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The effect of surfactants on growth and form of monodispersed iron oxide particles

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Abstract−The effects of added surfactants on the size and shape of the monodispersed iron oxide particles prepared by forced hydrolysis from aqueous ferric chloride solutions were investigated by transmission electron microscopes. When the concentration of ferric chloride solutions increased, either the particle growth displayed clear delays or only a reaction intermediate of β-FeOOH was made. The cation and the amphoteric surfactant formed a spherical α-Fe_2O_3 within 12 hours regardless of the added concentration, and the anion delayed the growth of its particles or simply made the β-FeOOH as the concentration increased.

Key words: Hydrolysis, Surfactant, Monodispersed, Iron Oxide Particles

INTRODUCTION

Iron oxide particles are a subject of considerable importance, because of industrial applications such as in catalysts, pigments, magnetic materials, and ceramic production parts. The production of monodispersed particles is also studied in fields involving colloids [Matijevic, 1981; Shaw, 1992].

The production of iron oxide particles is related to several variables: pH of an aqueous solution, temperature, time, anion and iron ion concentration, and ion intensity. Different particles may result from the change of only one of these variables [Matijevic and Scheiner, 1978; Matijevic et al., 1975; Matijevic, 1977; Moriyama, 1975].

Heller et al. discovered β-FeOOH, Spiro such as ferric hydroxides, and from the late 1960s, the discovery of various types of monodispersed iron oxide particles has succeeded by using forced hydrolysis, thermal decomposition of complex compounds, homeogenous precipitation, phase transformation, and aerosol-based chemical reactions.

The dispersion stability of the surfactants of monodispersed iron dioxide has been studied by Moriyama, Corkill and Meguro for a long time, but the influence of activators on the shapes and sizes of particles in forced hydrolysis has not been studied systematically as much [Corkill et al., 1966; Meguro et al., 1983].

In this research we studied the effect of adding surfactants which have an effect on particle shape in the production process of monodispersed iron ion by forced hydrolysis method from ferric chloride aqueous solution.

It was standardized to the given particle without the addition of any surfactant, and then we studied the particle size, composition, and shape in the case of changing kinds and concentrations of surfactants by TEM and XRD.

EXPERIMENTAL

$FeCl_3 \cdot 6H_2O$ used of analytical grade purity was supplied by Junsei Chemical. The surfactants of given concentration and 0.02 M $FeCl_3$ aqueous solution were added in a 500 ml erlenmeyer flask. This teflon-covered flask was aged in the thermostat which kept up 100±2 °C temperature.

For surfactants, industrial chemicals circulated in the markets today were added in their original forms. Also, secondary distilled water was used for the experiment.

Added concentrations of surfactants were 0.1, 0.5, 1.0 g/*l*. After aging, they were taken out in the thermostat, refrigerated quickly and maintained at room temperature. Iron oxide which is dispersed and precipitated in the solution was separated, washed by a centrifugal separator, and then dried at room temperature.

Iron oxide particles were dispersed well in methanol and were analyzed by TEM and XRD.

The reaction product of this experiment is α-Fe_2O_3 and β-FeOOH. The results of XRD are shown in Fig. 1 (α-Fe_2O_3 2θ: 24.3, 33.3, 35.7, 41.0, 49.5, 54.2, 62.5, 64.1, β-FeOOH 2θ: 17.3, 27.3, 34.7, 35.7, 39.8, 47.0, 52.5, 56.2).

