

Decomposition of H₂O with M-Ferrite (M=Cu and Ni) for H₂ generation

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The ferrites, NiFe₂O₄ and CuFe₂O₄, reduced by CH₄ were applied to H₂O decomposition for H₂ generation. In the reduction of the ferrites using CH₄ up to 1073 K, H₂ and CO were generated by partial oxidation of CH₄ above 973 K. The weight of CuFe₂O₄ and NiFe₂O₄ reduced almost the same amount at 1073 K. The reduction of CuFe₂O₄ at 1073 K formed the mixture of Cu, Fe, and FeO, while NiFe₂O₄ changed to the mixture of Ni-Fe alloy and FeO at the same temperature. The amount of the H₂O decomposition with the reduced CuFe₂O₄ was larger than that with the reduced NiFe₂O₄ in the oxidation of the reduced ferrites using H₂O up to 1073 K. In this reaction, H₂O was decomposed by oxidation of Fe and FeO. However, the metallic Cu and Ni were not oxidized and remained to a metallic state at 1073 K. The H₂O decomposition reaction with the reduced ferrites by CH₄ is an excellent process preparing useful gas such as H₂ and CO, and decomposing H₂O.

Key words: Decomposition of H₂O, H₂ generation, Cu and Ni ferrite.

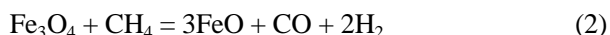
Introduction

A direct (or one step) H₂O decomposition is conceptually a simple method to generate H₂. However, The direct H₂O decomposition is impractical because it requires very high temperatures [1, 2]. So, a two-step H₂O decomposition using a metal oxide to decompose H₂O at lower temperature has been proposed [3-5]. Recently, studies using ferrites as the metal oxides to decompose H₂O and CO₂ have been progressed actively [6-9]. This reaction is using a property of the ferrite that takes place easily the redox reaction because the Fe ion exists as both bivalence and trivalence species.

A carbon compound or CH₄ as a reducing agent are used to reduce the ferrite at a low temperature [10, 11]. The reduction of the ferrite with a carbon compound such as coal to produce CO gas proceeds according to the following reaction [12-14];

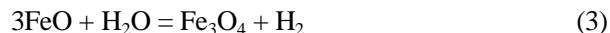


Also, the use of CH₄ as a reducing agent of the ferrite has the advantages producing syngas (mixture of H₂ and CO) by the partial oxidation of CH₄, and producing the ferrite reduced by the reduction of CH₄ [15, 16]. The overall reaction can be represented as:



The ferrite reduced by carbon compound or CH₄ de-

composes easily H₂O to H₂ even at low temperature:



In this paper, NiFe₂O₄ and CuFe₂O₄ prepared by co-precipitation were reduced by CH₄ and the reduced ferrites were applied to the H₂O decomposition for H₂ generation.

Experimental Procedures

Preparation of ferrite

NiFe₂O₄ and CuFe₂O₄ powders were prepared by a co-precipitation method. The requisite quantities of FeCl₃, NiCl₂, and CuCl₂ (first grade, Kanto Co.) were dissolved in distilled water. An aqueous solution of 5 N KOH was added dropwise to the solution of metallic chlorides maintaining a pH of 10. The precipitate was stirred at 353 K for 6 h. The product was filtered and washed with distilled water several time and dried at 373 K for 12 h. The dried ferrite powder was calcined for 2 h at 1173 K. The ferrites were analyzed by X-ray diffraction (XRD, McScience, M18SHF-SRA) to monitor their structure.

Reduction and H₂O decomposition reaction of ferrite

Ni- and Cu-ferrite were reduced by CH₄ gas (99.9%) in a Cahn Vacuum-Electrobalance System (TGA, Cahn Instruments Inc., Cahn 2000). The ferrite powder (50 mg) was placed in a platinum crucible in a quartz tube (25 mm outer diameter). The CH₄ was introduced at room temperature by a gas distribution system with mass flow controllers (Matheson Co.). The ferrite was heated

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by a halogen-lamp heater under the flow CH_4 gas ($60 \text{ ml minute}^{-1}$) at the heating rate of 10 K minute^{-1} to 1073 K . In the reduction reaction of ferrite with CH_4 , the product gases were analyzed with a quadruple-mass spectrometry (MS, Balzers, MSC 200). After the reduction, the reduced ferrite was analyzed by XRD.

