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The Preparation of Monodispersed α-Iron(III) Oxide Particles from 2,2′-Bipyridineiron(II) Complex

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Monodispersed α-iron(III) oxide (hematite) particles were produced from an iron(II) chloride/2,2′-bipyridine system in the presence of potassium nitrate at elevated temperatures, 90—100 °C. An aqueous solution of 2,2′-bipyridineiron(II) complex directly gave spherical hematite particles (0.35 μm in size with a relative standard deviation of 0.09) under the conditions of 1.0×10^{-3} mol dm^{-3} $FeCl_2$, 3.0×10^{-3} mol dm^{-3} 2.2′-bipyridine, 6.0×10^{-3} mol dm^{-3} HCl, and 5.0×10^{-2} mol dm^{-3} KNO_3 at 100 °C for 8 h. The oxidation of iron(II) ions would be slower than the dissociation of the complex and precipitation during the course of aging. The hematite particles grew through the polynuclear layers mechanism. Iron(II) sulfate/2,2′-bipyridine mixed solutions were also capable of yielding monodispersed particles, though they were a mixture of hematite and α-iron(III) hydroxide oxide (goethite). The points of zero charge (PZC) of these particles were estimated as pH 7.7 and 7.5 for those obtained from the iron(II) chloride and sulfate/2,2′-bipyridine systems, respectively.

The preparation and characterization of monodispersed particles of metal oxide and hydrous oxide have been extensively studied by forced hydrolyses.[1-8] Monodispersed α-iron(III) oxide (hematite) particles have been prepared by aging acidified iron(III) salt solutions at elevated temperatures through the conversion of β-iron(III) hydroxide oxide, β-FeOOH, previously deposited.[2,4,5] On the other hand, an iron(III) chloride/glycine system directly gave monodispersed hematite particles through forced hydrolysis.[9,10] In the latter case, the glycinatoiron(III) complex acts as a soluble reservoir for hydroxoiron(III) complexes at higher temperatures.

In the present work, monodispersed iron(III) oxide and hydroxide oxide particles were prepared by the forced hydrolysis of 2,2′-bipyridineiron(II) complex solutions in the presence of potassium nitrate as an oxidizing agent. Furthermore, the growth process and surface characterization of the monodispersed particles are discussed.

Experimental

Materials. All of the reagents used in this work were of guaranteed grade and employed without further purification. A small amount of iron(III) species in iron(II) chloride and sulfate solutions was reduced with iron of 99.9% in purity (≈200 mesh) and corresponding acid. An aliquot of the iron(II) salt solution was passed through a column charged with an H-type cation-exchange resin (Amberlite IR 120B). Then a concentration of acid, thus replaced, was titrated in order to determine the total number of moles of iron(II) and acid. The concentration of the iron(II) species was determined spectrophotometrically with 2,2′-bipyridine. All of the solutions were previously filtered through a Membrane filter (0.2 μm in pore size) and then deoxygenated by bubbling nitrogen before use.

Procedures. A mixed solution of iron(II) salt, 2,2′-bipyridine, corresponding acid, and potassium nitrate was tightly sealed in a screw-capped glass tube at specified concentrations and then aged at 100±1 and and 90±1 °C for 8—72 h in a thermostatted air oven. The produced particles were centrifuged at 1160 g and washed repeatedly with doubly distilled water using ultrasonic equipment. The morphology and size of the particles were observed with a scanning electron microscope (model ALPHA-10S). The particles were identified using an X-ray diffractometer (model Geigerflex RAD IIIA).

The mixed solution was also aged at 100±0.5 °C for 14 h in an oil bath in order to study the growth process of monodispersed hematite particles from the concentration changes of the iron species remaining in the solution. The aged solution was quenched to room temperature at regular intervals and centrifuged to remove precipitates, followed by filtration through a Membrane filter (0.1 μm in pore size). The total concentration of the iron(II) and (III) species was determined spectrophotometrically with 2,2′-bipyridine after reducing the iron(III) species to iron(II) with hydroxylamine hydrochloride. The concentration of the iron(II) species was separately determined after masking the iron(III) ions with sodium ethylenediaminetetraacetate.

