Mechanism of M Ferrites (M = Cu and Ni) in the CO_2 Decomposition Reaction

Hyun-Chang Shin and Seung-Chul Choi

Department of Materials Science and Engineering, Ajou University, San 5, Wonchun-dong, Paldal-gu, Suwon, Kyunggi-do, South Korea 442-749

Kwang-Deog Jung and Sung-Hwan Han*

Cleantech Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, South Korea 130-650

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M ferrites (M = Ni and Cu) were prepared for the CO_2 decomposition reaction. The mechanisms of reduction and oxidation of M ferrites were investigated by thermogravimetric analysis and X-ray diffraction experiments. Cu ferrite showed excellent redox properties compared to those of Ni ferrite. Cu ferrite lost its oxygen atoms from the lattice by the H_2 reduction at 473 K, which was 150 K lower than the temperature at which Ni ferrite did. The reduction of Cu ferrite at 1073 K formed the mixture of metallic Cu, FeO, and α-Fe, while Ni ferrite gave a Ni−Fe alloy at the same temperature. Reaction of the reduced ferrites with CO_2 oxidized the ferrites by suppling oxygen atoms from CO_2. The oxidation temperature of the reduced Cu ferrite was 200 K lower, and the weight recovery was faster than that of Ni ferrite. The oxidation with CO_2 at 1073 K could not regenerate their original states and produced the mixture of Fe_3O_4 and metallic Cu and Ni. On the basis of the understanding of the Cu ferrite redox behaviors, a new mechanism for the CO_2 decomposition reaction was proposed.

Introduction

The decomposition of carbon dioxide (CO_2) into carbon or carbon monoxide (CO) has been one of the possible target technologies for the utilization of CO_2 and the mitigation of greenhouse effects. Sacco and Reid[1] reported the decomposition of CO_2 on a clean steel wool producing H_2O, CH_4, CO, and carbon. Recently, Tamaura and Tabata reported that oxygen-deficient M ferrites (M = Ni, Mn, Zn, etc.) with the spinel structure were prepared by the H_2 reduction (eq 1) and the oxygen-deficient M ferrites easily reduced CO_2 into carbon[2−9] (eq 2). The redox cycles were repeated up to 11 times.[10]

$$MFe_2O_4 + H_2 = MFe_2O_{4-\delta} + \delta H_2O \qquad (1)$$

$$MFe_2O_{4-\delta} + CO_2 = MFe_2O_4 + CO_{2-\delta} \qquad (2)$$

They assumed the formation of oxygen-deficient sites in M ferrite by the H_2 reduction and the reversible phase change during the redox reaction. Nonetheless, the structural changes of M ferrite at the respective redox steps were not clearly understood. Herein, we found that the reaction mechanisms of eqs 1 and 2 were not appropriate for the redox reaction of M ferrites. We have investigated the redox mechanism of M ferrites in detail. The H_2 reduction of M ferrites separated metallic Ni and Cu followed by the formation of Fe_3O_4. As the reduction temperature increased, Fe_3O_4 was further reduced to FeO and metallic Fe. The reduced M ferrite was oxidized in turn by CO_2 at 1073 K to regenerate Fe_3O_4. Interestingly, the metallic Ni and Cu were not oxidized in the oxidation step and remained in the metallic state. Cu ferrite had excellent low-temperature properties for the production of the reduced ferrite and the decomposition of CO_2 with it.

Experimental Section

Chemicals. $NiCl_2$, $CuCl_2$, and $FeCl_3$ (first grade) were purchased from Kanto Co. and used without further purification. H_2 (5%) in Ar and CO_2 (99.9%) were used for the redox reaction of ferrite.

Instruments. X-ray diffraction (XRD) experiments were performed with a McScience, M18SHF-SRA X-ray diffractometer (Cu Kα). Thermogravimetric analysis (TGA) was carried

* To whom correspondence should be addressed. Tel: +822-958-5212. Fax: +822-958-5219. E-mail: hansungh@kistmail.kist.re.kr.