The H_2O decomposition reaction was performed with the same experimental apparatus as the one for the reduction process. The water was evaporated by passing Ar gas (99.99% , $60 \text{ ml minute}^{-1}$) through water was introduced into the system at a heating rate of 10 K minute^{-1} to 1073 K . For the H_2O decomposition reaction, the product gases were analyzed by a quadruple-mass spectrometry. The ferrite structures were analyzed by XRD after the H_2O decomposition reaction.

Results and Discussion

Reduction property of M -ferrite ($M=Cu$ and Ni)

The ferrites calcined for 2 h at 1173 K were confirmed to be $CuFe_2O_4$ and $NiFe_2O_4$ with the spinel structure by XRD (Fig. 1). The redox behaviors of the prepared ferrites were investigated by TGA and XRD.

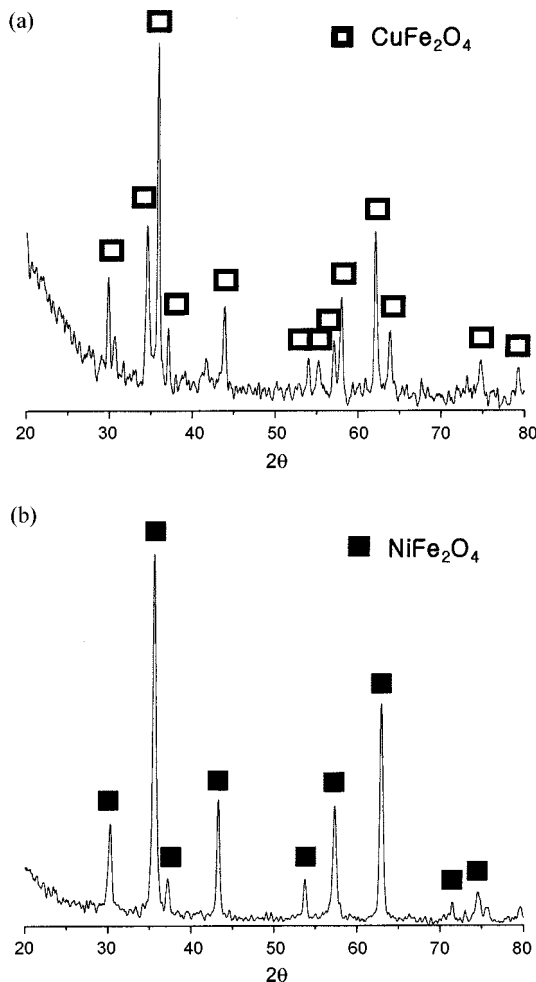


Fig. 1. XRD patterns of ferrites calcined for 2 h at 1173 K after preparation using a co-precipitation method; (a) $CuFe_2O_4$, and (b) $NiFe_2O_4$.

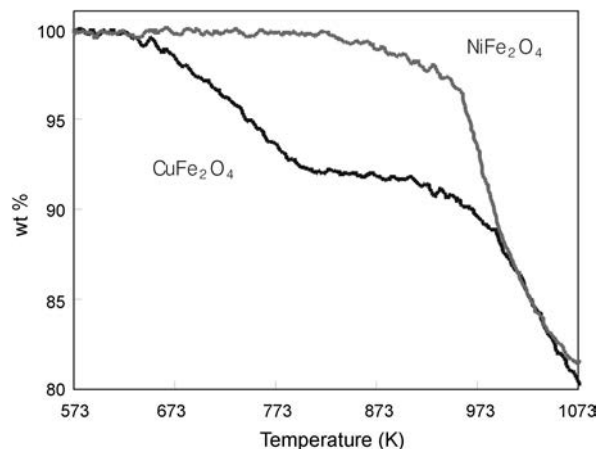


Fig. 2. TGA curves of $CuFe_2O_4$ and $NiFe_2O_4$ under CH_4 gas atmosphere.

