NiFe₂O₄ 금속산화물의 열화학싸이클에 의한 물분해 수소생산기술

한상범*, 강태범, 주오심*, 정광덕*†**
*한국과학기술연구원, 청정에너지연구센터
** 상명대학교, 자연과학대학

Thermo-chemical Cycle with NiFe₂O₄ for Water-Splitting to Produce Hydrogen

Sang Bum Han*, Tae Bum Kang, Oh-Shim Joo*, Kwang-Deog Jung*†**

Korea Institute of Science and Technology
Clean Energy Reseach Center,
7 Hongy-dong Jongro-gu, Seoul, 110-743, Korea
** *SangMyung University, College of Natural Sciences*

ABSTRACT

금속산화물의 열화학싸이클에 의한 수소생산 소재중 안정성이 우수하고 물분해 수소생산능이 비교적 우수한 NiFe₂O₄를 합성하여 열화학수소생산공정 적용시 최적화의 조건에 대하여 검토하였다[1]. 합성한 NiFe₂O₄는 격자상수가 8.34 Å이었고, 뫼스바우어에 의해 구조는 Ni이 페라이트 구조인 AB₂O의 B위치에 주로 위치하는, A 및 B의 상대적 흡수강도가 57.9:42.1인 역스피넬구조를 보이고 있다. 이러한 구조의 NiFe₂O₄의 열적환원은 610 °C부터 시작하여 1200 °C에 이르는 동안 약 1.1 wt% 의 무게감소가 관찰된다. 물에 의한 산화과정에서 수소가 발생하게 되는데, 1200 °C이하의 환원온도 에서 가능한 수소생산량은 약 0.45 cm³/g·cycle 이었다. 산화·환원의 반복과정에서 NiFe₂O₄의 XRD 에 의한 구조변화는 관찰되지 않아 매우 안정한 구조를 갖는다는 것을 보여주었다. 수소생산을 위한 무게당 싸이클당 수소생산양은 산화·환원과정의 온도범위가 가장 중요하였고 물의 접촉시간은 중요한 요소가 되지 않았다. 열적 환원과정에서 많은 양의 수소생산성능을 보이기 위해서는 1200 °C이상의 고온을 필요로 하는 것을 보여주었다.

KEY WORDS : thermo-chemical cycle(열화학 싸이클), thermal reduction(열적 환원), water oxidation(물산화반응), hydrogen production(수소생산), ferrites(페라이트), NiFe₂O₄(니켈페라이트)
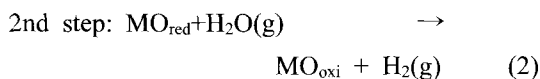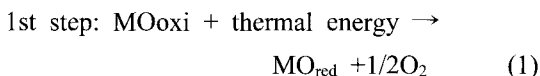
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†Corresponding author : jkdcat@kistmail.kist.re.kr

1. Introduction

Water can be directly decomposed into

hydrogen and oxygen by the thermal dissociation at the temperature of 2200-3000 °C. Generated hydrogen and oxygen gas has to be separated at high temperatures to prevent the recombination of hydrogen and oxygen, which impose one of barriers on practical applications. Therefore, several two-steps and multi-step water splitting methods have been studied to split water at lower temperatures: thermo-chemical cyclic processes, photo-catalytic, photo-chemical and photo-biological processes [1-8].

A two step water splitting process, using metal oxides as a redox couple MO$_{red}$/MO$_{oxi}$, has been studied by several authors[2,5]. It can be written as:

1st step: MOoxi + thermal energy $\rightarrow$
$$MO_{red} + 1/2O_2 \qquad (1)$$
2nd step: MO$_{red}$+H$_2$O(g) $\rightarrow$
$$MO_{oxi} + H_2(g) \qquad (2)$$

Fe$_3$O$_4$/FeO redox couple was proposed for hydrogen production by the two-step cycle and water splitting was conducted at 2000 °C [9].