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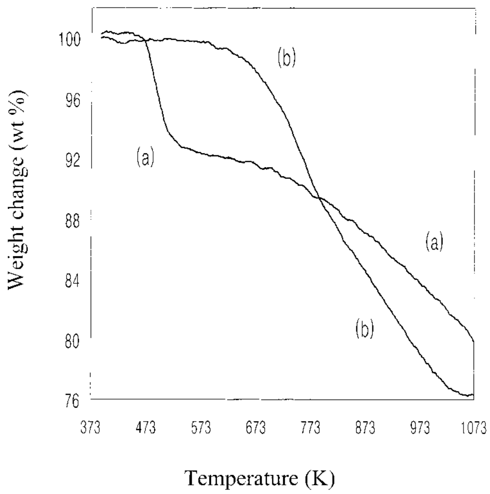

Figure 1. TGA curves on the reduction of M ferrites: (a) $CuFe_2O_4$; (b) $NiFe_2O_4$. Experimental conditions: 5% H_2 in Ar, a heating rate of 10 K/min, and a flow rate of 60 mL/min.

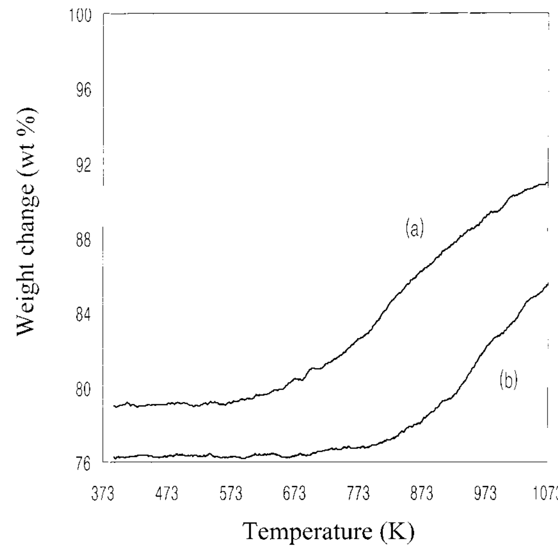

Figure 2. TGA curves on the CO_2 decomposition with reduced M ferrites: (a) reduced Cu ferrite; (b) reduced Ni ferrite. Experimental conditions: 100% CO_2, a heating rate of 10 K/min, and a flow rate of 60 mL/min.

out with a Cahn vacuum-electrobalance system (Cahn 2000). Samples (50 mg) were loaded on a platinum crucible in a quartz reactor and heated by a halogen lamp. Gases were supplied by a gas distribution system with mass flow controllers (Matheson Co.). The CO_2 decomposition products were analyzed by a quadrupole mass spectrometer (Balzers MSC 200, MS-Cube).

Preparation of Cu and Ni Ferrites. Cu ferrite ($CuFe_2O_4$) and Ni ferrite ($NiFe_2O_4$) were prepared by a coprecipitation of the corresponding metallic chlorides. The aqueous solution of KOH (5 N) was added dropwise to the solution of metallic chlorides, maintaining pH 10. The reaction mixture was stirred at 353 K for 6 h. The precipitate was filtered and washed with water and acetone several times. The product was then dried at 373 K for 12 h and calcined at 1073 K for 2 h. The ferrites were analyzed by an XRD to monitor their structures.

Reduction of Ferrites. Cu(II) and Ni(II) ferrites were reduced by 5% H_2 in Ar in a Cahn vacuum-electrobalance system. The ferrite powder (50 mg) was placed in a platinum crucible in a quartz tube (1 in. o.d.), and H_2 was introduced at room temperature. The ferrite was heated by a halogen-lamp heater under H_2 gas (60 mL/min) at the heating rate of 10 K/min to 1073 K. After the reduction, the reduced ferrite was analyzed by an XRD experiment.

Decomposition of CO_2 with Reduced Ferrite. The decomposition of CO_2 was performed with the same Cahn vacuum-electrobalance system as the one of the reduction process. CO_2 gas (60 mL/min) was introduced into the system at a heating rate of 10 K/min to 1073 K. CO_2 decomposition products were analyzed by a quadrupole mass spectrometer. Ferrite structures were analyzed by XRD experiments after the decomposition reaction.

