

# CO<sub>2</sub> decomposition using metal ferrites prepared by co-precipitation method

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**Abstract**—To catalytically decompose the greenhouse gas, CO<sub>2</sub>, spinel structure M-ferrites (M=Co, Ni, Cu, Zn) were synthesized by chemical co-precipitation using metal salts and sodium hydroxide as starting materials. The crystallite size of the newly-prepared M-ferrites increased and the BET surface area decreased with increasing calcination temperature. A thermal analysis of the reduction and reoxidation of M-ferrites indicated that substitution of divalent transition metals (i.e., Cu, Ni and Co) into Fe<sub>3</sub>O<sub>4</sub> improved the reduction kinetics in the order of Cu>Ni>Co. ZnFe<sub>2</sub>O<sub>4</sub> was the most difficult compound to completely reduce due to its stable structure. Commercial samples of the reduced Fe<sub>3</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> showed an increase in mass through the reoxidation process, but it was much more difficult for oxygen atoms to enter the structure of the reduced samples of NiFe<sub>2</sub>O<sub>4</sub> and CuFe<sub>2</sub>O<sub>4</sub>. The M-ferrites in a batch type reactor showed better efficiency than the commercial Fe<sub>3</sub>O<sub>4</sub>. Also found was that CoFe<sub>2</sub>O<sub>4</sub> showed a high regeneration potential, although it required a higher critical reaction temperature. NiFe<sub>2</sub>O<sub>4</sub> and CuFe<sub>2</sub>O<sub>4</sub> were excellent candidate materials for CO<sub>2</sub> decomposition at lower temperatures.

Keywords: Carbon Dioxide, Metal Ferrite, Co-precipitation, Catalytic Reduction

## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is the most prominent greenhouse gas in the earth's atmosphere. A fair number of researchers have, over the years, produced a series of separation and capture technologies to control the atmospheric level of CO<sub>2</sub>. Decomposition of CO<sub>2</sub> into carbon has been a targeted technology since Sacco and Reid [1] reported its decomposition using clean steel wool [1]. However, no major breakthrough in CO<sub>2</sub> decomposition efficiency occurred until Tamaura and Tabata [2] presented that CO<sub>2</sub> could be decomposed to C with an efficiency of nearly 100% at about 300 °C on oxygen-deficient magnetite (Fe<sub>3</sub>O<sub>4-δ</sub>) in the early of 1990s [2]. Thereafter, oxygen-deficient ferrites (MFe<sub>2</sub>O<sub>4</sub>, where M is a bivalent metal) have consistently been studied as plausible catalysts for CO<sub>2</sub> decomposition [3-6]. The ferrites must first be reduced and then are reoxidized by CO<sub>2</sub>. During the reduction by H<sub>2</sub>, oxygen ions (O<sup>2-</sup>) present at the surface or those that migrate to the surface react with the adsorbed H<sub>2</sub> and thereby form H<sub>2</sub>O, leaving behind empty oxygen sites in the structure. To maintain the electrical neutrality of the compound, trivalent iron ions (Fe<sup>3+</sup>) are reduced to divalent ions (Fe<sup>2+</sup>) when Fe<sup>3+</sup> accepts the electrons released from the reaction. As a result, metal ferrites (MFe<sub>2</sub>O<sub>4</sub>) are transformed to an oxygen-deficient structure with the formula MFe<sub>2</sub>O<sub>4-δ</sub>. Subsequently, Fe<sup>2+</sup> in MFe<sub>2</sub>O<sub>4</sub> is oxidized by CO<sub>2</sub>, which will be reduced to carbon atoms. At the same time, O<sup>2-</sup> fills the empty sites that formed after

the H<sub>2</sub> reduction. Then, oxygen-deficient MFe<sub>2</sub>O<sub>4-δ</sub> gradually recovers to normal MFe<sub>2</sub>O<sub>4</sub>. However, the reactions of CO<sub>2</sub> decomposition generally require temperatures above 300 °C [7].

To lower the reaction temperature and to increase the CO<sub>2</sub> decomposition rate, we explore the substitution of a group of transition metals such as Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> into the bivalent iron metal ions (Fe<sup>2+</sup>) in magnetite using the co-precipitation method. The prepared metal ferrites are then characterized focusing on CO<sub>2</sub> decomposition under batch or continuous flow conditions.

## EXPERIMENTAL

### 1. Sample Preparation and Characterization

Ferrite catalysts were prepared by a co-precipitation process as described in our previous work [8]. The starting iron oxide was Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and the metal precursors included Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (DAEJUNG CHEMICALS & METALS CO., LTD. Korea). Bivalent metal salts of Co, Ni, Cu and Zn and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in distilled water with gentle stirring. The precipitates, which had been obtained by precipitation with NaOH solution, were aged at 60 to 65 °C (resulting in a pH of 11 to 13) for 30 minutes. Each sample was dried at 130 °C and then heated at different temperatures.

The prepared catalysts were closely characterized in terms of chemical and physical properties. Chemical compounds could be found through X-ray powder diffraction (XRD) analysis using a Rigaku Instrument (JP/D/M AX-2500H diffractometer, Japan) with Cu K $\alpha$  radiation at 40 kV and 30 mA over the range, 2 $\theta$ =15°-70°, of which scanning speed was 3°/min. To investigate the thermal characteristics, TGA curves were simultaneously recorded from 25 °C to 800 °C in air with a flow rate of 100 ml/min at a 10 °C/min heat-

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<sup>\*</sup>This article is dedicated to Prof. Sung Hyun Kim on the occasion of his retirement from Korea University.