The redox cycle using 2 kW of solar energy was attempted to produce hydrogen[10]. Ni cation-excess ferrite was shown to be effective on CO2 reduction by thermo-chemical cycle and was suggested to be applicable to hydrogen production[11]. The thermo-chemical cycles with the errites including Ni cation-excess ferrite were tested to produce hydrogen[12-14]. The redox cycle of ZrO$_2$-supported Co(II)-ferrite was utilized to produce 8 Ncm^3/g of hydrogen (the reduction at 1400 °C and the oxidation at 100 °C) but the reduced samples were pulverized between each cycles. On the other hand, the thermo-chemical cycle with ZnO/Zn couple was also attempted to produce a large amount of hydrogen production at the temperature above 1400 °C[15]. The combination system of ZnO/Zn/ferrite was conducted to lower the reaction temperature[16]. Nowadays, thermo-chemical cycles using VHTR (very high temperature cooled reactor) has been studied to produce hydrogen using the high temperature near 1000 °C as well as that of the solar furnace, since the importance of the hydrogen production by a themo-chemical cycle has been emphasized. Recent water splitting with ferrites showed the maximized H$_2$ production with the NiFe$_2$O$_4$ in the repeated cycles of thermal reduction and water oxidation[1]. In this study, the optimum reaction condition to produce hydrogen was scrutinized with Ni-ferrite. The optimum condition were discussed with TPR (temperature programmed reduction) patterns.

2. Experimental

NiFe$_2$O$_4$ samples were synthesized by a solid state reaction as previously reported. For a solid state preparation, required amounts of NiO and Fe$_2$O$_3$ (First Grades, Aldrich Chemical Company, Inc.) was ball-milled with zirconia ball in the distilled water for 2 weeks. The mixture was filtered and dried at 100 °C for 24 h in air. The powder samples were calcined at 1100 °C for 16 h in air. The structures of the calcined samples were characterized by a X-ray diffractometry
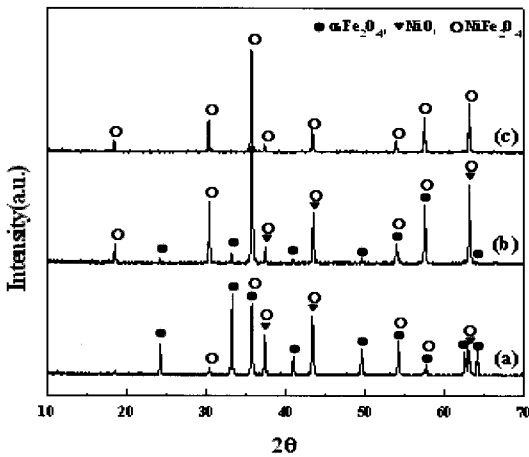
Fig. 1. XRD patterns of NiFe₂O₄ calcined at: (a) 700°C, (b) 900 °C, and (c) 1100 °C.

(McScience, M18SHF-SRA X-ray diffractometer, CuKα, 40 kV 20 mA) and Mössbauer spectroscopy. The lattice parameters of NiFe₂O₄ samples were calculated by the Nelson-Riley method. Mossbauer spectra were recorded at room temperature with ^{57}Co source diffused in metallic Rh, which was oscillated in constant acceleration mode (conventional electromechanical type).Fig. 1. XRD patterns of NiFe₂O₄ calcined at: (a) 700°C, (b) 900 °C, and (c) 1100 °C.

The NiFe₂O₄ sample was placed in a quartz reactor and He gas was passed through the reactor for the reduction of the sample in a flow rate of 100 cm³/min. The reactor temperature was ramped to 1200 °C with a heating rate of 20 °C/min and cooled down to 800oC. Then, 0.3 cm³/min of liquid H₂O was evaporated and passed through the activated Ni ferrite with He gas of a flow rate of 100 cm³/min at 800 °C. The excess H₂O in the products was trapped in a condenser of which the temperature maintained at 0 °C with ice.

The cycles of thermal reduction and water oxidation were carried out repeatedly. The gases evolved in the reaction were detected by a mass spectrometry (MS, Balzers MSC 200 MS-Cube). The amounts of evolved hydrogen and oxygen were calibrated with the standard gas injection into mass spectrometer after the reaction. The oxygen content changes of Ni-ferrite during the thermal reduction were determined by a microbalance (TGA, Cahn 2000 Electrobalance) in a separate experiment. After the water splitting step, a variety of the crystal phase for sample was identified by the X-ray diffractometry.