The reductions of ferrites were monitored by the weight decrease during the reduction using CH_4 gas up to 1073 K (Fig. 2). In this reaction, the weight of $CuFe_2O_4$ decreased showing a two-stage reduction. One stage of the reduction started at 623 K and decreased by about 7 wt\% up to 813 K . The other stage of the reduction started at 913 K and decreased by about 20 wt\% up to 1073 K . There are 4 oxygen atoms in $CuFe_2O_4$, and the total weight percentage of oxygen atoms in

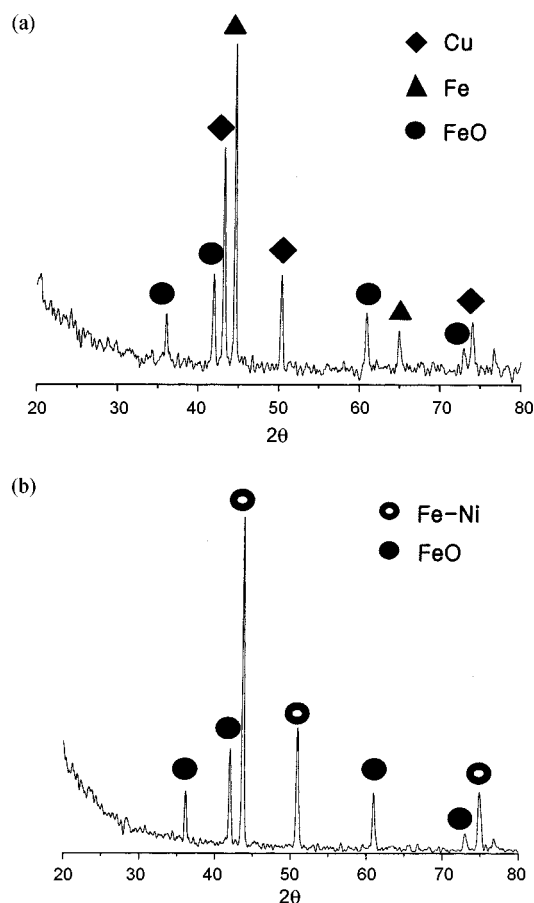


Fig. 3. XRD patterns of reduced ferrites at 1073 K using CH_4 ; (a) $CuFe_2O_4$, and (b) $NiFe_2O_4$.

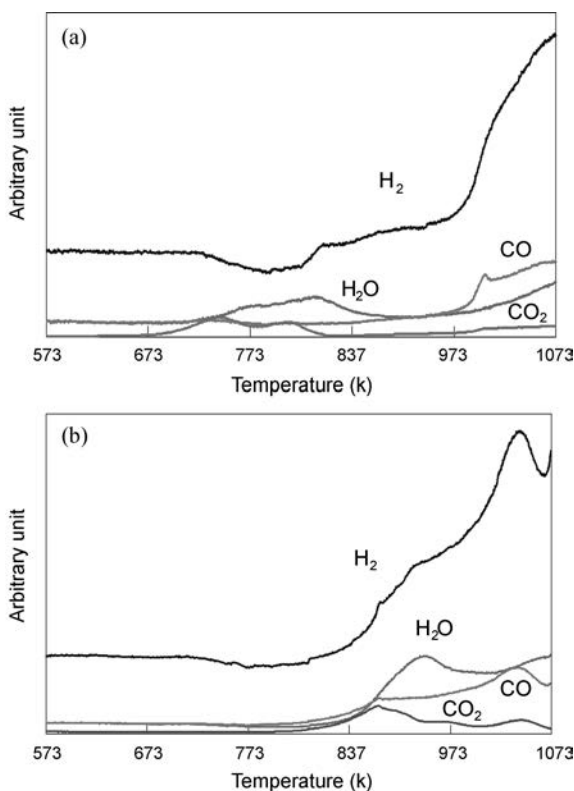


Fig. 4. Concentration changes of product gases while reduction of ferrites using CH_4 ; (a) CuFe_2O_4 , and (b) NiFe_2O_4 .

CuFe_2O_4 is 26.7%. So, the weight loss of 20 wt% means that 3 oxygen atoms in CuFe_2O_4 were eliminated. This TGA result was incorporated in to XRD data (Fig. 3(a)). The phases of the reduced CuFe_2O_4 were observed to be a mixture of FeO , metallic Cu and $\alpha\text{-Fe}$ because 3 oxygen atoms in the CuFe_2O_4 were eliminated in the reduction up to 1073 K.