Results and Discussion

Reduction of Cu(II) and Ni(II) Ferrites. The reduction behaviors of Cu(II) and Ni(II) ferrites were investigated by TGA experiments. The reductions of ferrites were monitored by the weight loss during hydrogenation (Figure 1). The weight decreased to form reduced ferrite (the term "oxygen-deficient" was not proper to describe the situation) as the temperature increased up to 1073 K. The Ni ferrite showed a single reduction stage above 623 K followed by a relatively fast weight decrease to 1023 K. The weight percentage of oxygen in Ni ferrite was 27.2%. Above 1023 K, there was a 24% weight decrease, which meant the complete reduction of the system. The weight decrease slowed above 1023 K because of the complete elimination of oxygen from the system. The elimination of oxygen from Ni ferrite generated a Ni−Fe alloy, which was characterized by an XRD experiment.

On the other hand, Cu ferrite performed a two-stage reduction: one at 473 K with a sharp decrease and the other starting from 673 K. The first reduction of Cu ferrite was accompanied by a drastic 7% weight decrease to 523 K. After the first reduction stage, Cu ferrite gave a stable intermediate plateau in the TGA spectrum between 473 and 723 K. It is important to notice that the first reduction temperature was 150 K lower than that of Ni ferrite. The reduction temperature of 473 K was the lowest one ever reported as far as we know. The weight percentage of an oxygen atom in Cu ferrite is 6.7%. The weight loss of 7% at the first stage meant the elimination of one oxygen atom from the ferrite structure and the formation of metallic Cu. The formation of metallic Cu was further monitored by an XRD experiment.

The second reduction stage exhibited a slow weight decrease up to 1073 K. The weight loss due to the oxygen elimination became 20 wt % at 1073 K. There are four oxygen atoms in Cu ferrite, and the total weight percentage of oxygen atoms in Cu ferrite is 26.7%. The weight loss of 20% meant that three oxygen atoms in Cu ferrite were eliminated, leaving only one oxygen atom behind at 1073 K. The elimination of three oxygen atoms from the ferrite generated FeO along with metallic Cu and Fe. The formation of FeO and metallic Cu and α-Fe was further confirmed at the next XRD experiment.

CO_2 Decomposition with Reduced Ferrites. CO_2 decomposition reactions were performed by introducing 99.9% CO_2 into the reduced M ferrites (M = Ni and Cu) which were reduced up to 1073 K in 5% H_2 in Ar. Weight changes were monitored by TGA experiments (Figure 2). As the temperature increased, CO_2 oxidized the reduced ferrites and supplied oxygen to the reduced ferrite, producing carbon and CO. As shown in Figure 2, the reduced Ni ferrite started to react with CO_2 at

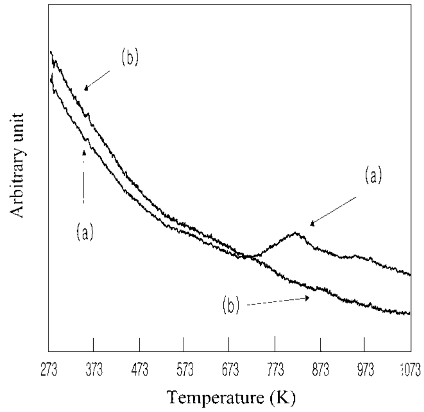

Figure 3. Mass signal intensities during CO_2 decomposition with reduced Cu ferrite: (a) CO; (b) CO_2.

800 K and increased its weight to 1073 K. After the reaction with CO_2, the 9% weight increment was observed at 1073 K, recovering 85% of the original Ni ferrite weight. The 9% weight increment was equivalent to 1.3 oxygen atoms, which meant that the original ferrite was not completely recovered by the oxidation of CO_2 at 1073 K.