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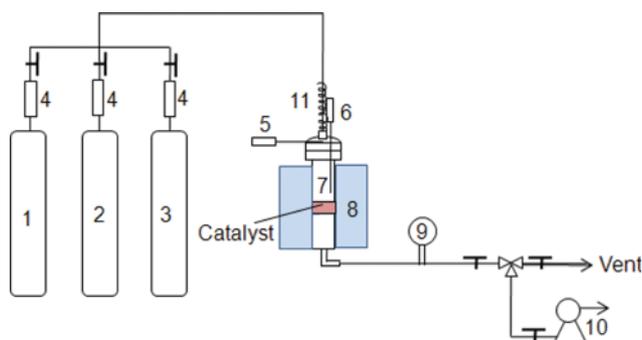


Fig. 1. Schematic experimental set-up for catalyst activation and CO<sub>2</sub> decomposition.

- |                        |                            |
|------------------------|----------------------------|
| 1. H <sub>2</sub> gas  | 7. Stainless reactor       |
| 2. CO <sub>2</sub> gas | 8. Electric furnace        |
| 3. He gas              | 9. Digital pressure sensor |
| 4. Flow meter          | 10. Vacuum pump            |
| 5. Safety valve        | 11. Preheater              |
| 6. Thermocouple        |                            |

ing rate using a thermogravimetric analyzer (TGA-DSC, STA N-1000, SCINCO, Japan). Specific surface area was evaluated using BET (Brunauer, Emmett and Teller; BEL-SORP max, Japan) and the average crystallite size was calculated by Scherrer equation [9]:

$$D = K\lambda / \beta \cos\theta \quad (1)$$

where D is the mean crystallite dimension, K is the shape factor (=0.9),  $\lambda$  is the x-ray wavelength, typically 1.54 Å,  $\beta$  is the line broadening at half the maximum intensity (FWHM) in radians, and  $\theta$  is the Bragg angle.

## 2. Decomposition of CO<sub>2</sub>

Experimental work including catalyst activation and CO<sub>2</sub> decomposition was carried out in a conventional batch type shown in Fig. 1. Continuous flow tests of reduction and reoxidation were also observed using thermal gravimetric analysis (TGA-DSC, STA N-1000, SCINCO, Japan). Major test factors that influence the activation of the catalyst and decomposition reaction were the reduction time, H<sub>2</sub> flow rate and reaction temperature.

### 2-1. Batch Reactor

Sample catalysts were activated in a stainless steel tube reactor (21.9 mm inner diameter; 190 mm length). The reactor was kept warm in an electric furnace under a supply of inert helium gas. When the temperature reached the setpoint, H<sub>2</sub> gas (200 cc/min) was injected through the reactor at different temperatures.

Decomposition of CO<sub>2</sub> using the hydrogen-reduced magnetite and ferrites was followed the reduction process. The residual H<sub>2</sub> gas was removed by flowing He through the reactor for about 10 minutes. After evacuation of the reactor using a vacuum pump, pure CO<sub>2</sub> was fed into the reactor until it reached atmospheric pressure (1.01-1.03 kg/cm<sup>2</sup> depending on the weather conditions).

The inner pressure was continuously recorded by a digital pressure sensor. The pressure was used to monitor the CO<sub>2</sub> decomposition rate because the moles of gas are related to the pressure based on the ideal gas equation.

### 2-2. Continuous Flow Reaction

Newly made M-ferrites (M=Co, Ni, Cu, Zn) were also tested

under a continuous flow in the TGA. Samples were preheated from room temperature to 300 °C under N<sub>2</sub> flow and then cooled to 50 °C to minimize the effect of water on weight change. Every sample was first reduced by 10% H<sub>2</sub> in a N<sub>2</sub> atmosphere with a flow rate of 100 ml/min at a 5 °C/min heating rate up to 600 °C. After the reduction, H<sub>2</sub> flow was turned off and the samples were cooled to 50 °C. Then, CO<sub>2</sub> gas (100 ml/min) was introduced into the system at the same heating rate of 5 °C/min. The initial weight of the samples in all cases was recorded after preheating.

## RESULTS AND DISCUSSION

Oxygen-deficient metal ferrites were synthesized by using co-precipitation and were characterized focusing on the chemical structure and specific surface area. Spinel ferrites consist of AB<sub>2</sub>O<sub>4</sub>, where A is a divalent atom and B is trivalent. The O<sup>2+</sup> in this structure reacted with H<sub>2</sub> and resulted in a structure of AB<sub>2</sub>O<sub>4- $\delta$</sub>  which can react with CO<sub>2</sub>. Several researches attempted to transform Fe<sub>3</sub>O<sub>4</sub> to Fe<sub>3</sub>O<sub>4- $\delta$</sub>  through the reduction process. As CO<sub>2</sub> is decomposed to C, however, the structure returns to Fe<sub>3</sub>O<sub>4</sub> again [8]. To enhance the catalytic activity, a few metal elements (Co, Ni, Cu and Zn) were used as 'A' in the AB<sub>2</sub>O<sub>4</sub> structure. The active metal elements for CO<sub>2</sub> decomposition were evaluated in a batch or a continuous process.

