heated to around 1273K for different time, and then water was bumped quantitatively into the pre-heater, generated steam reacts with the sample. Excess water was removed by a water trap or by a dehydration tube. The evolved O₂ and H₂ gases were detected by gas chromatography (GC). The sample was analyzed by XRD before and after reacting with water.

Figure 1. Schematic illustration of experimental setup
3. RESULTS AND DISCUSSION

In our previous work, CuFe$_2$O$_4$ was prepared and preliminarily applied in a 2-step water splitting process. It is found that doped CuFe$_2$O$_4$ may have lower decomposition than undoped CuFe$_2$O$_4$. In the process of preparation of MnFe$_2$O$_4$, we found that the thermal stability of MnFe$_2$O$_4$ was not as good as other doped ferrite. Based on this information, it is reasonable to deduce that Mn-doped CuFe$_2$O$_4$ has lower thermal decomposition temperature than CuFe$_2$O$_4$ while its theoretical oxygen-deficient value after activation is close to that of CuFe$_2$O$_4$. Therefore, we attempted to synthesize Mn-doped CuFe$_2$O$_4$, and to investigate its thermochemical characteristics and employ it to the 2-step water-splitting cycle.

**XRD of the Mn$_x$Cu$_y$Fe$_2$O$_4$**

Figure 2 shows the XRD patterns of Mn$_x$Cu$_y$Fe$_2$O$_4$ with various Mn/Cu molar ratios. The molar ratio of Mn/Cu is 1/9, 3/7, and 5/5 respectively, the molar ratio of (Cu+Mn)/Fe is fixed on 1/2. Fig. 2 (a) shows the XRD patterns of Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ and undoped CuFe$_2$O$_4$. It was shown that they have the same spinel structure. When the Mn/Cu ratio increased to 3/7, the XRD pattern shows apparent difference with that of CuFe$_2$O$_4$, as shown in (b). Apart from characteristic peaks of CuFe$_2$O$_4$, many other peaks appear. Compare with standard XRD library, it was confirmed these peaks are attributed to FeFe$_2$O$_4$ and impurities, such as Fe$_2$O$_3$ and Mn$_2$O$_3$. When the Mn/Cu ratio increased to 5/5, the XRD shows that the sample does not include either Mn$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ or CuFe$_2$O$_4$ with spinel structure, but mainly consist of mixtures of FeFe$_2$O$_4$, Fe$_2$O$_3$ and Mn$_2$O$_3$. These facts indicate that the increase of Mn amount gradually impact the structure of Mn$_x$Cu$_y$Fe$_2$O$_4$. To remain the spinel structure of the copper ferrite, the Mn/Cu molar ratio should be kept below 3/7. In the following water-splitting experiment, Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ was used as the cycle material.

![XRD patterns of Mn$_x$Cu$_y$Fe$_2$O$_4$](image.png)
Fig. 2 XRD patterns of ferrites with various Mn/Cu molar ratio

TG-DTA characteristics of Mn_{0.1}Cu_{0.9}Fe_{2}O_{4}

TG and DTA curves were recorded for Mn_{0.1}Cu_{0.9}Fe_{2}O_{4} in flowing N\textsubscript{2} atmosphere with heating rate at 10 K.min\textsuperscript{-1}. To compare the thermal decomposition characteristics of Mn_{0.1}Cu_{0.9}Fe_{2}O_{4} and CuFe\textsubscript{2}O\textsubscript{4}, their TG (a) and DTA (b) curves are shown in the same figure, Figure 3.
Figure 3. TG-DTA curves of Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ and CuFe$_2$O$_4$

Figure 3(a) shows TG curves of Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ and CuFe$_2$O$_4$. It could be observed that Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ start to decompose when temperature raised to around 730 °C, while the starting decomposition temperature of CuFe$_2$O$_4$ is about 800 °C, indicating that doped Mn in copper ferrite leads to the lower thermal stability. Figure 3(b) shows the DTA curves of Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ and CuFe$_2$O$_4$. For both compound, a strong endothermic peak appears as the temperature raised to 1146 °C, indicating the spinel structures of these ferrites changed and formation of new species when temperature is higher than this point. These facts mean that when temperatures are between 730 to 1146 °C for Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ and between 800 to 1160 °C, the spinel structure of these ferrites could be remained. The weight loss is caused by releasing of oxygen in crystal lattice. The weigh loss for Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ and CuFe$_2$O$_4$ is 2.709 and 2.705. During this stage, the ferrites changed to their corresponding oxygen deficient one, i.e., Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_{4-\delta}$ and CuFe$_2$O$_{4-\delta}$, the corresponding maximum $\delta$ value is 0.405 and 0.406 respectively. Therefore, it could be concluded that adulteration of appropriate amount of Mn in CuFe$_2$O$_4$ bring about lower decomposition temperature while keep the spinel structure and similar maximum $\delta$ value.

**Oxygen releasing and water splitting**

The process was implemented in a device shown in Fig. 1. A charge of 5 g of Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ power (100-200mesh) was loaded in the quartz reactor. During the activation step (O$_2$ releasing), the reactor was heated to about 1173K and a flow of 100 mL/min of N$_2$ was passed through the sample at slightly above ambient pressure. O$_2$ was detected with GC, and the pressure in the quartz tube was measured by pressure gauge. After activation for desired time, O$_2$ can not be detected any more, the reactor was cooled to 873K and quantitative amount of water was pumped and vaporized into the reactor, until the pressure reached to 1 atm. Afterwards, the reactor temperature was raised to 1073K. Gas samples were collected at 2 minutes interval. Figure 5 shows the GC spectrum of gas sample taken from the reactor after 8 minutes reaction with steam. The results showed that H$_2$O was split and H$_2$ evolved in the process. By repeating both activation and water splitting steps following the same procedures, the cycling capability of the (Mn,Cu) ferrite was confirmed.
4. SUMMARY

2-step thermochemical water splitting cycle based on Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ was developed. The preparation conditions, crystal structure and thermal characteristics of Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ were studied. Results show that the spinel type (Mn,Cu) ferrite could be easily prepared by co-precipitation method. The TG-DTA curve of Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ indicates that the ferrite began to lose lattice oxygen at ~750°C in nitrogen. In addition, the water splitting cycle with Mn$_{0.1}$Cu$_{0.9}$Fe$_2$O$_4$ was demonstrated; and oxygen and hydrogen generated in the process were detected by GC. The cycling capability of the (Mn,Cu) ferrite was proved.

REFERENCES

[7] Ehrensberger K, Kuhn P, Shklover. V. Temporary phase segregation processes during the oxidation of (Fe0.7Mn0.3)0.990 in N2-H2O atmosphere. Solid state ionics, 1996 90:75-81