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Characterization of wet processed (Ni, Zn)-ferrites for CO_2 decomposition

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Ultrafine (Ni, Zn)-ferrites were prepared by two different methods of coprecipitation and hydrothermal synthesis, and their oxygen-deficient ferrites (ODF) produced by hydrogen reduction were investigated on the efficiency of CO_2 decomposition. The crystalline sizes of (Ni, Zn)-ferrites were less than 30 nm with high Brunauer–Emmett–Teller (BET) surface areas, ranging from 77 to 172 $m^2\ g^{-1}$. The (Ni, Zn)-ferrites by hydrothermal synthesis resulted in smaller crystalline sizes, higher BET surface areas and better efficiencies of CO_2 decomposition than by coprecipitation. Compared with the binary $NiFe_2O_{4-\delta}$ ferrite, the ternary $(Ni_x, Zn_{1-x})\ Fe_2O_{4-\delta}$ ferrites showed higher efficiency for CO_2 decomposition, indicating a potential catalyst for the reduction of CO_2 emission in the environmental atmosphere. © *2001 Kluwer Academic Publishers*

1. Introduction

The mitigation of CO_2 emission in atmosphere has been an important environmental concern in order to minimize the so-called 'greenhouse effect' of global warming. The reduction of CO_2 has been extensively studied by many research groups using chemical, photochemical, and biological methods [1–4]. Recently, it was shown that CO_2 can be actively decomposed to carbon and oxygen around 300°C on the surface of the oxygen-deficient ferrites represented by $Me_xFe_{3-x}O_{4-\delta}$, where δ expresses the oxygen deficiency [5]. The oxygen-deficient ferrite (ODF) is formed by hydrogen reduction at about 300°C,

$$Me_xFe_{3-x}O_4 + \delta H_2 \rightarrow Me_xFe_{3-x}O_{4-\delta} + \delta H_2O. \qquad (1)$$

Then, the ODF is highly reactive to decompose CO_2 to carbon and oxygen as follows,

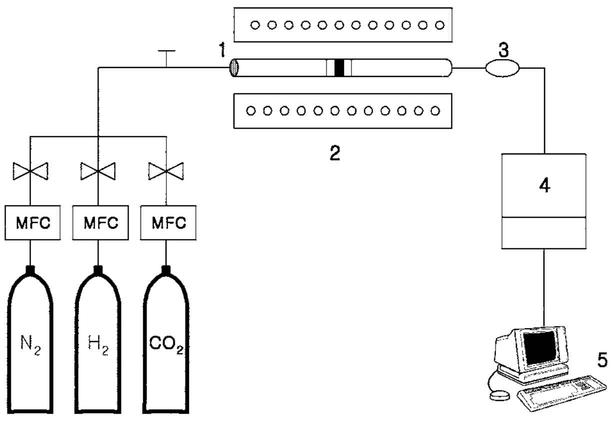
$$\begin{aligned} &Me_xFe_{3-x}O_{4-\delta} + (\delta/2)CO_2 \\ &\quad \rightarrow Me_xFe_{3-x}O_4 + 1/2\delta C(s). \end{aligned} \qquad (2)$$

Crystallographically, Me(II)-bearing ferrites have the spinel structure with the general formula $Me^{2+}O \cdot Fe_2^{3+}O_3$, where Me^{2+} is a divalent metallic ion such as Fe^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, etc. Mixed ferrites can also be fabricated in which the divalent cation may be a mixture of ions (e.g., $Ni_{1-x}Zn_xFe_2O_4$), so that a wide range of composition is possible [6, 7].

Until now, oxygen-deficient Zn(II)-; Mn(II)-, Co(II)- and Ni(II)-bearing ferrites have been widely studied for CO_2 decomposition reactivity which is significantly different with processing methods and compositions [8, 9]. Particularly, CO_2 decomposition efficiency was highly improved by using ultrafine-particled ferrites with high specific surface area [10, 11]. Ferrites, $Me_xFe_{3-x}O_4$ can be fabricated by a solid-state reaction. However, the conventional solid-state reaction at high temperature (above 1000°C) produces a coarse grained ferrite which results in a low CO_2 decomposition reactivity. In order to obtain ultrafine ferrites many different kinds of wet processing methods such as oxidation method, coprecipitation, hydrothermal synthesis, spray drying and freeze-drying methods have been studied [12–15]. Among those, coprecipitation and hydrothermal synthesis resulted in ultrafine particles of Ni-bearing ferrites with a mean crystalline size smaller than 50 nm [11, 16]. In the present study ultrafine powders of the ternary (Ni, Zn)-ferrites were synthesized by coprecipitation and hydrothermal methods, and their efficiencies on CO_2 decomposition to carbon and oxygen were investigated.