A specific surface area was measured using a modified BET analyzer (model SA1000). The surface charge density of the particles was determined by ordinary potentiometric titration as follows: a sample of 0.40 g was suspended in 50.0 cm^3 of 4.00×10^{-3} mol dm^{-3} potassium hydroxide solution. The suspension was titrated very slowly (≈30 h) with 5.00×10^{-3} mol dm^{-3} nitric acid at 25±0.1 °C under an ionic strength of 0.10 mol dm^{-3} (KNO_3) in a nitrogen atmosphere.

A surface analysis was carried out in order to identify the species adsorbed on the surface of particles using an X-ray photoelectron spectroscope (XPS), model ESCALAB Mk II.

Results

Formation of Monodispersed Hematite Particles from Iron(II) Chloride/2,2′-Bipyridine System. Figure 1 shows the concentration domain of iron(II) chloride and hydrochloric acid for making iron(III) oxide particles by forced hydrolysis at 100±1 °C for 24 h under fixed concentration ratios of $[\mathrm{bpy}]/[FeCl_2]=3.0$ and $[KNO_3]/[FeCl_2]=50$, respectively. Monodispersed spherical particles were directly produced under a

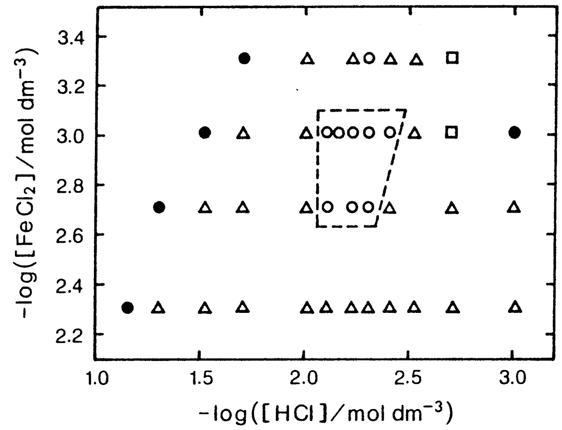

Fig. 1. Concentration domain of FeCl$_2$ and HCl for making hematite particles by forced hydrolysis at 100 °C for 24 h. Conditions: [bpy]/[FeCl$_2$]=3.0, [KNO$_3$]/[FeCl$_2$]=50. Symbols: ○; spherical, □; flower-like, △; irregular, ●; no precipitation. A dashed line indicates the composition range for monodispersed spherical particles.

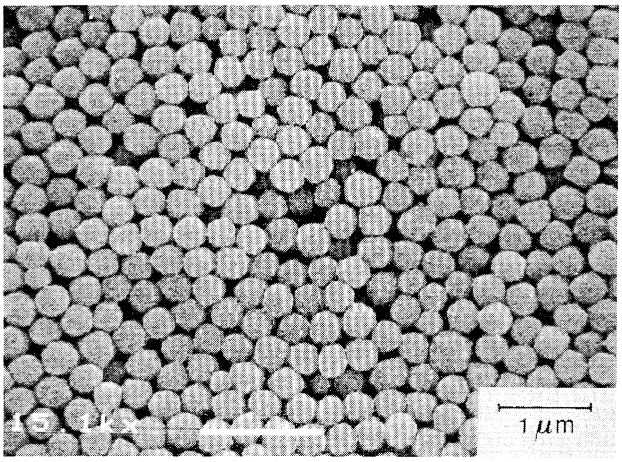

Fig. 2. Scanning electron micrograph of monodispersed spherical hematite particles prepared by forced hydrolysis at 100 °C for 8 h. Conditions: $[\mathrm{FeCl_2}]=1.0\times10^{-3}$, $[\mathrm{bpy}]=3.0\times10^{-3}$, $[\mathrm{HCl}]=6.0\times10^{-3}$, $[\mathrm{KNO_3}]=5.0\times10^{-2}$ mol dm^{-3}.

limited set of conditions (indicated by ○). No particles were observed, even after aging for 72 h, in the region indicated by ●.