On the other hand, the decomposition of CO_2 with the reduced Cu ferrite occurred at 200 K lower than the temperature at which decomposition with Ni ferrite did. CO_2 started to react with the reduced Cu ferrite from 600 K, increasing the weight of the ferrite with a sigmoidal pattern. As the reaction temperature reached 1073 K, the rate of weight increase slowed and formed a plateau, indicating the formation of a stable phase. The weight increase was 11%, and 91% of the original Cu ferrite weight was recovered by the CO_2 oxidation reaction. At the reduction process, 20% weight loss (equivalent to 3 oxygen atoms) was monitored. The 11% weight recovery meant 1.6 oxygen atoms supply to the Cu ferrite. Therefore, the oxygen shortage of 9.0% from the original ferrite meant a 1.3 oxygen atom shortage, suggesting the formation of metallic Cu and Fe_3O_4 (eq 3). Cu was not oxidized to its oxide form as in the case of the oxidation of the reduced Ni ferrite. The final oxidation stage was also analyzed by the XRD experiment in the following section.

$$CuFe_2O_4 \rightarrow Cu + {}^2/_3Fe_3O_4 + {}^4/_3O \qquad (3)$$

Off-Gas Analysis from the CO_2 Decomposition Reaction. The off-gas from the CO_2 decomposition reaction was analyzed by a quadupole mass spectrometry (Figure 3). As a logical product from the CO_2 decomposition reaction, CO ($m/e = 28$) was monitored. In the off-gas stream of the Ni ferrite oxidation with CO_2, only a trace amount of CO was detected, indicating that both of the oxygen atoms of the CO_2 molecule were reacted with the reduced Ni ferrite, leaving carbon as a main product on the ferrite surface. The formation of carbon on Ni ferrite was anticipated because Ni was a well-known metallic component for the carbon formation in many catalytic reactions.[11]

It is worthwhile to notice that CO was produced from CO_2 decomposition with the reduced Cu ferrite as shown in Figure 3. The CO production temperature was well correlated to the weight increasing temperature in the TGA spectrum. The formation of CO continued to 1073 K. The formation of CO from CO_2 gave the important meaning that the carbon deposition was minimized on the ferrite surface. The carbon formation on the ferrite surface is a fatal problem for the reversibility of the redox cycle because it covers the ferrite surface, blocks the gas diffusion, and inhibits the CO_2 decomposition reaction. Therefore, Cu ferrite is an excellent candidate for the practical application of the redox cycle of CO_2 decomposition. Moreover, the formation of CO from CO_2 has an additional meaning other than the prevention of the carbon deposition on the ferrite surface. CO is a valuable chemical feedstock in the chemical industry.[12,13] Its formation from CO_2 will provide an opportunity for utilization of the ferrite-related process.

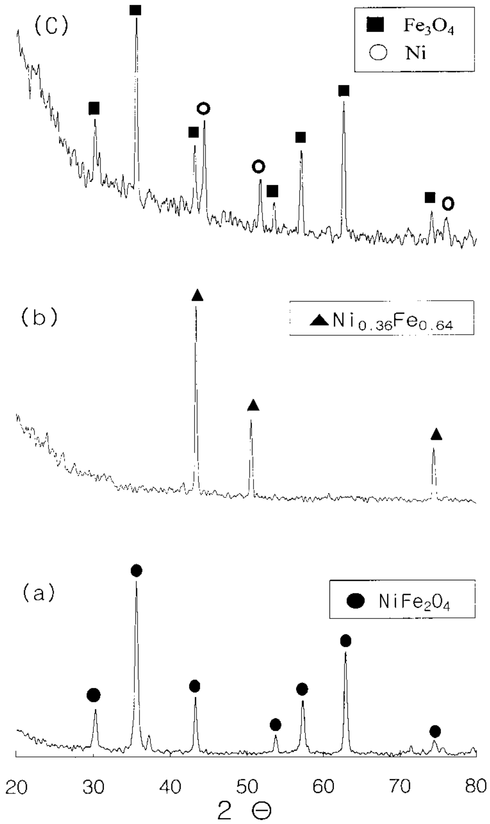

Figure 4. XRD patterns of Ni ferrite: (a) calcination; (b) reduction to 1073 K; (c) CO_2 decomposition to 1073 K.