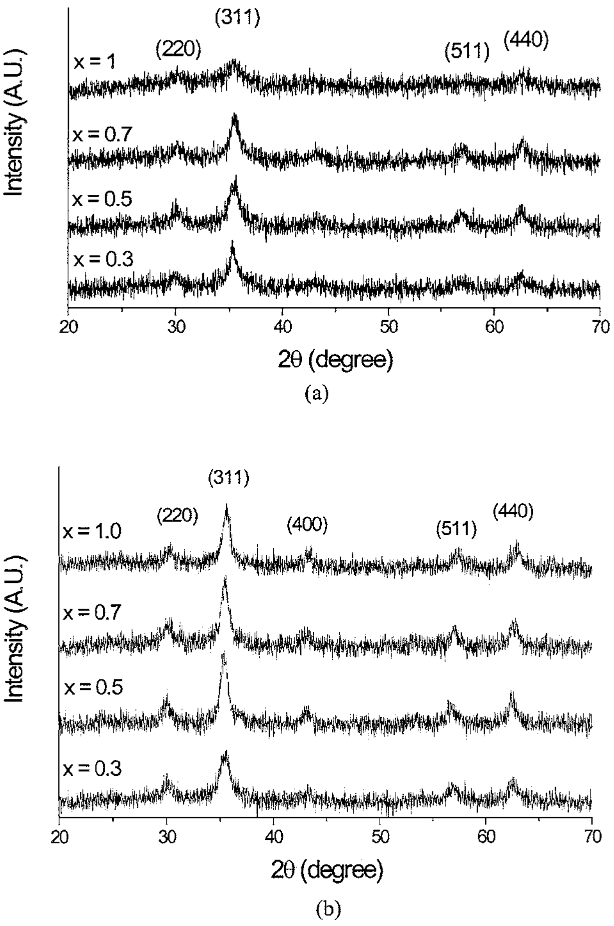
2. Experimental

Ultrafine (Ni, Zn)-ferrites were synthesized by two different wet processings of coprecipitation and hydrothermal methods. Appropriate amounts of $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_2 \cdot 6H_2O$ were dissolved at 60°C in distilled water (150 ml) which was degassed by passing N_2 gas. In coprecipitation, the mixed nitrate solution was added to the 1.2 mol NaOH solution (150 ml) which was kept at 60°C with stirring. The pH of the mother solution was kept at 9.0. In hydrothermal synthesis, the mixed solution (150 ml) was neutralized with the 3.0 mol NaOH to be a pH of about 9.0 and treated in autoclave at 160°C for 5 hrs. The precipitated products were separated by centrifuging around 10000 rpm, followed by washing



1. Reaction cell with ferrite powder 2. electrical furnace 3. syringe 4. gas chromatography 5. computer

Figure 1 Schematic diagram of the experimental apparatus for CO_2 decomposition reaction.



(a)

(b)

Figure 2 X-ray diffractograms of (N$_x$, Zn$_{1-x}$)-ferrites by (a) coprecipitation and (b) hydrothermal synthesis.

with distilled water and ethanol, and dried in vacuum at 60°C for 20 hrs. Finally, dried powders were heated at 300°C in N_2 atmosphere for one hour to eliminate H_2O and any −OH remnants [10].

The chemical compositions of synthesized ferrites were analyzed by inductively coupled plasma (ICP) spectroscopy and energy dispersive spectroscopy (EDS). The crystalline characterization was done by x-ray diffractometry with Cu K_α radiation (Zeifert 3000) and transmission electron microscopy (TEM). The Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption (Shimadzu, Micromeritics 2400).

