The Carbon Dioxide Decomposition Reaction with $(Ni_xCu_{1-x})Fe_2O_4$ Solid Solution

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The mechanisms of the redox reaction of $(Ni_xCu_{1-x})Fe_2O_4$ solid solution were investigated by thermo-gravimetric analysis and X-ray diffraction experiments. The redox reaction was accelerated by a kind of a substituted divalent metal such as Ni and Cu. $(Ni_xCu_{1-x})Fe_2O_4$ showed excellent reduction reaction with increasing Ni content and excellent CO₂ decomposition with increasing Cu content. The CO₂ decomposition ability of the reduced $(Ni_xCu_{1-x})Fe_2O_4$ showed the maximum value at x = 0.5. CO₂ was decomposed by oxidation of oxygen deficient FeO (FeO_{1- δ}, $0 \le \delta \le 1$). The $(Ni_{0.5}Cu_{0.5})Fe_2O_4$ solid solution is an excellent candidate for the practical application of the CO₂ decomposition.

Introduction The decomposition of carbon dioxide (CO₂) into carbon or carbon monoxide (CO) has been one of the possible target technologies for the utilization of CO₂ and the mitigation of greenhouse effects. Sacco and Reid reported the decomposition of CO₂ on clean steel wool [1]. Recently, Tamaura reported that oxygen-deficient Mferrites (M = Ni, Mn, Zn, etc.) of the spinel structure were prepared by the reduction of H₂ (Eq. (1)), and the oxygen-deficient M-ferrites easily reduced CO₂ into carbon [2– 9] (Eq. (2)):

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

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

They assumed the formation of oxygen deficient sites in M-ferrite by the H₂ reduction and the reversible phase change during the redox reaction. Herein, we found that the reaction mechanisms of Eqs. (1) and (2) were not appropriate for the redox reaction of M-ferrites [10]. In addition, we found that NiFe₂O₄ and CuFe₂O₄ showed excellent reduction reaction and CO₂ decomposition, respectively. In this study, (Ni_xCu_{1-x})Fe₂O₄ solid solution was prepared and the redox reaction for CO₂ decomposition was investigated.

Experimental NiCl₂, CuCl₂, and FeCl₃ (First Grades, Kanto Chemical Co.) were used for preparing $(Ni_xCu_{1-x})Fe_2O_4$ (x = 0.25, 0.5, and 0.75) by a coprecipitation of the

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corresponding metallic chlorides. Aqueous solution of KOH (5 N) was added dropwise to the solution of metallic chlorides maintaining pH 10. The reaction mixture was stirred at 80 °C for 6 h. The precipitate was filtered and washed with water and acetone several times. The product was then dried at 100 °C for 12 h and calcined at 800 °C for 2 h. The ferrites were analyzed by XRD (McScience, M18SHF-SRA X-ray diffractometer, CuK α), Cu-K $_{\alpha}$, to monitor their structures.

 $(Ni_xCu_{1-x})Fe_2O_4$ was reduced by 5% H₂ in Ar in a Cahn vacuum electrobalance system. The ferrite powder (50 mg) was placed in a platinum crucible in a quartz tube (1 inch outer diameter), and H₂ was introduced at room temperature. The ferrite was heated by a halogen lamp heater under H₂ gas (60 ml/min) at the heating rate of 10 °C/min to 800 °C. Gases was supplied by a gas distribution system with mass flow controllers (Matheson Co.). After the reduction, the reduced ferrite was analyzed by XRD.

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 the heating rate of 10 °C/min to 800 °C. The concentration change of the product gas during CO_2 decomposition reaction was analyzed by a quadruple mass spectrometer. Ferrite structures were analyzed by XRD experiments after the decomposition reaction.