Figure 2 shows an example of monodispersed spherical particles obtained at 100±1 °C for 8 h under the conditions given in the figure (an initial pH 2.2 and a final pH 2.3). The average size of these particles was estimated as being 0.35 μm, with a relative standard deviation of 0.09. The spherical particles would be polycrystals or aggregates of well-crystallized fine hematite[11] particles, judging from X-ray powder diffractometry and their morphology. On the other hand, flower-like particles (Fig. 3) were produced under the conditions shown by □, which consisted of mixtures of α-iron(III) hydroxide oxide (goethite)[12] and hematite.

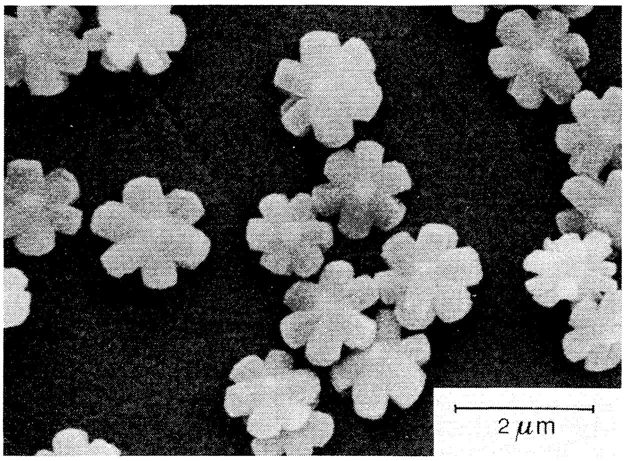

Fig. 3. Scanning electron micrograph of flower-like partilces obtained at 100 °C for 24 h. Conditions; $[\mathrm{FeCl_2}]=5.0\times10^{-4}$, $[\mathrm{bpy}]=1.5\times10^{-3}$, $[\mathrm{HCl}]=2.0\times10^{-3}$, $[\mathrm{KNO_3}]=2.5\times10^{-2}$ mol dm^{-3}.

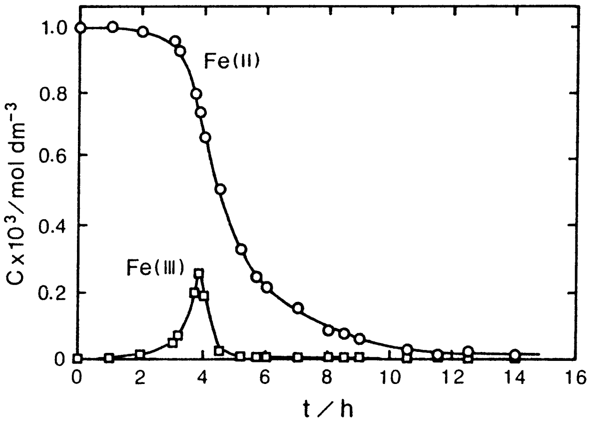

Fig. 4. Concentration changes in Fe(II) and (III) species in supernatant solution during forced hydrolysis at 100 °C in 2,2′-bipyridine/iron(II) chloride system. Conditions: $[\mathrm{FeCl_2}]=1.0\times10^{-3}$, $[\mathrm{bpy}]=3.0\times10^{-3}$, $[\mathrm{HCl}]=6.0\times10^{-3}$, $[\mathrm{KNO_3}]=5.0\times10^{-2}$ mol dm^{-3}.