### 1. Characterization

Calcination is an essential step in the preparation of catalytic ferrites by chemical co-precipitation. Calcination temperature plays a key role in determining the crystalline type and particle size of the M-ferrites. The dried precipitates were calcined at 350 °C and 500 °C, respectively, for 2 hours. The XRD patterns of the M-ferrites are shown in Fig. 2 to Fig. 5. As shown, the appearance of hematite (Fe<sub>2</sub>O<sub>3</sub>) became apparent after heat treatment up to 500 °C. In the oxygen-deficient phase of magnetite, iron oxide can be restructured to hematite if it is sufficiently thermally treated. High temperature heating facilitated the formation of M-ferrites and resulted in improved consolidation. In the case of CuFe<sub>2</sub>O<sub>4</sub>, another oxide form, CuO was detected at over 400 °C as previously shown by Lv

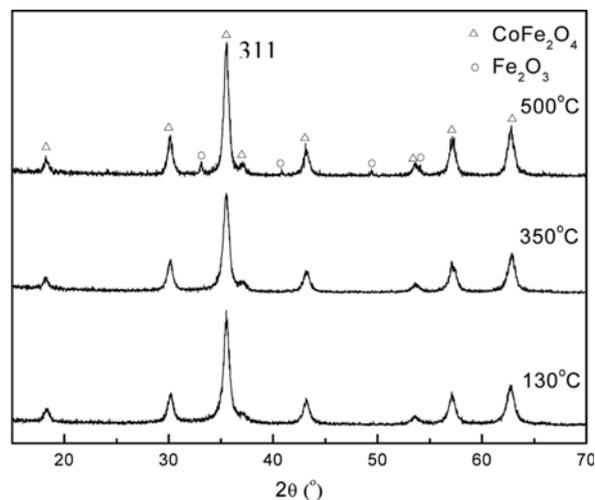


Fig. 2. XRD profiles of CoFe<sub>2</sub>O<sub>4</sub> with calcination temperature.

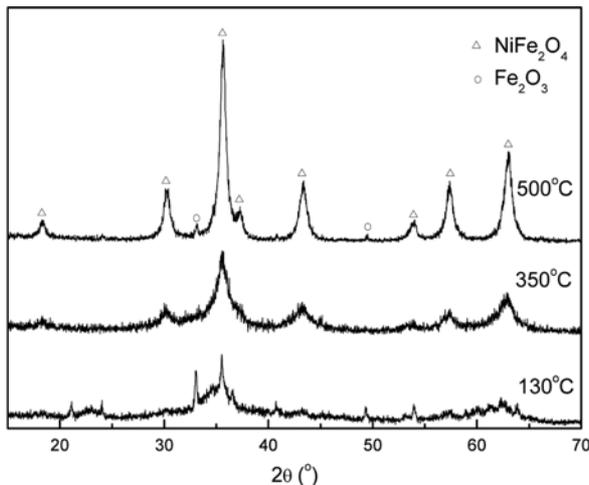


Fig. 3. XRD profiles of NiFe<sub>2</sub>O<sub>4</sub> with calcination temperature.

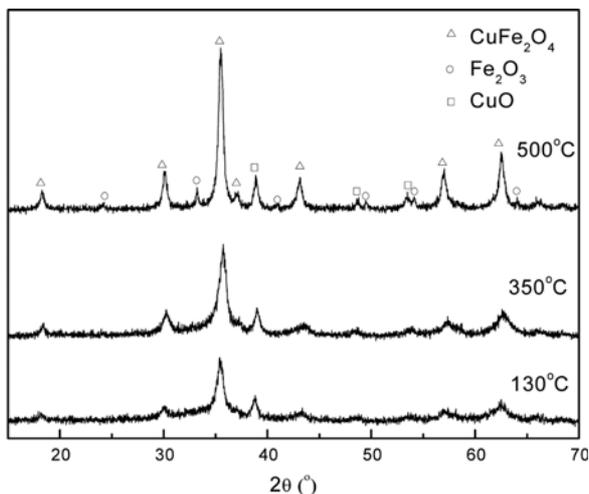


Fig. 4. XRD profiles of CuFe<sub>2</sub>O<sub>4</sub> with calcination temperature.

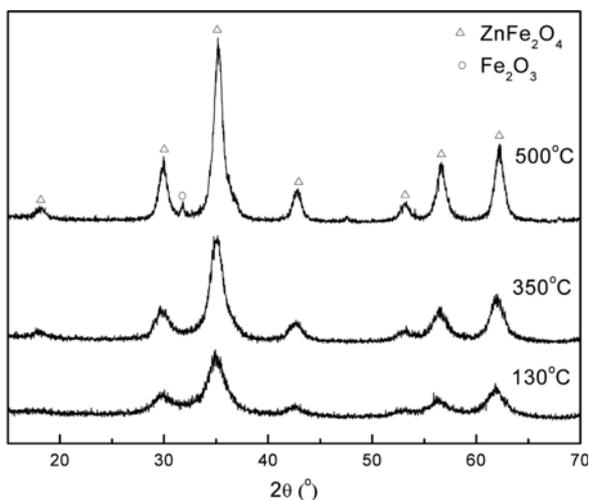


Fig. 5. XRD profiles of ZnFe<sub>2</sub>O<sub>4</sub> with calcination temperature.

et al. [10].