Redox Mechanism of M Ferrite. The redox behaviors of M ferrites were monitored by XRD experiments. Three samples of Ni ferrite were investigated: (a) calcination, (b) the reduction at 1073 K, and (c) the CO_2 decomposition reaction at 1073 K. The XRD spectrum after calcination showed a typical spinel structure of $NiFe_2O_4$ (Figure 4a). As the reduction temperature increased to 1073 K, Ni ferrite was reduced, and the spinel structure disappeared, generating a Ni−Fe alloy (Figure 4b). The formation of the Ni−Fe alloy coincided with the TGA experiment (Figure 1b). The weight of the ferrite decreased 24% by the H_2 reduction, which

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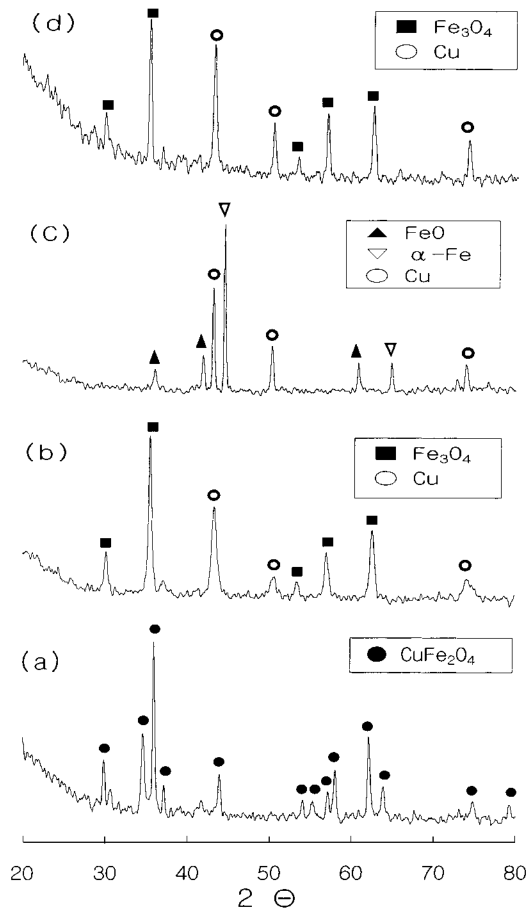

Figure 5. XRD patterns of Cu ferrite: (a) calcination; (b) reduction to 573 K; (c) reduction to 1073 K; (d) CO_2 decomposition to 1073 K.

indicated the elimination of more than 3.6 oxygen atoms from the system. One of the stable phases of the Fe−Ni alloy is $Fe_{0.64}Ni_{0.36}$, which was identical to the phase shown in Figure 4b. The composition from the reduction of Ni ferrite at 1073 K was calculated to be $Fe_{0.62}Ni_{0.38}$ based on TGA results. The ratio $Fe_{0.64}Ni_{0.36}$ from the XRD peak pattern of the Fe−Ni alloy showed a good agreement with the composition of $Fe_{0.62}Ni_{0.38}$ from the TGA experiment.

The reduced Ni−Fe alloy was oxidized by the CO_2 decomposition reaction. The oxidation of the Ni−Fe alloy generated the mixture of metallic Ni and Fe_3O_4 (Figure 4c). *Interestingly, the metallic Ni was not oxidized and remained in a metallic state even at 1073 K in the presence of CO_2.* Fe_2O_3 oxide, which was a thermodynamic stable phase, was not produced, but Fe_3O_4, which was a metastable phase, was a main iron oxide product. The redox pattern is summarized in eq 4.

$$NiFe_2O_4 \rightarrow Ni^0 + Fe_3O_4 \leftrightarrow Ni{-}Fe \qquad (4)$$

However, Cu ferrite demonstrated a quite different redox pattern. Four different samples were explored: (a) calcination, (b) reduction at 573 K, (c) reduction at 1073 K, and (d) CO_2 decomposition at 1073 K. The XRD spectrum after calcination showed a typical spinel structure of $CuFe_2O_4$ (Figure 5a). Different from the case of Ni ferrite, the reduction at 573 K produced a mixture of metallic Cu and Fe_3O_4 (Figure 5b). As the temperature increased to 573 K, there was a 8% weight loss in the TGA experiment, which was equivalent to the weight of 1.2 atoms of oxygen (Figure 1a). The phase transition of $CuFe_2O_4$ to metallic Cu and Fe_3O_4 needs a $^4/_3$ (1.33) atomic oxygen loss (eq 3). The results from the XRD experiment were well correlated to the weight loss in the TGA experiments. The phase after the elimination of 1.2 oxygen atoms (mixture of metallic copper and Fe_3O_4) was thermally stable up to 673 K.