RESULTS AND DISCUSSION

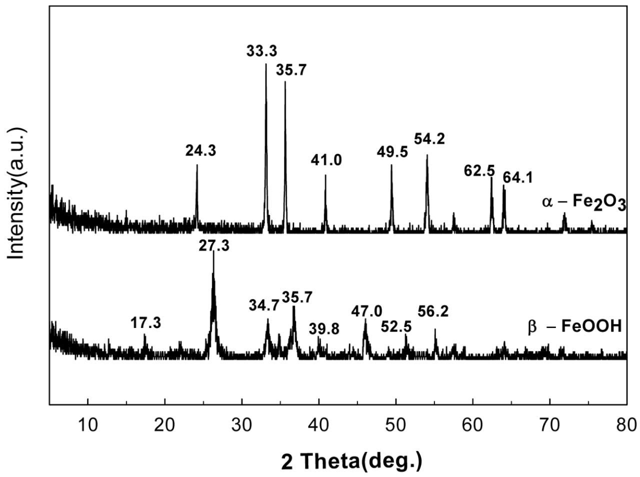

Fig. 1. X-ray diffraction(XRD) spectra of α-Fe_2O_3 and β-FeOOH.

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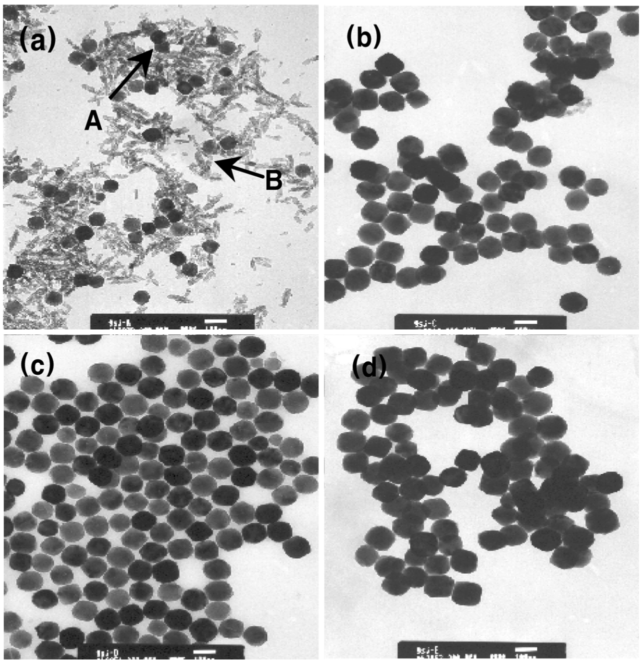

Fig. 2. Transmission electron micrographs (TEM) of α-Fe_2O_3 particles obtained by aging 0.02 M $FeCl_3$ aqueous solution at 100 °C.
(a) 12 hrs (A: α-Fe_2O_3, B: β-FeOOH), (b) 24 hrs, (c) 36 hrs, (d) 48 hrs

0.02 M $FeCl_3$ aqueous solution was matured for 48 hrs at 100 °C, spherical shapes α-Fe_2O_3 were made by hydrolysis. 0.02 M $FeCl_3$ aqueous solution underwent a forced hydrolysis, β-FeOOH was made first. As time passed, β-FeOOH dissolved and disappeared to make α-Fe_2O_3.

We knew that these particles were α-Fe_2O_3 from X-ray analysis results. The concentration of $FeCl_3$ aqueous solution was increased, particle-like rods were made, and identified as β-FeOOH from X-ray analysis result. This process can be seen in Figs. 2. and 3.

The more that $FeCl_3$ aqueous solution concentration was increased, the particle growth was delayed. Even if β-FeOOH is generated, β-Fe_2O_3 is not generated well.

The concentration of the surfactants that was added to 0.02 M $FeCl_3$ aqueous solution was altered by 0.1-1.0 g/*l* in order to study the influence of the surfactants. It was fermented for 48 hours at 100 °C to make a spherical α-Fe_2O_3 particle.

In the cation and amphoteric surfactants, the more the concentration of surfactant increased, the reaction time was decreased. And the reaction was finished in 12 hours. In case of increasing the reaction time, on the contrary, particle size was increased for a lump together. This process can be seen in Fig. 5.