The reflection peak at (311), which was found near  $2\theta=35^\circ$ ,

Table 1. Average crystalline size and BET surface areas of the M-ferrites

Sample	Calcination temperature (°C)	Average crystallite size (nm)	BET surface area (m <sup>2</sup> /g)
CoFe <sub>2</sub> O <sub>4</sub>	350	12.9	64.68
	500	14.4	54.42
NiFe <sub>2</sub> O <sub>4</sub>	350	5.3	127.90
	500	11.8	43.73
CuFe <sub>2</sub> O <sub>4</sub>	350	10.7	55.82
	500	18.2	25.7
ZnFe <sub>2</sub> O <sub>4</sub>	350	5.6	86.45
	500	8.9	39.89

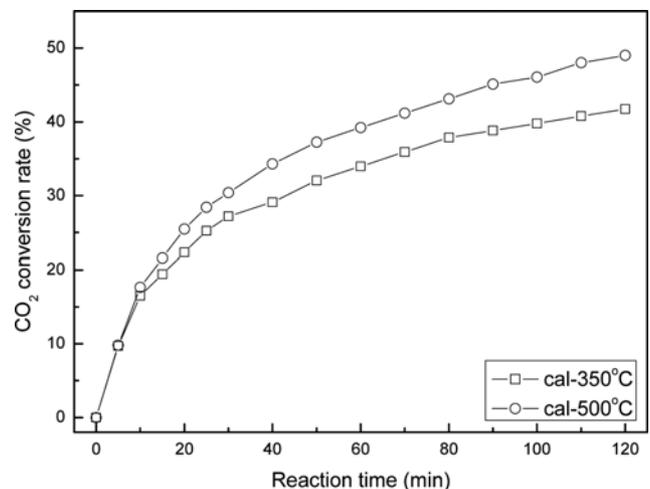


Fig. 6. Decomposition of CO<sub>2</sub> with calcination temperature by reduced CoFe<sub>2</sub>O<sub>4</sub>.

represents the spinel ferrite according to the JCPDS (Joint Committee on Powder Diffraction Standards) card. The intensity of the 311-reflection peak increased with an increase in annealing temperature. This indicates that the crystallinity of the products can be improved by increasing the calcination temperature.

While the crystallinity increased, the BET specific surface area decreased with increasing calcination temperature as shown in Table 1. A decrease in surface area usually occurs due to clogging effect during high temperature treatment [11,12]. This process stabilizes the surface chemical structure. The completed crystal ferrites were 5 nm to 20 nm in size, and these small sizes contributed to the high catalytic activity and CO<sub>2</sub> decomposition [13].

## 2. CO<sub>2</sub> Decomposition by M-ferrites in a Batch Reactor

The activation of the materials and CO<sub>2</sub> decomposition using the hydrogen-reduced ferrites were investigated in batch processes at various reaction temperatures with a H<sub>2</sub> reduction time of 2 hours.

### 2-1. Effect of Calcination Temperature on Catalytic Activity

Calcination at 500 °C made the crystalline structure more stable as forming metallic ferrites, which was already observed in XRD diffractograms. Higher temperatures increased the sizes of the M-ferrite crystallites, and the sizes distributed from 5.3 μm to 18.2

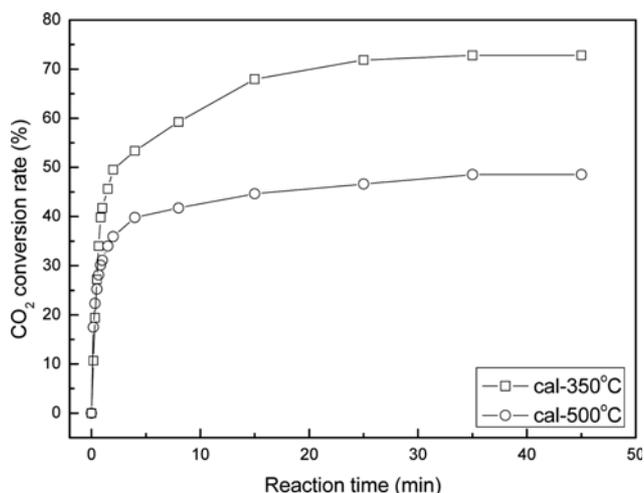


Fig. 7. Decomposition of CO<sub>2</sub> with calcination temperature by reduced NiFe<sub>2</sub>O<sub>4</sub>.