Concentration Change in Iron Species during Growth of Monodispersed Spherical Hematite Particles in Iron(II) Chloride/2,2′-Bipyridine System. The concentrations of iron species in a supernatant solution were determined at 100±0.5 °C for 14 h in order to elucidate the growth process of monodispersed hematite particles under the conditions given in Fig. 2. Figure 4 shows the concentration changes in both the iron(II) and iron(III) species as a function of the aging time. The concentration of iron(II) species decreased after 1.7 h, as the release and oxidation of iron(II) ions were enhanced. However, the iron(III) species steeply increased up to a maximum value, 2.5×10^{-4} mol dm^{-3}, at 3.8 h and then drastically decreased. At the same time, the particles were generated, following a rapid decrease in the total iron concentration. The concentration of iron(III) species reached a critical supersaturation for spontaneous and rapid nucleation at 3.8 h, followed by a negligibly small concentration of iron (III) species after 4.5 h. The oxidation of iron(II) to the trivalent state, in general, takes place slowly in the presence of nitrate ions, even in a neutral solution.[13] Thus, this process would be a rate-determining step during the growth of hematite particles after iron(II) ions have been released through the dissociation of the 2,2′-bipyridineiron(II) complex.

It has been confirmed that hydroxoiron(III) complexes act as the precursors of iron(III) oxide particles.[14,15] An appropriate supersaturation of hydroxoiron(III) complexes should be maintained in order to produce monodispersed particles[16,17] without secondary nucleation. Thus, the conditions given in the present work would satisfy the above criteria.

Growth Process of Spherical Hematite Particles. The growth process of the spherical hematite particles was examined by following the total concentration of iron species in the supernatant solution during the course of aging (Fig. 4). The reaction degree, α, is defined as

$$\alpha=(C_0-C)/(C_0-C_f), \tag{1}$$

where C_0, C_f, and C are the initial and final concentrations of the iron species, and that at reaction time t, respectively.

Nielsen[18] has proposed that a change in the reaction degree, $d\alpha/dt$, can be expressed by the following equation for the growth of particles through a polynuclear layers mechanism as:

$$d\alpha/dt=KC^{(m+2)/3}\alpha^{2/3}, \tag{2}$$

where the parameters, K and m, stand for the apparent rate constant under the given conditions and the exponent of the concentration dependence for the surface nucleation, respectively.

Parameters m and K[19] were numerically estimated as being 3.53 and 8.53×10^5 by a least-squares method using logarithmic values of $d\alpha/dt$, C, and α. Figure 5 shows the results calculated from Eq. 2 by the Runge-Kutta method using the parameters obtained above. The values, thus obtained (solid curve), agreed well with those observed in a rather wide range of the reaction degree from around 0.1 to 0.9. Similar numerical treatments were also made for the mononuclear layer and diffusion mechanisms. However, calculated values for both the mechanisms did not fit with the experimental ones. Thus, the monodispersed spherical hematite particles would grow through the polynuclear layers mechanism in the iron(II) chloride system, though they were polycrystals or aggregates.

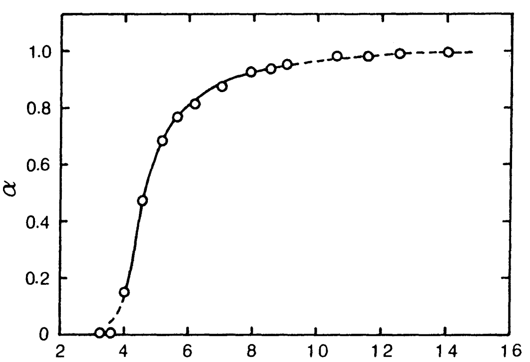

Fig. 5. Change in reaction degree during forced hydrolysis at 100 °C. Conditions: $[FeCl_2]=1.0\times10^{-3}$, $[bpy]=3.0\times10^{-3}$, $[HCl]=6.0\times10^{-3}$, $[KNO_3]=5.0\times10^{-2}$ mol dm^{-3}.

Precipitation of Iron(III) Hydrous Oxide Particles from Iron(II) Sulfate/2,2′-Bipyridine System. Mixed solutions were aged at 100±1 °C for 24 h under the fixed conditions of 5.0×10^{-3} mol dm^{-3} iron(II) sulfate and $[KNO_3]/[FeSO_4]$ ratio of 50, varying concentrations of sulfuric acid from 1.0×10^{-3} to 1.0×10^{-1} mol dm^{-3} and 2,2′-bipyridine from 5.0×10^{-3} to 2.0×10^{-2} mol dm^{-3}.