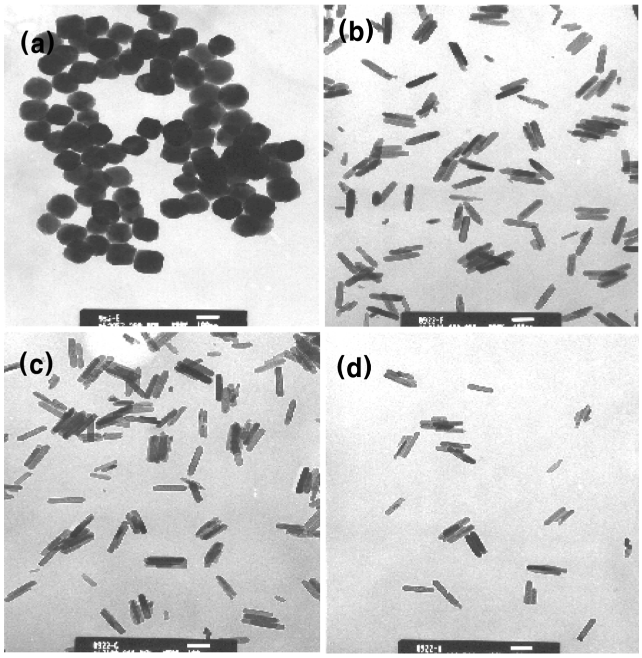

Fig. 3. Transmission electron micrographs (TEM) of α-Fe_2O_3 particles obtained by aging $FeCl_3$ aqueous solution at 100 °C for 48 hrs.
(a) 0.02 M/*l*, (b) 0.05 M/*l*, (c) 0.8 M/*l*, (d) 1.0 M/*l*

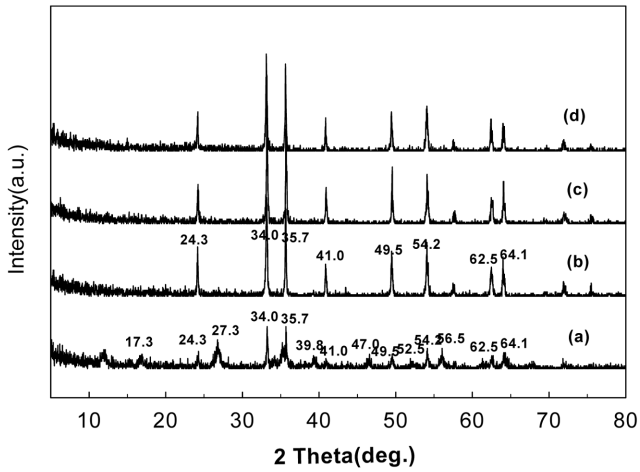

Fig. 4. X-ray diffraction (XRD) spectra of α-Fe_2O_3 particles obtained by aging 0.02 M $FeCl_3$ aqueous solution at 100 °C for 48 hrs.
(a) 12 hrs, (b) 24 hrs, (c) 36 hrs, (d) 48 hrs

In anion surfactant, other types were shown according to chemical composition.

Table 1. Components of surfactants used for manufacture of α-Fe_2O_3

Common name	Type	Chemical component	Producer
MICONIUM DSDM75	Cation	Dimethyldioctadecyl ammonium chloride	Miwon Chem.
MITAIN CA	Amphoteric	*N*-Covoamidopropyl-*N*,*N*-dimethylglycine	Miwon Chem.
Pionin NDA-50	Anion	Sodium dodecylbenzene sulfonate	Cosel Chem.
Pionin CLS	Anion	Calcium ligno sulfonate	Cosel Chem.

Table 2. Properties of products formed with concentration of reactants

$FeCl_3$ conc. (M/*l*)	Product				
	Time (hr)	Color	Particle shape (TEM)	Particle size (TEM)	Crystal structure (XRD)
0.02	48	Dull red	Sphere (Trigonal)	100 nm	α-Fe_2O_3
0.05	48	Yellow	Rod (Tetragonal)	L : 150 nm, L/W=3.5 : 1	β-FeOOH
0.08	48			L : 150 nm, L/W=3.5 : 1	β-FeOOH
0.10	48			L : 140 nm, L/W=3.5 : 1	β-FeOOH