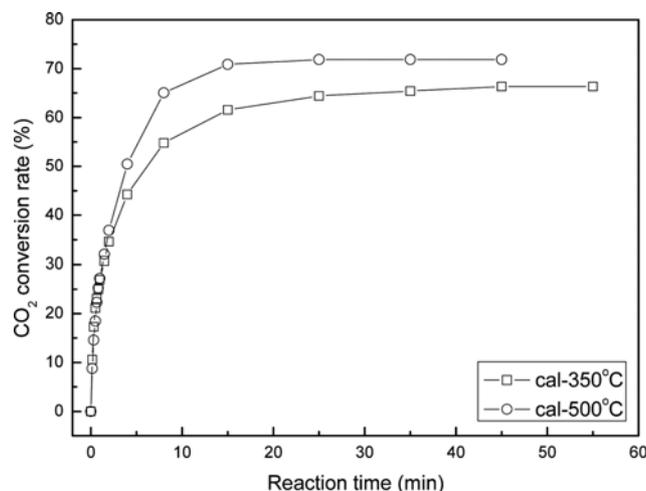


Fig. 9. Decomposition of CO<sub>2</sub> with calcination temperature by reduced ZnFe<sub>2</sub>O<sub>4</sub>.

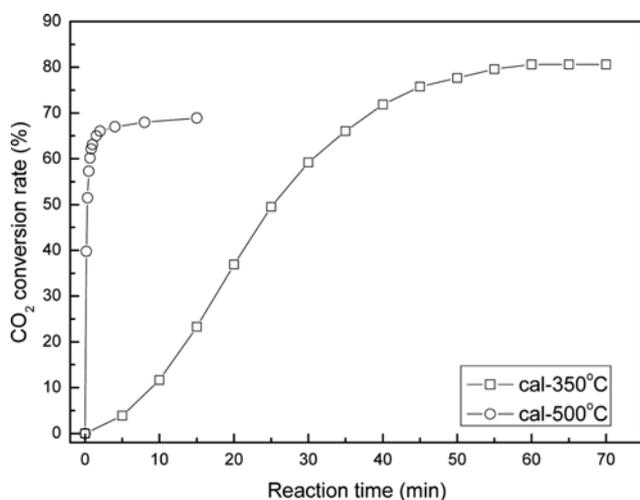


Fig. 8. Decomposition of CO<sub>2</sub> with calcination temperature by reduced CuFe<sub>2</sub>O<sub>4</sub>.

μm depending on the metal precursors, and this also influenced specific surface area (Table 1).

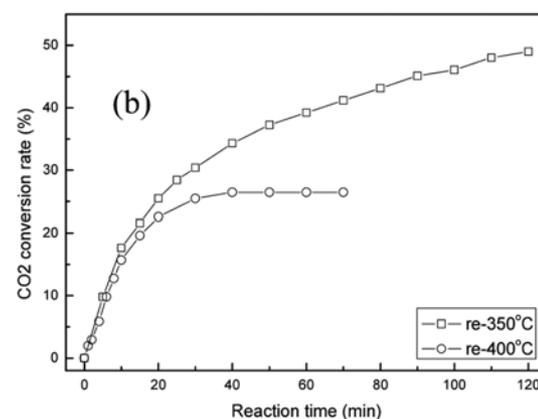
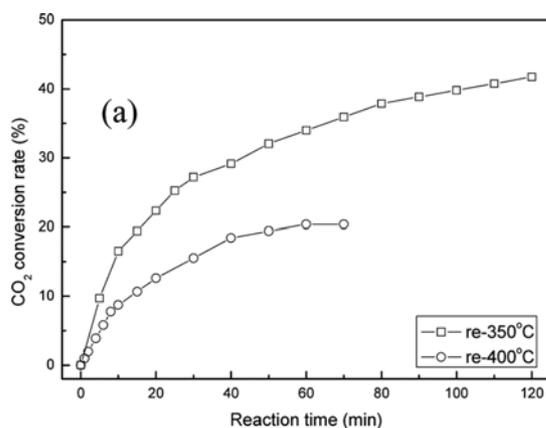


Fig. 10. Decomposition of CO<sub>2</sub> with reaction temperature by reduced CoFe<sub>2</sub>O<sub>4</sub>-calcined at (a) 350 °C and (b) 500 °C.

The ferrites were activated at 200 °C to 400 °C, depending on the empirical characteristics of each metal element. Decomposition of CO<sub>2</sub> was attempted at the same temperature used for the catalyst activation. Figs. 6 to 9 show that high temperature calcination resulted in increased decomposition of CO<sub>2</sub> except for the nickel ferrite (Fig. 7). Nickel ferrite showed a different trend from other metal ferrites. The sample calcined at 350 °C obtained a higher decomposition efficiency than that obtained from the 500 °C heat treatment. This behavior might be attributed to the large specific surface area despite the more obvious spinel crystallite forms. As seen earlier in Fig. 3, nickel impregnated ferrite consisted of apparent crystalline peaks when calcined at 500 °C. However, the heat treatment at 350 °C did not lead to the complete form of metallic compounds. Insufficient calcination resulted in amorphous M-ferrite, which may have a large volume of unstable pores with a large specific surface area. It might improve the interactions between CO<sub>2</sub> molecules on the ferrite surface.

