

Synthesis of Silica-Coated Cobalt Ferrite Nanoparticles Using Water-in-Oil Microemulsion

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ABSTRACT

Silica-coated cobalt ferrite nanoparticles ($\text{CoFe}_2\text{O}_4\text{-SiO}_2$) were prepared using a water-in-oil microemulsion consisting of water, polyoxyethylen(15)cetyether (surfactant) and cyclohexane (oil). Co-Fe hydroxide precursors were synthesized in the microemulsion solution, where hydrolysis of tetraethylorthosilicate was performed to produce SiO_2 . The samples thus obtained were calcined at various temperatures ranging from 500 to 1000°C. X-ray diffraction patterns showed a peak corresponding to the (311) plane of CoFe_2O_4 . From TEM observations, the CoFe_2O_4 particles (ca. 2–5 nm) were located nearly at the center of spherical SiO_2 particles (ca. 30–35 nm) and the size distribution of the CoFe_2O_4 particles was very narrow. The magnetic properties were determined at room temperature by applying a magnetic field of 15 kOe. The magnetization increased with increasing calcination temperature. The saturation magnetization was 2.4 emu/g at the calcination temperature of 1000°C. However, the coercivity had a low value because the particle size of CoFe_2O_4 was smaller than the critical size, below which the material becomes superparamagnetic.

Key words: Cobalt ferrite, Silica-coated nanoparticles, Microemulsion, Magnetic properties

1. INTRODUCTION

Magnetic ferrite materials such as magnetite and cobalt ferrite have attracted the attention of many researchers⁽¹⁻³⁾ because of their promising applications in magnetic recording, sensors, and magneto-optical devices. Cobalt ferrite (CoFe_2O_4) has been prepared by sol-gel^(4,5) and precipitation methods⁽⁶⁾. However, the broad size distribution of its magnetic particles is a serious limitation for electric devices^(7,8), because the particle size affects the magnetic properties. The difficulty of obtaining uniform-sized magnetic nanoparticles results from the fact that the nanoparticles easily aggregate during preparation, e.g., the nucleation and calcination stages. Moreover, these magnetic materials need to be coated with silica (SiO_2) or alumina (Al_2O_3) for protection against erosion and

corrosion⁽⁹⁾.

We have developed a method for preparing supported metal catalysts using a water-in-oil (w/o) microemulsion⁽¹⁰⁾. As this work progressed, we were able to obtain SiO_2 -coated rhodium nanoparticles using a specific microemulsion system (polyoxyethylene(15)cetyether / cyclohexane / water system)^(11,12). In this study, SiO_2 -coated cobalt ferrite ($\text{CoFe}_2\text{O}_4\text{-SiO}_2$) nanoparticles were prepared using a w/o microemulsion. The advantages of these particles are their uniform particle size and the fact that they are SiO_2 -coated. In this paper, we report the synthesis of $\text{CoFe}_2\text{O}_4\text{-SiO}_2$ nanoparticles and their structural and magnetic properties.