Table 3. Properties of products formed with concentration of surfactants

Surfactant	Product					
	Conc. (gr/*l*)	Time (hr)	Color	Particle shape (TEM)	Particle size (TEM)	Crystal structure (XRD)
None	-	24	Dull red	Sphere (Trigonal)	100 nm	α-Fe_2O_3
MDSDM75	0.1	12	Red	"	"	"
(Cation)	0.5	12	"	"	"	"
	1.0	12	"	"	"	"
MITAIN CA	0.1	12	"	"	"	"
(Amphoteric)	0.5	12	"	"	"	"
	1.0	12	"	"	"	"
Pionin NDA	0.1	12	Dull red	"	"	"
(Anion)	0.5	48	Yellow	Rod (Tetragonal)	-	β-FeOOH
	1.0	48	-	-	-	-
Pionin CLS	0.1	12	Dull red	Sphere (Trigonal)	100 nm	α-Fe_2O_3
(Anion)	0.5	12	"	Rod (Tetragonal)	50-60 nm	β-FeOOH
	1.0	48	-	-	-	-

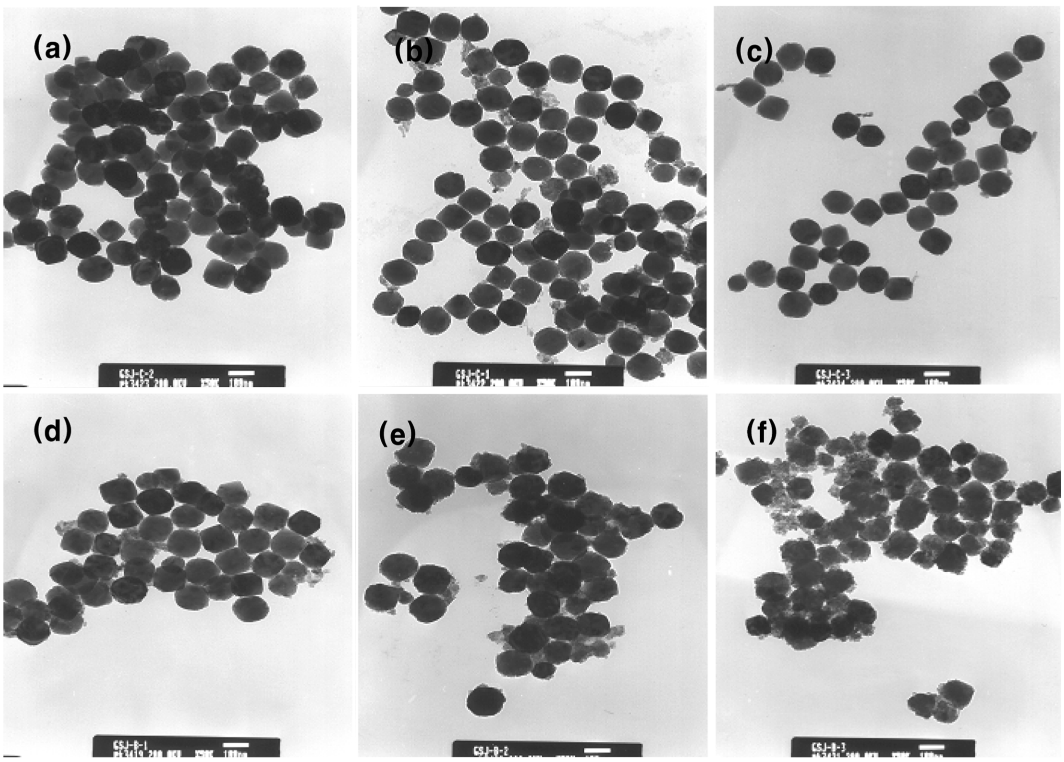

Fig. 5. Transmission electron micrographs (TEM) of α-Fe_2O_3 particles obtained by aging 0.02 M $FeCl_3$ aqueous solution containing MDSDM 75 and MITAIN CA at 100 °C for 12 hrs.
MDSDM 75 (a) 0.1 g/*l*, (b) 0.5 g/*l*, (c) 1.0 g/*l*, MITAIN CA (d) 0.1 g/*l*, (e) 0.5 g/*l*, (f) 1.0 g/*l*.