Results and Discussion The XRD spectrum of $(Ni_xCu_{1-x})Fe_2O_4$ after the calcination showed a typical spinel structure. The reduction behaviors of $(Ni_xCu_{1-x})Fe_2O_4$ were investigated by TGA experiments. The reduction of ferrites was monitored by the weight loss (Fig. 1). The weight decreased to form reduced ferrite as the temperature increased to 800 °C. The weight loss of $(Ni_{0.25}Cu_{0.75})Fe_2O_4$ was observed from 250 °C, but the weight loss of $(Ni_{0.5}Cu_{0.5})Fe_2O_4$ and $(Ni_{0.75}Cu_{0.25})Fe_2O_4$ occurred at 100 °C higher than the temperature at which reduction of $(Ni_{0.25}Cu_{0.75})Fe_2O_4$ did. In the reduction reaction of $(Ni_xCu_{1-x})Fe_2O_4$ to 800 °C, the weigh loss of $(Ni_{0.25}Cu_{0.75})Fe_2O_4$, $(Ni_{0.5}Cu_{0.5})Fe_2O_4$, and $(Ni_{0.75}Cu_{0.25})Fe_2O_4$ were 19%, 21%, and 22%, respectively. The reduction patterns of $(Ni_xCu_{1-x})Fe_2O_4$ did correspond to the NiFe₂O₄ which performed a one-stage reduction [10]. In the result of Fig. 1, it was found that starting temperature of the reaction and total weight loss of $(Ni_xCu_{1-x})Fe_2O_4$ was increased with increasing Ni content in $(Ni_xCu_{1-x})Fe_2O_4$.



Fig. 1. TGA curves of the reduction of $(Ni_xCu_{1-x})Fe_2O_4$: (a) $(Ni_{0.25}Cu_{0.75})Fe_2O_4$, (b) $(Ni_{0.5}Cu_{0.5})Fe_2O_4$, and (c) $(Ni_{0.75}Cu_{0.25})Fe_2O_4$. Experimental

conditions: 5% H₂ in Ar, heating rate $10 \,^{\circ}$ C/min, and flow rate 60 ml/min

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There are four oxygen atoms in each ferrite, which has the spinel structure. When x is 0 to 1, the total weight percentage of oxygen atoms in $(Ni_xCu_{1-x})Fe_2O_4$ is 26.7% to 27.2%, respectively. So, the weight loss of about 20% meant that three oxygen atoms in $(Ni_xCu_{1-x})Fe_2O_4$ were eliminated, leaving only one oxygen atom behind at 800 °C. The

 $(Ni_xCu_{1-x})Fe_2O_4$ were eliminated, leaving only one oxygen atom behind at 800 °C. The elimination of three oxygen atoms from the ferrite generated FeO along with metallic Cu or Ni and Fe. The formation of FeO, metallic Ni or Cu and Fe were further confirmed by XRD.

As the reduction temperature increased to 800 °C, a phase change of $(Ni_xCu_{1-x})Fe_2O_4$ was observed in the XRD spectrum (Fig. 2). Phases of reduced $(Ni_{0.25}Cu_{0.75})Fe_2O_4$ were α -Fe, FeO and Cu. At 800 °C, there was a 20% weight loss in the TGA experiment, which was equivalent to the loss of three oxygen atoms. The elimination of three oxygen atoms from $(Ni_{0.25}Cu_{0.75})Fe_2O_4$ should give a mixture of Cu, FeO, and α -Fe phases. In the $(Ni_{0.5}Cu_{0.5})Fe_2O_4$ and $(Ni_{0.75}Cu_{0.25})Fe_2O_4$ reduced up to 800 °C, the spinel structure disappeared, generating metallic Fe–Ni and some FeO due to a decrease over 20% of total weight by the H₂ reduction.

The important point to note is that the metallic Cu and α -Fe phases existed as separate ones in the reduced (Ni_{0.25}Cu_{0.75})Fe₂O₄ compared with forming a Ni–Fe alloy in the reduced (Ni_{0.75}Cu_{0.25})Fe₂O₄. In the metallic state of Ni and Fe, Ni dissolved into Fe to form a stable isomorphous system of Ni–Fe phase. However, in the metallic state of Fe and Cu, the alloy formation was inhibited in the presence of the miscibility gap, and Fe and Cu existed as separated phases [11].

The CO₂ decomposition reactions were performed by introducing 99.9% CO₂ into the reduced (Ni_xCu_{1-x})Fe₂O₄ which were reduced up to 800 °C with 5% H₂ in Ar. The weight changes were monitored by TGA experiments (Fig. 3). With the temperature increasing, CO₂ oxidized with the reduced ferrites and supplied oxygen to the reduced ferrite producing carbon and CO. As shown in Fig. 3, the reduced (Ni_{0.25}Cu_{0.25})Fe₂O₄ started to react with CO₂ from 400 °C and the other reduced ferrites (x = 0.5 and 0.75) started to react from 500 °C. Hence, it is found that oxidizing temperature of the reduced (Ni_xCu_{1-x})Fe₂O₄ was increased with increasing Ni content in (Ni_xCu_{1-x})Fe₂O₄. After the reaction with CO₂, the weight recovering percentages of reduced (Ni_xCu_{1-x})Fe₂O₄ were 90% (x = 0.75), 91% (x = 0.25), and 91.5% (x = 0.5) of the original (Ni_xCu_{1-x})Fe₂O₄ at



800 °C. The CO₂ decomposition ability of the reduced (Ni_xCu_{1-x})Fe₂O₄ showed the maximum value at x = 0.5.