2. EXPERIMENTAL

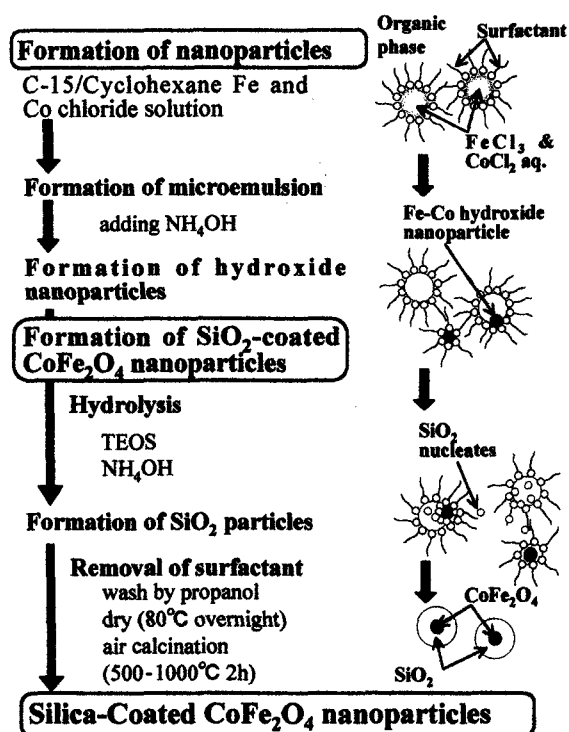


Fig. 1. Preparation procedure for SiO_2 -coated CoFe_2O_4 nanoparticles.

Table I. Preparation conditions for SiO_2 -coated CoFe_2O_4 nanoparticles.

Aqueous phase	TEOS	Time	
		Preparation of hydroxide particle	TEOS hydrolysis
CoCl_2 0.3 M \times 1.4 cc	15 g	1 h	1 h
FeCl_3 0.3 M \times 2.8 cc			

A procedure for preparing SiO_2 -coated CoFe_2O_4 nanoparticles is shown in Fig. 1, and the preparation conditions are listed in Table I. A w/o microemulsion system with polyoxyethylen(15)ecetyler (C-15, $\text{C}_{16}\text{H}_{33}(\text{OC}_2\text{H}_4)_{15}\text{OH}$) as the surfactant, cyclohexane as the oil phase and aqueous solutions of CoCl_2 and FeCl_2 as the water phase was used. The microemulsion was prepared by dissolving aqueous solutions of CoCl_2 and FeCl_2 in stoichiometric proportions (see Table I) in a C-15 / cyclohexane solution. The concentration of the CoCl_2 and FeCl_2 in water was 0.3 M and that of the C-15 in cyclohexane was 0.5 M. In the microemulsion solution, the cobalt-iron hydroxide complex nanoparticles were synthesized by adjusting the pH to approximately 9.0 with

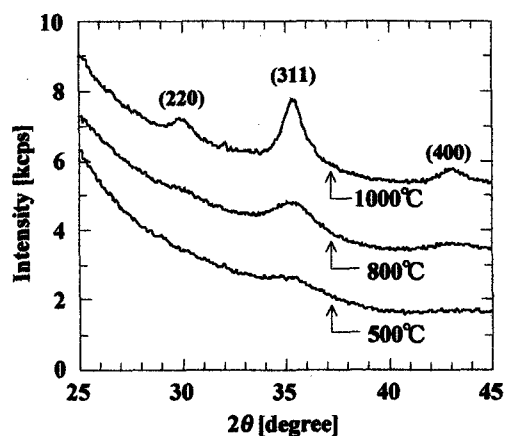


Fig. 2. X-ray diffraction pattern of CoFe_2O_4 - SiO_2 samples calcined at different temperatures.

NH_3 solution. Tetraethylorthosilicate (TEOS), as a SiO_2 source, and a dilute ammonium solution were added to the solution containing the cobalt-iron hydroxide complex nanoparticles, and the hydrolysis and polycondensation of TEOS was performed at 50°C . After hydrolysis for 1 h, the SiO_2 gel containing the cobalt-iron hydroxide complex nanoparticles was centrifuged, thoroughly washed with propanol, dried at 80°C overnight, and calcined under an air flow at 500°C for 2 hours to remove the surfactant. Finally, the samples thus prepared were calcined at 500 – 1000°C for 2 hours for complete conversion of the hydroxide into the magnetic ferrite (CoFe_2O_4).

The CoFe_2O_4 - SiO_2 nanoparticles thus prepared were inspected by transmission electron microscopy (TEM, Nihon Denshi JEM-2000FX). The particle size of the CoFe_2O_4 was measured from TEM photographs. The crystallinity and the magnetic properties of the nanoparticles were investigated as a function of the calcination temperature using an X-ray diffractometer (XRD, Rigaku Rint-2400) and a vibrating-sample magnetometer (VSM, Tamagawa Seisakushyo VSM-1550HGC).