The Fe_3O_4 was further reduced to FeO and α-Fe. As the reduction temperature increased to 1073 K, a mixture of three phases was observed in the XRD spectrum (Figure 5c): metallic Cu, FeO, and α-Fe. At 1073 K, there was a 20% weight loss in the TGA experiment (Figure 1a), which was equivalent to the loss of 3 oxygen atoms. The elimination of 3 oxygen atoms from $CuFe_2O_4$ should give the mixture of Cu, FeO, and α-Fe phases. The peaks from metallic Cu became sharp with an increase in the crystallinity. Interestingly, metallic Cu and α-Fe phases existed as separate ones compared to the reduction pattern of Ni ferrite forming a Ni−Fe alloy. In the metallic states of Ni and Fe, Ni dissolved into Fe to form a stable isomorphous system of a γ-$Fe_{0.64}Ni_{0.36}$ phase. However, in the metallic states of Fe and Cu, the alloy formation was inhibited in the presence of the miscibility gap, and Fe and Cu existed as a separated phase.[14]

The mixture of Cu ferrite reduced at 1073 K reacted with CO_2 at the same temperature. It gave a similar XRD pattern as that of Ni ferrite (Figure 5d), producing the mixture of metallic Cu and Fe_3O_4. Even at 1073 K, Cu was not oxidized to copper oxide in the CO_2 atmosphere. The XRD peaks from metallic Cu became sharp because of the thermal treatment at 1073 K. The behavior of Cu ferrite during the redox cycle can be depicted in eq 5. *Once Cu ferrite was reduced, Cu remained in a metallic state while Fe changed its oxidation state.*

$$CuFe_2O_4 \rightarrow Cu^0 + Fe_3O_4 \leftrightarrow Cu^0 + FeO \leftrightarrow Cu^0 + \alpha\text{-}Fe \qquad (5)$$

The Cu and Ni are well-known active metallic components in the reduction catalyst. Cu and Ni easily activate hydrogen molecules and sometimes become a center for the hydrogen spillover.[15−18] The incorporation of Cu and Ni in the ferrite structure kinetically facilitated the reduction of ferrite. Cu ferrite was more readily reduced and oxidized at low temperature than those of Ni ferrite particularly at the reduction step. Also Cu ferrite was tolerant of the carbon deposition from the CO_2 decomposition.

The formation of reduced ferrites at low temperature is strategically important to mitigate greenhouse effects originating from the CO_2 emission. Moreover, it is valuable to utilize CO_2 as a chemical feedstock. It can provide a methodology to utilize oxygen without the oxygen separation process from the air. The excellent

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reduction behavior of Cu ferrite could give us a new opportunity to utilize CO_2, mitigating the greenhouse effects.

Summary

The mechanisms of reduction and oxidation of M ferrites (M = Ni and Cu) were investigated. Cu ferrite lost oxygen atoms from the lattice by the H_2 reduction at 473 K, which was 150 K lower than the temperature at which Ni ferrite did. The reduction of Cu ferrite formed the mixture of metallic Cu, FeO, and α-Fe, while Ni ferrite gave a Ni−Fe alloy. Reaction of the reduced ferrites with CO_2 oxidized the ferrites by supplying oxygen atoms from CO_2. The oxidation temperature of the reduced Cu ferrite was 200 K lower, and a weight recovery was faster than that of Ni ferrite. The oxidation with CO_2 at 1073 K could not regenerate the original ferrites and produced the mixture of Fe_3O_4 and metallic Cu and Ni. On the basis of the understanding of the Cu ferrite redox behaviors, a new mechanism for the CO_2 decomposition reaction was proposed.

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