H_2 reduction and CO_2 decomposition reactions were carried out in a continuous flow gas. About 1.0 g of (Ni, Zn)-ferrite powders was placed in a quartz tube of 10 mm inner diameter heated by tubular electrical furnace as shown in Fig. 1. The H_2 reduction for making the oxygen-deficient ferrites was performed by passing a mixed gas of 8% H_2-92% N_2 through the ferrite powders at a flow rate of 100 ml/min at 300°C for a time ranging from 1 to 4 hrs. Then, after purging the reaction cell by N_2 gas, the CO_2 decomposition reaction were carried out in continuous flow of 10% CO_2-90% N_2 gases passing through the oxygen-deficient ferrite powders. All the gas flow rates were controlled by mass flow controllers (MFC). The efficiency of CO_2 decomposition was analyzed by using gas chromatography (Shimadzu, GC-8A) with thermal conductivity detector (TCD).

3. Results and discussions

Fig. 2 shows the X-ray diffractograms of the (Ni$_x$, Zn$_{1-x}$) Fe_2O_4 obtained by coprecipitation and hydrothermal synthesis, where the molar ratios of Fe and oxygen are assumed to be stoichiometric as a matter of convenience. All XRD patterns show a single phase of the cubic spinel structure. The peaks of the ferrites by hydrothermal method are narrower and stronger than those by coprecipitation. The peak broadening for the ferrites by coprecipitation indicates poor crystallinity, compared with those of hydrothermal method.

Fig. 3a and b show TEM micrographs of ferrite particles obtained by coprecipitation and hydrothermal method, respectively. The particles were nearly spherical and the crystalline size ranged from 10 to 20 nm for coprecipitation and from 5 to 10 nm for hydrothermal method. The BET surface areas of coprecipitation and hydrothermal method were 77–122 and 113–172 m^2/g, respectively. As Zn composition increased the BET surface area decreased in general, while lattice constant increased. Table I summarize the results of particle characterizations on the chemical composition, BET surface area, lattice parameter and crystalline size. The lattice parameters were calculated from the XRD peaks (220), (311), (400), (422), (511) and (440) of the spinel ferrites by using the Nelson–Riley function [17].

Fig. 4 shows the CO_2 decomposition performance of (Ni$_{0.5}$, Zn$_{0.5}$)$Fe_2O_{4-\delta}$ synthesized by coprecipitation as a function of the hydrogen reduction time. The mixed gas of 8% H_2-92% N_2 was passed through the 1.0 g ferrite at a flow rate of 100 ml/min at 300°C for a time ranging from 1 to 4 hrs; then CO_2 decomposition process was performed by passing the mixture of 10% CO_2-90% N_2 at a flow rate of 60 ml/min. The CO_2 decomposition performance on reduction time was estimated by measuring the time the exiting gas passed

TABLE I Chemical composition, BET surface area, lattice parameter and crystalline size of (Ni_xZn_{1-x}) Fe_2O_4 ferrites

Sample					
Method	x^a	Chemical composition	BET surface area (m^2/g)	Lattice constant (Å)	Crystalline size (nm)
Coprecipitation method	0.3	$(Ni^{2+}_{0.29}Zn^{2+}{}_{0.74})Fe^{3+}_{1.91}O_4$	79.1	8.4227	14 ± 1
	0.5	$(Ni^{2+}_{0.51}Zn^{2+}_{0.51})Fe^{3+}_{1.98}O_4$	77.6	8.4068	17 ± 1
	0.7	$(Ni^{2+}_{0.72}Zn^{2+}_{0.32})Fe^{3+}_{1.95}O_4$	89.5	8.3685	15 ± 1
	1.0	$Ni^{2+}_{1.02}$ $Fe^{3+}_{1.99}O_4$	122.1	8.3406	14 ± 1
Hydrothermal method	0.3	$(Ni^{2+}_{0.31}Zn^{2+}_{0.75})Fe^{3+}_{1.91}O_4$	121.8	8.4113	8 ± 0.5
	0.5	$(Ni^{2+}_{0.47}Zn^{2+}_{0.51})Fe^{3+}_{2.00}O_4$	113.2	8.4095	9 ± 0.5
	0.7	$(Ni^{2+}_{0.66}Zn^{2+}_{0.32})Fe^{3+}_{2.02}O_4$	127.5	8.3651	8 ± 0.5
	1.0	$Ni^{2+}_{0.98}$ $Fe^{3+}_{2.02}O_4$	172.4	8.3400	7 ± 0.5

$^a x$ is the initial molar ratio of the solution prior to the reaction.