#### 2-2. Effect of Reaction Temperature on Catalytic Reactivity

Figs. 10 to 13 show the CO<sub>2</sub> decomposition rates of each catalyst in terms of reaction temperature. The ferrites were calcined at 350 °C or 500 °C. The temperature used to activate the ferrite was

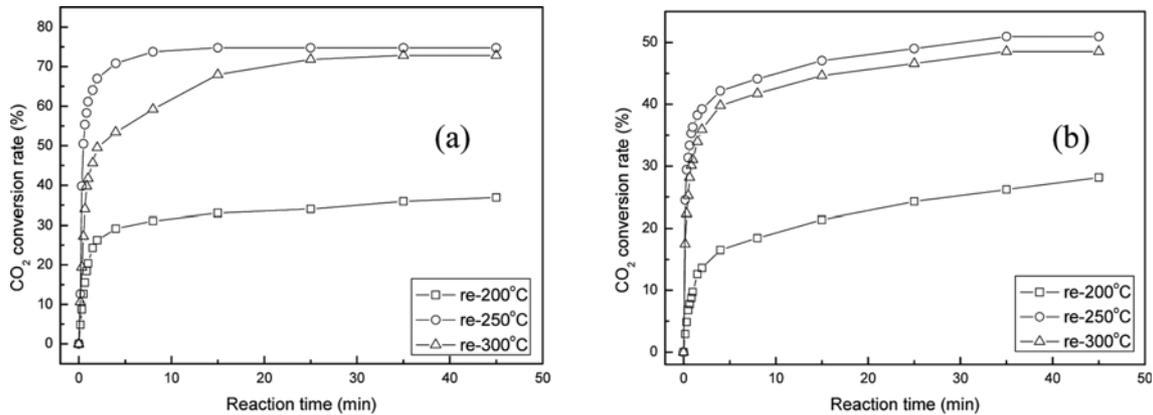


Fig. 11. Decomposition of CO<sub>2</sub> with reaction temperature by reduced NiFe<sub>2</sub>O<sub>4</sub>-calcined at (a) 350 °C and (b) 500 °C.

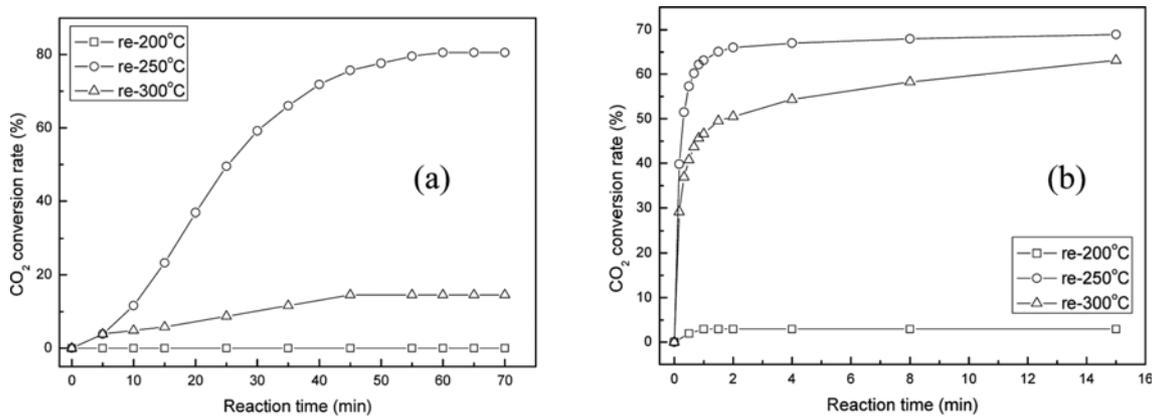


Fig. 12. Decomposition of CO<sub>2</sub> with reaction temperature by reduced CuFe<sub>2</sub>O<sub>4</sub>-calcined at (a) 350 °C and (b) 500 °C.

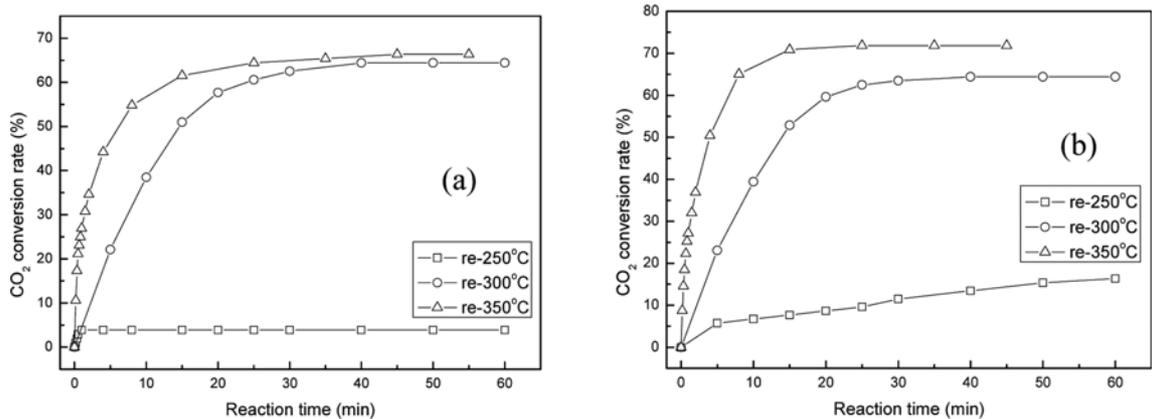


Fig. 13. Decomposition of CO<sub>2</sub> with reaction temperature by reduced (ZnFe<sub>2</sub>O<sub>4</sub>-calcined at (a) 350 °C and (b) 500 °C.

also used for the CO<sub>2</sub> decomposition reaction. The reaction temperature required to decompose CO<sub>2</sub> was found between 200 °C and 350 °C depending on the catalyst. This indicated that the substitution of metal ions of nickel, copper and zinc to iron in magnetite facilitated the CO<sub>2</sub> decomposition. However, the cobalt-based ferrite led to an increase in the reaction temperature as compared to the commercial Fe<sub>3</sub>O<sub>4</sub> (300 °C) as measured in a batch reaction. Experiments conducted for up to 2 hours showed maximum CO<sub>2</sub>

conversion rates of 48% for Co-ferrite, 76% for Ni-ferrite, 68% for Cu-ferrite, and 73% for Zn-ferrite. The initial conversion rate increased very steeply, then became almost constant after reaching the highest rate.