3. RESULTS AND DISCUSSION

X-ray diffraction patterns of the CoFe_2O_4 - SiO_2 nanoparticles calcined at different temperature are shown in Fig. 2. The sample calcined at 500°C showed a small peak around $2\theta=35^\circ$. On the other hand, at the calcination temperatures of 800°C and 1000°C , the

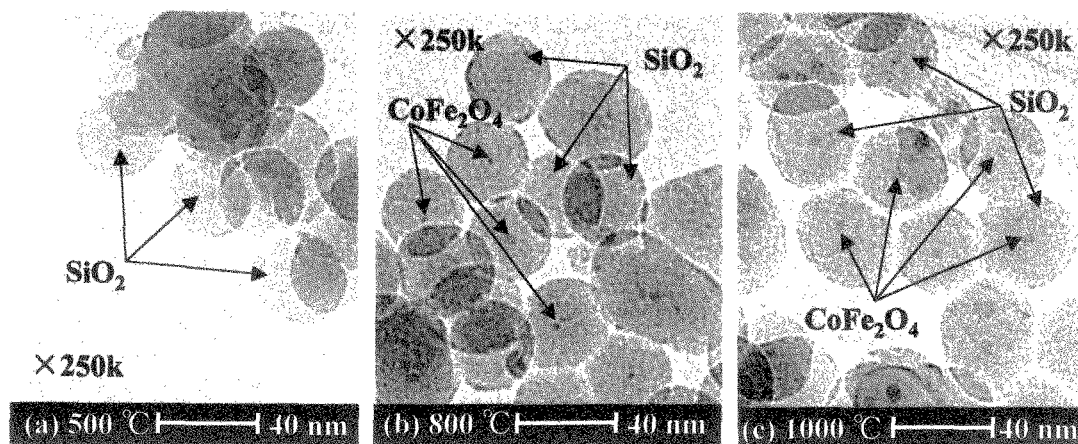


Fig. 3. TEM photographs of SiO_2 -coated CoFe_2O_4 nanoparticles prepared using microemulsion.

patterns clearly showed the peak corresponding to the (311) plane of CoFe_2O_4 ($2\theta=35.4^\circ$). As shown in the figure, the intensity of the peak increased with increasing calcination temperature. The increase in the intensity resulted from the formation of CoFe_2O_4 from Co-Fe hydroxide during calcination^(4,5).

The magnetic properties of particles depend on their particle size. Therefore, the materials used for electric devices should be ultrafine with narrow size distributions. Figures 3(a)–3(c) show TEM photographs of CoFe_2O_4 - SiO_2 nanoparticles calcined at 500°C, 800°C and 1000°C. At the calcination temperature of 500°C, CoFe_2O_4 particles could not be observed. On the other hand, at the calcination temperatures above 800°C (Figs. 3(b) and 3(c)), the CoFe_2O_4 particles could be observed, and they were located nearly at the center of uniform, spherical SiO_2 particles. The concentration of CoFe_2O_4 , which was evaluated from the total weight of the CoFe_2O_4 - SiO_2 nanoparticles and an amount of Co and Fe ions added (see Table I), was approximately 3.5 wt%. Although the overall size of the spherical SiO_2 particles was almost identical regardless of the calcination temperature, the average size of the centered CoFe_2O_4 particles increased from 2.0 nm to 5.5 nm with increasing calcination temperature from 800°C to 1000°C. These results indicated that the Co-Fe hydroxide nanoparticles were covered with SiO_2 during the TEOS hydrolysis, as described in Fig. 1, and that the conversion of the hydroxide into the magnetic oxide of CoFe_2O_4 took place