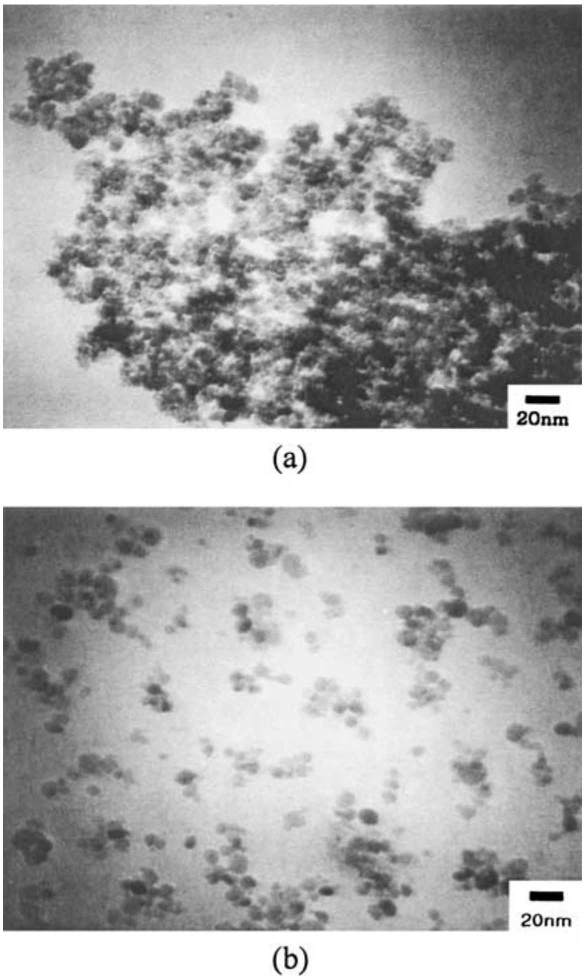


Figure 3 Transmission electron micrographs of synthesized $(Ni_{0.5}, Zn_{0.5})Fe_2O_4$ powders by (a) coprecipitation (b) hydrothermal methods.

through the reduced ferrite reader 5% CO_2 (the system gradually loses CO_2 decomposition potential to the initial composition of 10% CO_2). As shown in Fig.4, CO_2 decomposition efficiency increases with the maximum value at about 3 hrs reduction, then decreases with the reduction time. Probably, the decrease of CO_2 decomposition performance over 3 hr reduction may be due to partial decomposition of the spinel ferrite to less reactive metallic iron phase (α-Fe) [18]. In the following experiments of CO_2 decomposition, hydrogen reduction of the ferrite was performed for 3 hrs according to the results of Fig. 4.

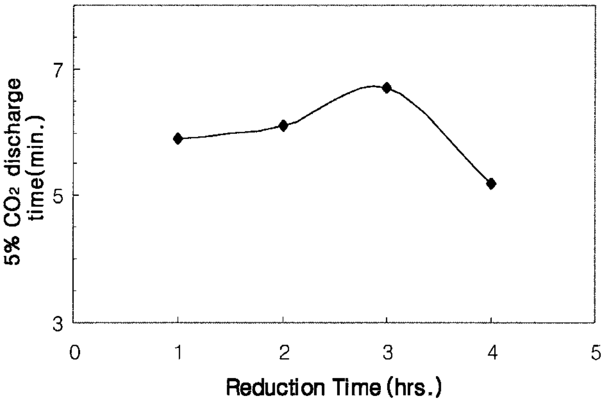


Figure 4 Effect of H_2 reduction time for the CO_2 decomposition of $(Ni_{0.5}, Zn_{0.5})$-ferrites at 300°C.