The reaction temperature was selected based on preliminary trials and error tests, and the decomposition reaction did not occur below the temperatures shown in each figure. An increase of 50 °C for activation and a reaction temperature from 200 °C to 250 °C in

NiFe<sub>2</sub>O<sub>4</sub> and CuFe<sub>2</sub>O<sub>4</sub> resulted in a substantial increase in the conversion rate. A slight decrease for both catalysts was found by additional heating to 300 °C. The zinc-impregnated ferrite showed a high conversion rate at 350 °C, which was quite higher than nickel and copper ferrites. The CO<sub>2</sub> conversion rate found when using the reduced ZnFe<sub>2</sub>O<sub>4</sub> consistently increased with increased reaction temperature. It might be because the ZnFe<sub>2</sub>O<sub>4</sub> had not been completely reduced under the current conditions at 500 °C, as will be discussed further below.

Using these catalysts, the decomposition reaction temperatures were lower than the conventional catalytic reactions due to the relatively simple decomposition mechanism, which occurred in two stages: diffusion and chemisorption of CO<sub>2</sub> [14]. Surface atoms of the activated catalysts might be unsaturated, leading to weak bonding force at the surface of solid catalyst. In this case, a higher temperature would result in a lower CO<sub>2</sub> adsorption capacity at the solid surface due to the higher Brownian motion [15]. On the other hand, an excessively high temperature during the reduction would result in less porous solid materials, which provide fewer active sites. Therefore, the optimum temperature for catalyst activation and CO<sub>2</sub> conversion could be associated with modified catalysts.

### 3. CO<sub>2</sub> Decomposition by M-ferrites under Continuous Flow

Fig. 14 shows the weight changes of commercial Fe<sub>3</sub>O<sub>4</sub> and M-ferrites prepared in this work with increasing temperature by thermo gravimetric analysis (TGA) in a 10% H<sub>2</sub> atmosphere. Theoretical and experimental weight changes for complete reduction early in

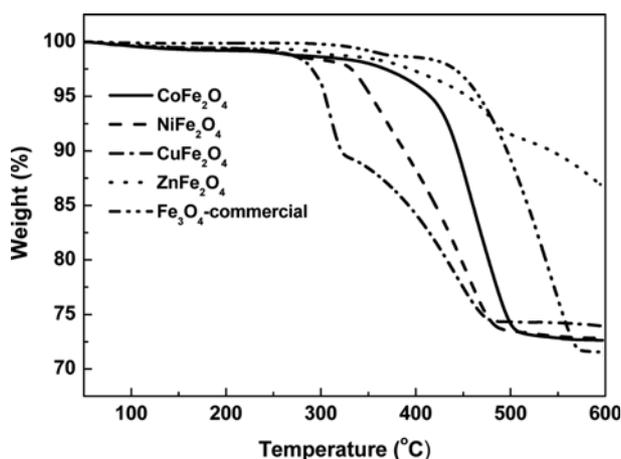
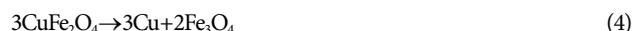


Fig. 14. TGA profiles of commercial magnetite and current M-ferrites under H<sub>2</sub>-atmosphere.

Table 2. Weight change relative to theoretical complete reduction and experimental results of commercial magnetite and M-ferrites

Reactions	Theoretical weight change (%)	Weight change in H <sub>2</sub> -TGA (%)
CoFe <sub>2</sub> O <sub>4</sub> →Co+2Fe	27.3	27.4
NiFe <sub>2</sub> O <sub>4</sub> →Ni+2Fe	27.3	27.2
CuFe <sub>2</sub> O <sub>4</sub> →Cu+2Fe	26.7	26.1
ZnFe <sub>2</sub> O <sub>4</sub> →Zn+2Fe	26.5	13.1
Fe <sub>3</sub> O <sub>4</sub> →3Fe	27.6	28.5