3. Results and Discussion

Fig. 1 shows the structural changes at the different calcination temperature of the mortared sample by a solid method by an X-ray diffractometer. The Figure shows that NiFe₂O₄ with a single phase of the spinel structure appears at the temperature above 1100 °C. The lattice constant of NiFe₂O₄ was calculated to be 8.34 Å by extrapolating the plot of each lattice constant a_0 versus the Nelson-Riley function.

The Mössbauer spectra of NiFe₂O₄ (AB₂O, ferrite) at a room temperature and 13 K were shown in Fig. 2. The spectra consist of two sextets. The sextet with the lower hyperfine field value can be assigned to the tetrahedral site (A site) and the sextet with the higher hyperfine field value can be assigned to the octahedral site (B site). The Mössbauer parameters for each site are listed in Table 1.

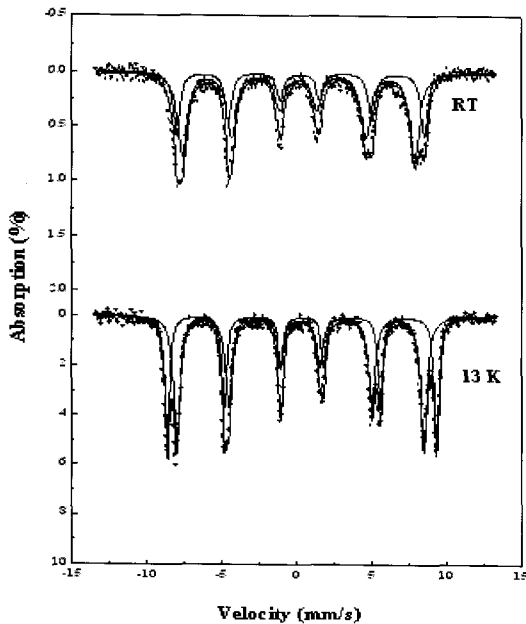The isomer shift value of B site Fe^{3+} ion is larger than that for A-site Fe^{3+} ions. It is well

Fig. 2. Mössbauer spectrum of NiFe$_2$O$_4$ at 13 K and room temperature

Fig 3. TPR profiles of NiFe$_2$O$_4$ while heating up to 1200 °C under He gas atmosphere

known that Ni^{2+} ions occupy preferentially B site to substitute Fe^{2+} ions, indicating that the NiFe$_2$O$_4$ is interpreted as an inverse spinel structure. Relative absorption intensity for the A and B sites of the prepared inverse spinel NiFe$_2$O$_4$ was 57.9: 42.1.

Fig. 3 shows TPR (temperature programmed reduction) profiles of NiFe$_2$O$_4$ at the temperature from 25 °C up to 1200 °C with a

Table 1 . Mössbauer parameters of NiFe2O4 at room temperature and 13K.

Temperature		HF (kOe)	Qs (mm/s)	δ (mm/s)	A (%)
Room temperature	A-Site	482.35	0.00	0.15	65.2
	B-Site	514.88	0.01	0.26	34.8
13K	A-Site	513.63	0.00	0.24	57.9
	B-Site	559.47	-0.01	0.37	42.1

ramping rate of 20 °C/min.

The first weight loss at about 200 °C in TGA can be attributed to the water desorption and the steady weight loss up to 1000 °C can be partly due to the removal of water residue and lattice oxygen. The fast weight loss can be assigned to oxygen removal from 1100 °C. The first thermal reduction of NiFe$_2$O$_4$ ranged from 600 to 820 °C, the second one was from 820 to 1000 °C and the last one started from 1100 °C. The sample weight decreased about 1.1 wt% up to 1200 °C. Table 2 shows hydrogen and oxygen production amount during the cycles of the different reduction and oxidation temperature. The amount of hydrogen, produced during water oxidation at 800 °C following the reduction at 1000 °C, was much less than that following the reduction up to 1200 °C. The amount of oxygen, evolved during the thermal reduction from 800 to 1200 °C, should be half of hydrogen, but was much less than the amount of stoichiometry. On the other hand, oxygen was rarely observed during the thermal

Table. 2. Hydrogen and Oxygen production with different redox temperatures.