Fig. 5a compares the CO_2 decomposition performance of $Ni_xZn_{1-x}Fe_2O_{4-\delta}$ [$x = 0.3$, 0.5, 0.7] ferrite with that of $NiFe_2O_{4-\delta}$ ($x = 1.0$) which were synthesized by hydrothermal method. The feed gas of 10% CO_2-90% N_2 was passed at a flow rate of 60 ml/min through the reaction cell held at 300°C in which 1 g-reduced ferrite was placed. $Ni_xZn_{1-x}Fe_2O_{4-\delta}$ ferrites kept decomposing CO_2 to carbon and oxygen for longer time than $NiFe_2O_{4-\delta}$ ($x = 1.0$). $Ni_xZn_{1-x}Fe_2O_{4-\delta}$ and $NiFe_2O_{4-\delta}$ ferrites decomposed CO_2 completely to carbon and oxygen up to 7 min and 5 min, respectively, afterwards their decomposition potentials disappeared gradually to be almost zero efficiency-state. Compositional variation of zinc from $1 - x = 0.3$ to 0.7 did not affect significantly the CO_2 decomposition efficiency. Fig. 5b compares the CO_2 decomposition performance of $Ni_xZn_{1-x}Fe_2O_{4-\delta}$ ($x = 0.5$) ferrites synthesized by two different methods of coprecipitation and hydrothermal synthesis. The ferrite by hydrothermal synthesis and coprecipitation continued to decompose CO_2 completely by 7 min and 5 min, respectively, indicating that the first shows better efficiency of the CO_2 decomposition than the latest. Better efficiency of the ferrite by hydrothermal synthesis might result from its higher surface area which plays as active medium for CO_2 adsorption on the surface of ferrites, as shown in Table I. Some researchers [19, 20] investigated the CO_2 decomposition performance of various oxygen deficient Zn-, Mn-, Co- and Ni-bearing ferrites among which the Ni-bearing ferrite showed better reactivity for CO_2

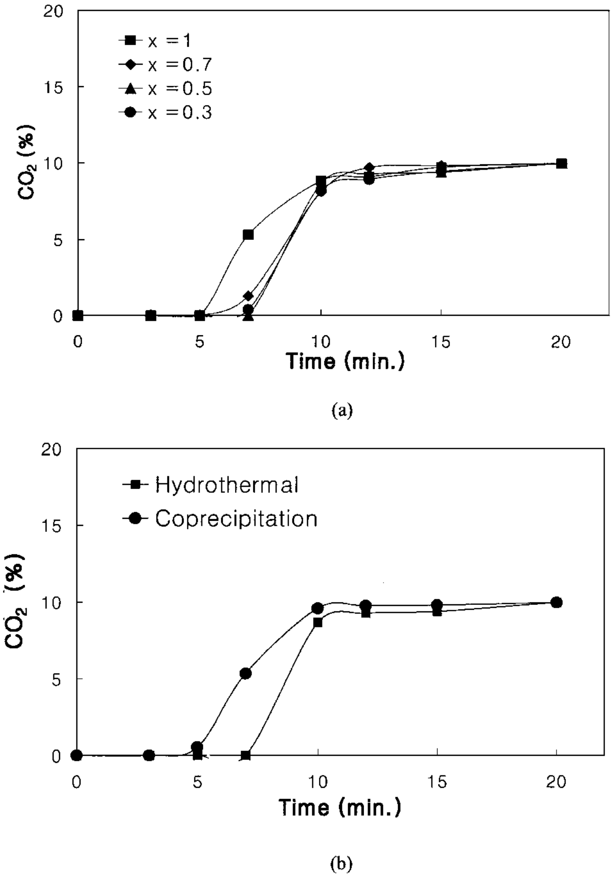


Figure 5 Comparison of CO_2 decomposition performance: (a) with respect to the variation of Zn for $\mathrm{Ni}_x\mathrm{Zn}_{1-x}\mathrm{Fe}_2\mathrm{O}_{4-\delta}$ synthesized by hydrothermal method ($x = 0.3, 0.5, 0.7, 0.1$), (b) for $(\mathrm{Ni}_{0.5}, \mathrm{Zn}_{0.5})\mathrm{Fe}_2\mathrm{O}_{4-\delta}$ synthesized by hydrothermal synthesis and coprecipitation.

decomposition than any others. In conclusion from the results as shown in Fig. 5a, the ternary compounds of oxygen deficient (Ni, Zn)-ferrites showed better efficiency of CO_2 decomposition than the binary Ni-ferrite. This imply that the ternary ferrite systems can be good candidates as catalytic materials for the mitigation of CO_2 emission to prevent air pollution.

4. Conclusions

Ultrafine (Ni, Zn)-ferrites with crystalline size less than 30 nm were synthesized by two wet processes of coprecipitation and hydrothermal methods. Oxygen-deficient (Ni, Zn)-ferrite synthesized by hydrothermal method showed better CO_2 decomposition performance than that of coprecipitation. Also, oxygen-deficient ternary (Ni, Zn)-ferrites are more reactive on CO_2 decomposition to carbon and oxygen than the binary Ni-ferrite.

Acknowledgments

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