The weight of NiFe_2O_4 decreased by about 18.5 wt% from 823 K to 1073 K showing a single reduction stage. The weight percentage of oxygen in NiFe_2O_4 is 27.2 %. The weight loss of 18.5 wt% means that about 2.7 oxygen atoms in the NiFe_2O_4 were eliminated at 1073 K. So, a mixture phase of FeO and Fe-Ni alloy in reduced Ni -ferrite was observed by XRD (Fig. 3(b)). In the XRD pattern of the reduced ferrites, Ni -ferrite formed a Fe-Ni alloy but Cu -ferrite existed as phases separated Cu and Fe . In the metallic states of Ni and Fe , Ni dissolved into Fe to form a stable isomorphous system. However, in the metallic states of Cu and Fe , the alloy formation was inhibited in the presence of the miscibility gap, and Fe and Cu existed as a separated phase [17].

When ferrites were reduced by CH_4 , the product gases were analyzed by a quadruple-mass spectrometry (Fig. 4). In the reduction under 973 K, CH_4 was oxidized by oxygen in the ferrites, and CO_2 and H_2O were generated. However, in the reduction above 973 K, the partial oxidation reaction of CH_4 progressed and a syngas such as H_2 and CO was generated. Then the reduction of the ferrite using CH_4 at 973 K is a useful

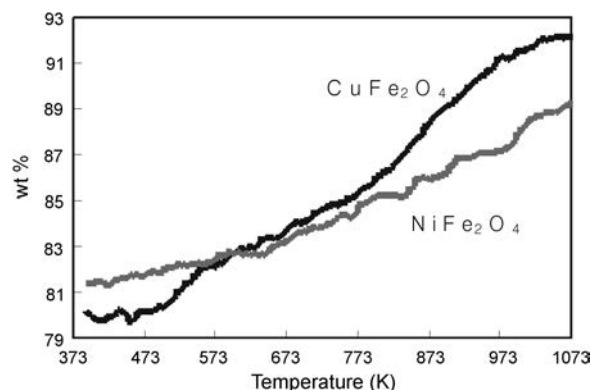


Fig. 5. TGA curves of reduced CuFe_2O_4 and NiFe_2O_4 for H_2O decomposition.

process to produce a syngas and the reduced ferrite.

H_2O decomposition for H_2 generation with reduced M-ferrite

The H_2O decomposition reactions for H_2 generation were performed by introducing H_2O evaporated with Ar gas ($60 \text{ ml minute}^{-1}$) into the reduced ferrite. The weight changes of H_2O decomposition for H_2 generation were monitored by TGA (Fig. 5). As the temperature increased, the reduced ferrites were oxidized by decom-

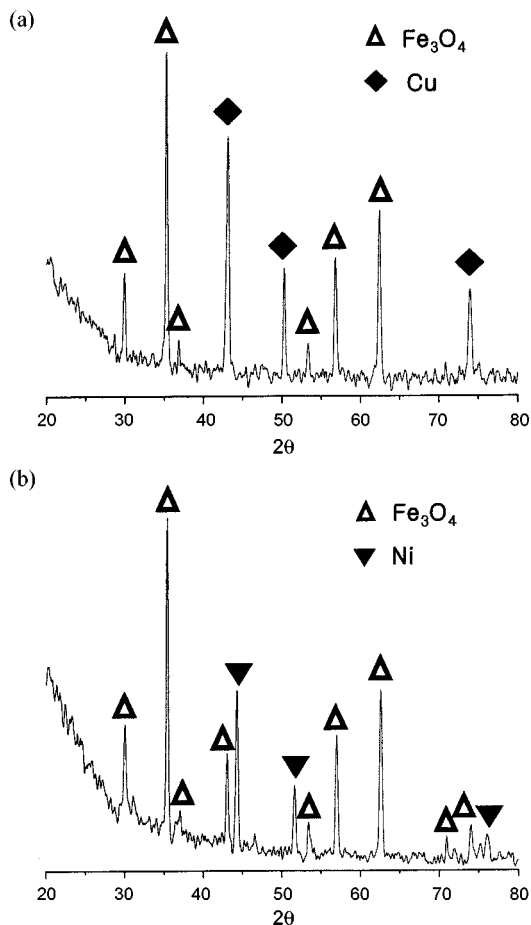


Fig. 6. XRD patterns of oxidized ferrites after H_2O decomposition at 1073 K; (a) CuFe_2O_4 , and (b) NiFe_2O_4 .

position of H_2O . As shown in Fig. 5, the decomposition of H_2O with the reduced CuFe_2O_4 occurred from 463 K. The weight of the reduced CuFe_2O_4 was increased to 12 wt% at 1073 K. It recovered to 92% of the original CuFe_2O_4 weight by the H_2O oxidation reaction. The 12% weight recovery means that 1.8 oxygen atoms were supplied to the reduced Cu-ferrite. The oxygen shortage of 8% from the original CuFe_2O_4 means a 1.2 oxygen atom shortage. The result was confirmed by XRD (Fig. 6(a)). After the H_2O decomposition reaction, the reduced CuFe_2O_4 was transformed to a mixture of metallic Cu and Fe_3O_4 phase. This result shows that H_2O decomposition was progressed by oxidation of FeO and Fe. While Cu was not oxidized to its oxide form and remained in a metallic state even at 1073 K in the presence of H_2O .