The off-gas from the CO_2 decomposition reaction was analyzed by a quadruple mass spectrometer (Fig. 4). As a logical product of the CO_2 decomposi-

Fig. 2. XRD patterns of $(Ni_xCu_{1-x})Fe_2O_4$ reduced up to 800 °C by 5% H₂ in Ar: (a) $(Ni_{0.25}Cu_{0.75})Fe_2O_4$,

- (b) $(Ni_{0.5}Cu_{0.5})Fe_2O_4$, and
- (c) $(Ni_{0.75}Cu_{0.25})Fe_2O_4$



Fig. 3. TGA curves of the CO₂ decomposition with reduced $(Ni_xCu_{1-x})Fe_2O_4$: (a) $(Ni_{0.25}Cu_{0.75})Fe_2O_4$, (b) $(Ni_{0.5}Cu_{0.5})Fe_2O_4$, and (c) $(Ni_{0.75}Cu_{0.25})Fe_2O_4$. Experimental

conditions: 100% CO₂, heating rate 10° C/min, and flow rate 60 ml/min

tion reaction, CO (m/e = 28) was monitored. It is worthwhile to notice that CO was produced from CO₂ decomposition with the reduced (Ni_{0.5}Cu_{0.5})Fe₂O₄ as shown in Fig. 3. The formation of CO from CO₂ 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 and blocks the gas diffusion and inhibits the CO₂ decomposition reaction.

The reduced $(Ni_xCu_{1-x})Fe_2O_4$ was oxidized by the CO₂ decomposition reaction. In the reaction, the oxidation of reduced $(Ni_xCu_{1-x})Fe_2O_4$ generated a mixture of metallic Ni or Cu and Fe₃O₄ (Fig. 5). The important point to note is that Ni or Cu was not oxidized and remained in a metallic state while Fe changed its oxidation state at 800 °C in the presence of CO₂. The redox process was summarized as

$$MFe_2O_4 \to M + Fe_3O_4 \leftrightarrow M + FeO \leftrightarrow M + \alpha - Fe, \qquad (3)$$

where M is Cu and Ni.

Cu and Ni are well known active metallic components in the reduction catalyst. The incorporation of Cu and Ni in the ferrite structure kinetically facilitated the reduction of ferrite. The formation of reduced ferrites at lower temperature is strategically important



to mitigate green-house effects by CO_2 emission. Moreover, it is valuable to utilize CO_2 as a chemical feedstock. The excellent reduction behavior of $(Ni_{0.5}Cu_{0.5})Fe_2O_4$ could give us a new opportunity to utilize CO_2 mitigating greenhouse effects.

Fig. 4. Mass signal intensities of CO during CO_2 decomposition with reduced ($Ni_{0.5}Cu_{0.5}$)Fe₂O₄



Fig. 5. XRD patterns of $(Ni_xCu_{1-x})Fe_2O_4$ oxidized up to 800 °C by CO₂: (a) $(Ni_{0.25}Cu_{0.75})Fe_2O_4$, (b) $(Ni_{0.5}Cu_{0.5})Fe_2O_4$, and (c) $(Ni_{0.75}Cu_{0.25})Fe_2O_4$

Summary The redox reaction of $(Ni_xCu_{1-x})Fe_2O_4$ solid solution were studied. $(Ni_xCu_{1-x})Fe_2O_4$ (x = 0.25, 0.5, and 0.75) was prepared for the CO₂ decomposition reaction. The redox reactions of $(Ni_xCu_{1-x})Fe_2O_4$ were investigated by thermo-gravimetric analysis and X-ray diffraction experiments. $(Ni_xCu_{1-x})Fe_2O_4$ showed excellent reduction reaction with increasing Ni content and excellent CO₂ decomposition with increasing Cu content in $(Ni_xCu_{1-x})Fe_2O_4$. The CO₂ decomposition ability of the reduced $(Ni_xCu_{1-x})Fe_2O_4$ showed the maximum value at x = 0.5. CO₂ was decomposed by oxidation of oxygen deficient FeO (FeO_{1- δ}, $0 \le \delta \le 1$) and the redox reaction was accelerated by a substituted divalent metal such as Ni and Cu.

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