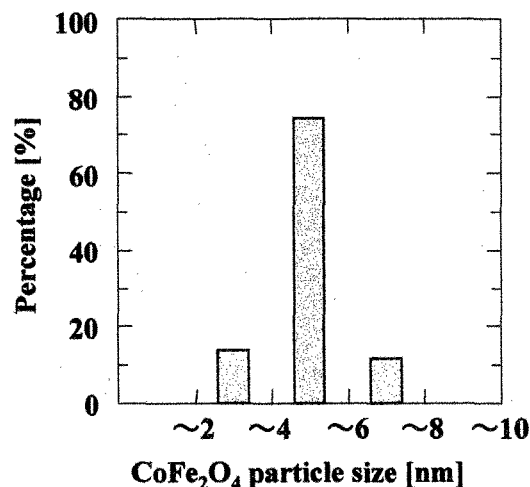


Fig. 4. Size distribution of CoFe_2O_4 nanoparticles calcined at 1000°C.

during calcination, as discussed above (see Fig. 2).

Figure 4 shows the size distribution of the CoFe_2O_4 particles calcined at 1000°C, obtained from TEM photographs. The size distribution of the CoFe_2O_4 particles was very narrow. The narrow size distribution is due to an inhibition of coagulation by the SiO_2 surrounding the CoFe_2O_4 particles. Since the CoFe_2O_4 nanoparticles were covered with SiO_2 , the motion and aggregation of the CoFe_2O_4 nanoparticles were physically restricted even though they were calcined at 1000°C^(11,12).

The magnetic properties were determined at room temperature by applying a magnetic field of 15 kOe. Fig. 5 shows magnetization curves of SiO_2 -coated CoFe_2O_4 nanoparticles calcined at 500°C, 800°C and 1000°C. The saturation magnetization increased with increasing

calcination temperature. The reason was that the particle size of CoFe_2O_4 increased with increasing calcination temperature. The saturation magnetization was 1.2 emu/g and 2.4 emu/g at the calcination temperatures of 800°C and 1000°C, respectively. On the other hand, the coercivity was as low as approximately 50 Oe because the particle size of CoFe_2O_4 was smaller than the critical size, below which the material becomes superparamagnetic⁽¹³⁾.

4. CONCLUSION

Silica-coated cobalt ferrite nanoparticles (CoFe_2O_4 - SiO_2) were prepared using a water-in-oil microemulsion consisting of water, polyoxyethylen(15)ecetyler (surfactant) and cyclohexane (oil). X-ray diffraction patterns showed peaks corresponding to CoFe_2O_4 . From TEM observations, the CoFe_2O_4 particles were located nearly at the center of spherical SiO_2 particles and the size distribution of CoFe_2O_4 particles was very narrow. The magnetization increased with increasing calcination temperature and the saturation magnetization was 2.4 emu/g at the calcination temperature of 1000°C.

ACKNOWLEDGEMENT

We thank the research laboratory of High Voltage Electron Microscope, Kyushu University, for the transmission electron micrograph. This work is partly supported by the Ministry of Education, Science, Sports, and Culture, Japan through a Grant-in-Aid for Exploratory Research, No. 11875172.

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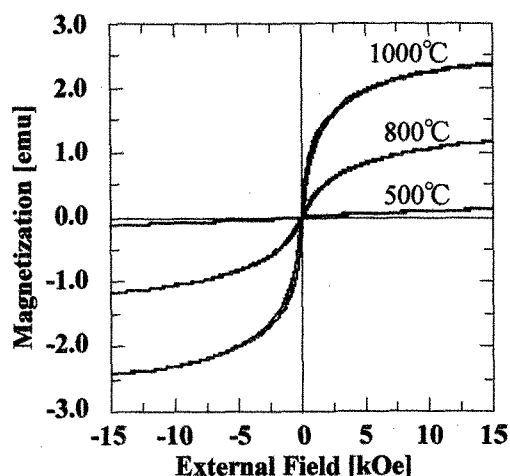


Fig. 5. Dependence of magnetic properties on calcination temperature for SiO_2 -coated CoFe_2O_4 nanoparticles.

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(Received December 17, 1999; Accepted March 30, 2000)