On the other hand, the reduced NiFe_2O_4 started to react with H_2O at 423 K and its weight increased by 7.5 wt% up to 1073 K. The 7.5% weight increment was equivalent to 1.1 oxygen atoms, which means that the original ferrite was not completely recovered by the oxidation with H_2O at 1073 K. After the oxidation reaction with H_2O , the reduced NiFe_2O_4 was changed to mixture of metallic Ni and Fe_3O_4 phase (Fig. 6(b)).

Concentration changes of reactant and product gas

during the H_2O decomposition were analyzed by quadrupole mass spectrometry (Fig. 7). As the temperature increased, H_2O oxidized the reduced ferrites and supplied oxygen to the reduced ferrites, producing H_2 . As shown in Fig. 7, the H_2 intensity from the reduced CuFe_2O_4 was observed to be stronger than that from the reduced NiFe_2O_4 in the H_2O decomposition reaction with the reduced ferrites. So, the reduced CuFe_2O_4 was more effective at H_2 generation than the reduced NiFe_2O_4 in the decomposition of H_2O .

Conclusion

The redox properties of NiFe_2O_4 and CuFe_2O_4 prepared by a co-precipitation process were studied. In the reduction reaction with CH_4 gas, CuFe_2O_4 was reduced at 623 K, which was 210 K lower than the temperature for NiFe_2O_4 . The reduced ferrite was oxidized by the H_2O decomposition and H_2 gas generated. The weight recovery of the reduced CuFe_2O_4 was much more than that of the reduced NiFe_2O_4 at 1073 K. In the redox reaction for the H_2 generation, CuFe_2O_4 showed excellent redox properties compared with those of NiFe_2O_4 , and CuFe_2O_4 was more effective at H_2 generation than NiFe_2O_4 in the decomposition of H_2O .

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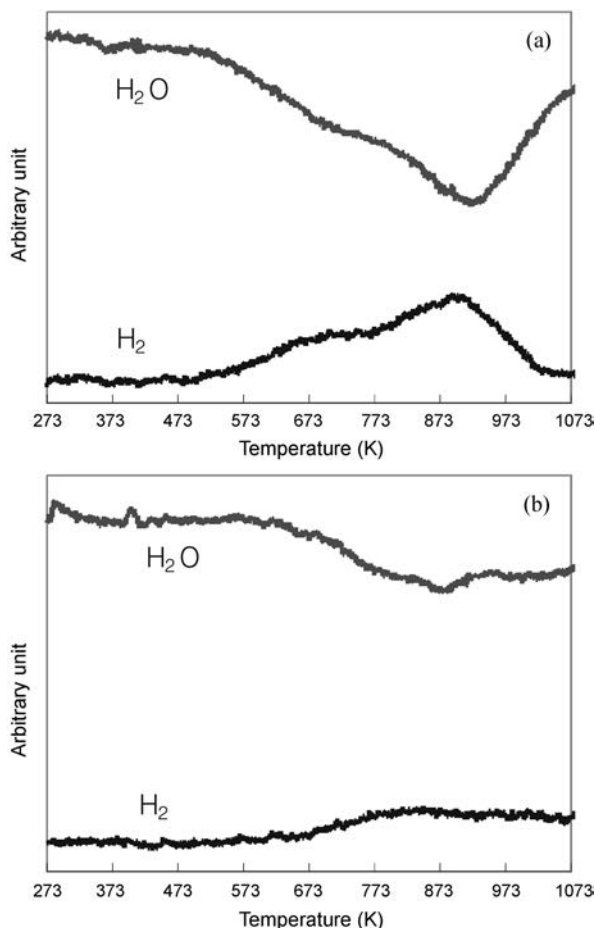


Fig. 7. Concentration changes of H_2O and H_2 while H_2O decomposition with reduced ferrites; (a) CuFe_2O_4 , and (b) NiFe_2O_4 .