this process are listed in Table 2. As mentioned previously, the reductions were completed before 600 °C for all the samples except for ZnFe<sub>2</sub>O<sub>4</sub>. The test samples of CoFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and CuFe<sub>2</sub>O<sub>4</sub> were almost completely reduced below 500 °C, which was a lower temperature than that of the commercial Fe<sub>3</sub>O<sub>4</sub>. These results indicated that substitution of divalent transition metals including Cu, Ni, Co into Fe<sub>3</sub>O<sub>4</sub> could promote the reduction kinetics in the order of Cu>Ni>Co. However, it was very difficult to reduce ZnFe<sub>2</sub>O<sub>4</sub> due to its stable structure as experienced in an open literature [15]. The XRD results in the aforementioned study revealed the appearance of ZnO and FeO at 650 °C. According to the elemental chemistry, Zn<sup>2+</sup> has an atomic orbital structure of 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3d<sup>10</sup>, which is very stable due to the saturation of the 3d orbital. This stability could hinder the complete reduction of ZnFe<sub>2</sub>O<sub>4</sub>. As seen in the TGA curves, both CuFe<sub>2</sub>O<sub>4</sub> and ZnFe<sub>2</sub>O<sub>4</sub> showed a two-step reduction behavior, while other samples were reduced without different phase transitions. In the first step of weight loss, CuFe<sub>2</sub>O<sub>4</sub> decreased by about 10% which was close to the theoretical value of 8.9% based on the following reaction:



It may be concluded that Cu first leached out from CuFe<sub>2</sub>O<sub>4</sub>, and the second weight loss arose due to the reduction of Fe<sub>3</sub>O<sub>4</sub>.

In the case of ZnFe<sub>2</sub>O<sub>4</sub>, the weight change was about 7% in the first step, which was close to the theoretical weight change of 6.6% based on:



The reduction was far from complete until the temperature reached 600 °C (Table 2). Therefore, ZnFe<sub>2</sub>O<sub>4</sub> was reduced to ZnO and FeO in the initial step.

The decomposition reaction of CO<sub>2</sub> with reduced commercial magnetite and M-ferrites was observed by introducing CO<sub>2</sub> flow. The metal alloy formed from the reduction process can be reoxidized by CO<sub>2</sub> as shown in Fig. 15. The critical temperature required for the reaction between CO<sub>2</sub> and metal alloy was in the following order: Fe<sub>3</sub>O<sub>4</sub><ZnFe<sub>2</sub>O<sub>4</sub><Co≈Ni≈Cu-ferrites. The weight of the fully reduced commercial Fe<sub>3</sub>O<sub>4</sub> increased rapidly from 350 °C to 500 °C and reached 97.8% of the initial weight. ZnFe<sub>2</sub>O<sub>4</sub> should

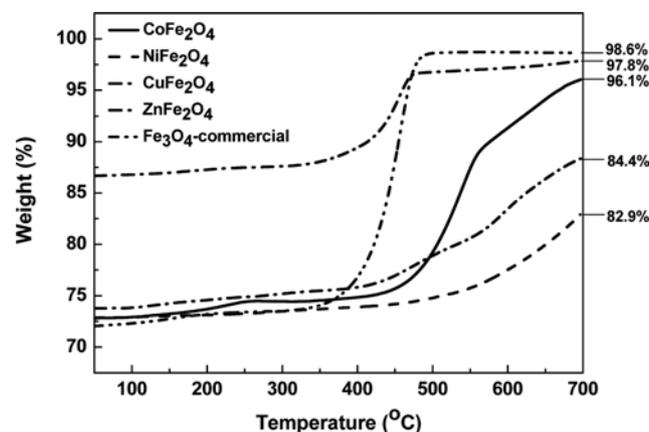


Fig. 15. TGA profiles of commercial magnetite and M-ferrites under CO<sub>2</sub> atmosphere.

have been easy to reoxidize to the initial weight (98.6%), but it was partly reduced to ZnO and FeO. The weight change of  $\text{CoFe}_2\text{O}_4$  in the  $\text{CO}_2$  atmosphere reflected a two-step reoxidation process, which was indicated by the turning point at about  $560^\circ\text{C}$  as deduced by Ma [16]. However, the weight of the reduced  $\text{NiFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  recovered and reached 82.9% and 84.4% of the initial samples, respectively, at the end of each process. It is much more difficult for oxygen atoms to enter the structure of the reduced samples to form the initial state during the reoxidation.

### CONCLUSIONS

Spinel M-ferrites ( $M=\text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) were successfully synthesized by chemical co-precipitation using metal salts and sodium hydroxide as start materials. The crystallinity of the newly-prepared M-ferrites increased with increasing calcination temperature. On the other hand, the crystallite size increased and BET surface area decreased as increasing the calcination temperature. TGA analyses for reduction and reoxidation processes of M-ferrites indicated that substitution of divalent transition metals Cu, Ni and Co in  $\text{Fe}_3\text{O}_4$  promoted the reduction kinetics in the order of  $\text{Cu} > \text{Ni} > \text{Co}$ . It was very difficult to completely reduce  $\text{ZnFe}_2\text{O}_4$  due to its stable structure. The commercial  $\text{Fe}_3\text{O}_4$  and the reduced  $\text{CoFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  showed increases in mass during the reoxidation process, and it was much more difficult for [O] to enter the structure of the reduced samples to form the initial states required for  $\text{NiFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$ . The performance of M-ferrites in a batch reactor presented some advantages over commercial  $\text{Fe}_3\text{O}_4$ .  $\text{CoFe}_2\text{O}_4$  showed quite a high regeneration potential, although it also showed a higher critical reaction temperature.  $\text{NiFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4$  were excellent in  $\text{CO}_2$  decomposition at lower temperatures.  $\text{ZnFe}_2\text{O}_4$  showed a totally different phase change from that of the other samples during the reaction.

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