Temperature window		Cycle. No				
		1	2	3	4	5
1200 °C~8 00°C	H_2 (mL/g)	0.49	0.44	0.41	0.39	0.45
	O_2 (mL/g)	0.88	0.12	0.09	0.08	0.09
1200 °C~ 700 °C	H_2 (mL/g)	0.62	0.44	0.58	0.40	0.26
	O_2 (mL/g)	1.97	0.27	0.27	0.27	0.31
1000 °C~8 00°C	H_2 (mL/g)	0.16	0.06	0.06	0.03	0.04
	O_2 (mL/g)	-	-	-	-	-

Table.3 Hydrogen production amount for $NiFe_2O_4$ with respect to the ferrite loadings.

Cycle No.	1	2	3	4	5
2g	0.64 cm^3	0.57 cm^3	0.53 cm^3	0.43 cm^3	0.40 cm^3
4g	1.98 cm^3	1.77 cm^3	1.67 cm^3	1.60 cm^3	1.81 cm^3
6g	2.54 cm^3	2.48 cm^3	2.37 cm^3	2.45 cm^3	2.38 cm^3
8g	3.30 cm^3	3.10 cm^3	3.15 cm^3	3.10 cm^3	3.21 cm^3

reduction from 800 to 1000 °C. TPR profiles in Fig. 3 showed two stage oxygen peaks during the thermal reduction up to 1000 °C and a monotonous increase in the evolved oxygen during the reduction from 1100 °C afterwards. The peak in the temperature ranges from 820 to 1000 °C in the TPR profile was small, indicating that oxygen evolution in the temperature ranges from 800 to 1100 °C can
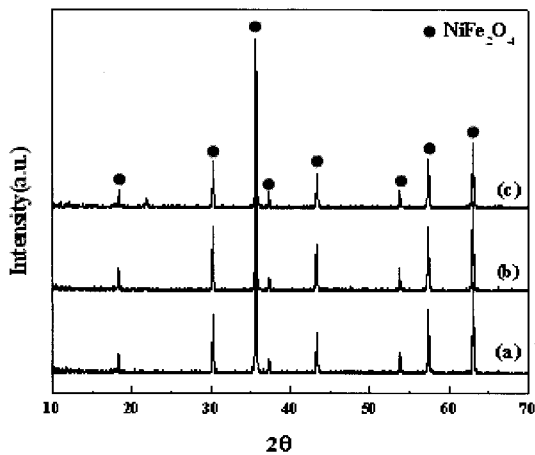
be minimized. The repeated redox cycles of 800~1200 °C shows almost the same hydrogen production in each cycle, indicating that $NiFe_2O_4$ is quite stable during the cycles. However, the oxidation at 700 °C following the reduction up to 1200 °C shows that amount of hydrogen production is fluctuating in each cycle. TPR profiles in Fig.3 shows that oxygen can be easily evolved at 700 °C, indicating that both hydrogen and oxygen can be co-produced at 700 °C. Therefore, it can be concluded that TPR profiles is very useful to select the redox temperature ranges to produce hydrogen by the redox cycle with ferrites.

Table 3 shows the amount of hydrogen production with respect to the contact time of water. The specific hydrogen production amount was not different with the change of the contact time, indicating that the specific hydrogen production amount per cycle by the thermo-chemical cycle would be determined not by kinetic terms, but by thermodynamic terms.

Fig. 4 shows the XRD patterns of the fresh and the used sample (after 5 cycles with the temperature window of 800~1200 °C). The crystal structure of the fresh sample was not

Fig. 4. XRD patterns of NiFe2O4: (a) Fresh state of NiFe2O4, (b) At 1200 °C reduction, and (c) After the redox reaction.

changed during the cycles, indicating that $NiFe_2O_4$ structure would be very stable.

4. Conclusion

The thermal behavior of $NiFe_2O_4$ prepared by a solid-state method was investigated for H_2 production by a two-step water splitting reaction. Oxygen release in $NiFe_2O_4$ started at 610 °C, a lot of Oxygen release up to 1200 °C and the weight loss was 1.1 wt% up to 1200 °C. The H_2O decomposition over $NiFe_2O_4$ catalyst proceeded via redox mechanism. When H_2O was decomposed, a lot of H_2 gas was evolved. $NiFe_2O_4$ produced H_2 volume of 0.45 cm^3/g a cycle on an average. The crystal structure of $NiFe_2O_4$ during the redox cycles was not changed.

Aknowlegement

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