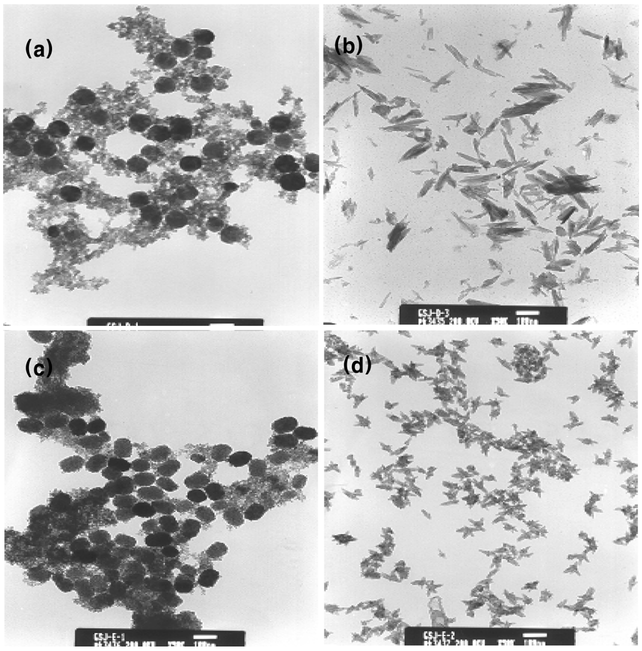

Fig. 6. Transmission electron micrographs (TEM) of α-Fe_2O_3 particles obtained by aging 0.02 M $FeCl_3$ aqueous solution containing Pionin NDA and Pionin CLS at 100 °C for 12 hrs. Pionin NDA (a) 0.1 g/*l*, (b) 0.5 g/*l*, Pionin CLS (c) 0.1 g/*l*, (d) 0.5 g/*l*.

Calcium ligno sulfonate reacted similarly to a cation. On the other hand, Sodium dodecylbenzene sulfonate was made α-Fe_2O_3, as well as the reaction intermediate of β-FeOOH, as the concentration increased, but not as easily. This process can be seen in Fig. 6.

When examined according to the reaction time, β-FeOOH was made first; small particles of α-Fe_2O_3 were made as β-FeOOH dissolved, and these particles assembled to a certain direction to form a spherical α-Fe_2O_3 particle.

Based on these results when 0.02 M $FeCl_3$ aqueous solution was being maintained for 48 hrs, at 100 °C, spherical shapes were made. Whereas rod-shaped β-FeOOH was formed at higher concentrations.

When a surfactant was added, either α-Fe_2O_3 was made easily or only β-FeOOH was made depending on the type of surfactant. Also, the easy formation of α-Fe_2O_3 shortened the reaction time to less than 12 hours. This result is probably because the surfactant reduced the surface tension strength of the reaction solution to increase the diffusion speed of the reaction materials.

CONCLUSIONS

The following results have been found by studying how the addition of a surfactant influenced the sizes and shapes of the particles when 0.02 M $FeCl_3$ aqueous solution was forcefully hydrolyzed in 100 °C temperature to produce an α-Fe_2O_3 particle:

1. When the concentration of $FeCl_3$ aqueous solution increased, either the particle growth displayed clear delays or only a reaction intermediate of β-FeOOH was made, but the making of α-Fe_2O_3 was not as easy.
2. The cation surfactant made a spherical α-Fe_2O_3 particle within 12 hours regardless of the added concentration.
3. The anion surfactant only made β-FeOOH as the concentration increased. However, it made almost no crystals within the 48-hour reaction time to display transparency, and no particle shapes could be observed through an electronic microscope.
4. Generalizing the above information, it is determined that the surfactant decreased the surface tension strength of the reaction solution to increase the diffusion speed of the reaction materials.

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