Spherical particles of a reasonably narrow size distribution were obtained only in a narrow composition range of sulfuric acid from 4.0×10^{-3} to 5.0×10^{-3} mol dm^{-3} (an initial pH 2.2—2.3) and $[bpy]/[FeSO_4]$ ratios between 2.7 and 3.3. Figure 6 shows an example of the particles comprising a mixtures of hematite and goethite, in contrast to the particles obtained in the iron(II) chloride system. Their average size was estimated as being 2.9 μm with a relative standard deviation of 0.12, much larger than those obtained in the chloride system.

Sulfate ions, in general, promote the polymerization of hydroxometal complexes, while the condensation reaction is much slower than the former.[20] Thus, hydroxoiron(III) complexes easily generate the goethite partly framed by -OH- bridges with the aid of sulfate ions, which lead to coprecipitated larger particles.

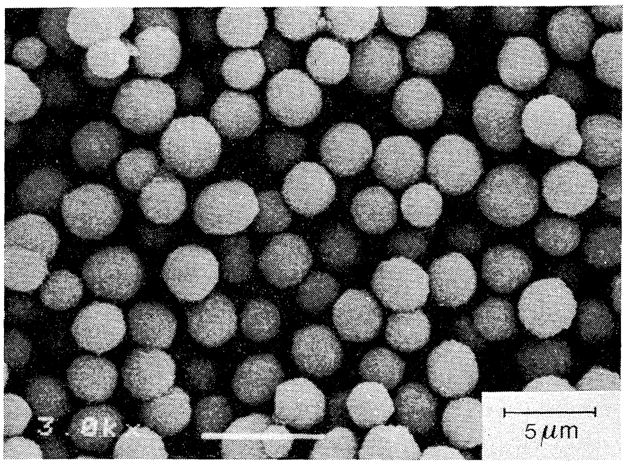

Fig. 6. Scanning electron micrograph of spherical particles obtained from 2,2′-bipyridine/iron(II) sulfate mixed solution at 100 °C for 8 h. Conditions: $[FeSO_4]=5.0\times10^{-3}$, $[bpy]=1.5\times10^{-2}$, $[H_2SO_4]=5.0\times10^{-3}$, $[KNO_3]=2.5\times10^{-1}$ mol dm^{-3}.

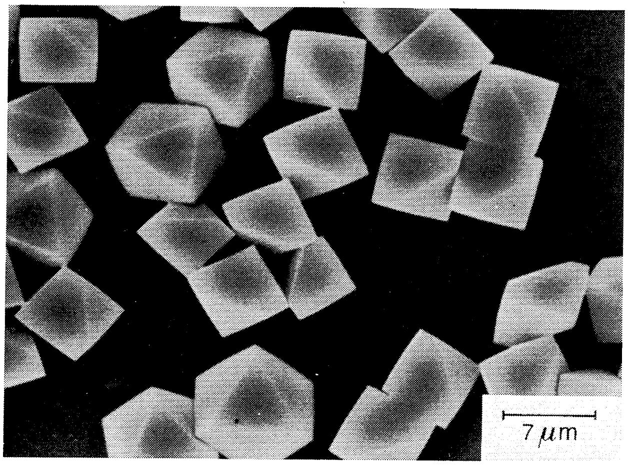

Fig. 7. Scanning electron micrograph of hydronium jarosite particles produced from 2,2′-bipyridine/iron (II) sulfate mixed solution at 100 °C for 72 h. Conditions: $[FeCl_2]=5.0\times10^{-3}$, $[bpy]=5.0\times10^{-3}$, $[H_2SO_4]=7.1\times10^{-2}$, $[KNO_3]=2.0\times10^{-1}$ mol dm^{-3}.

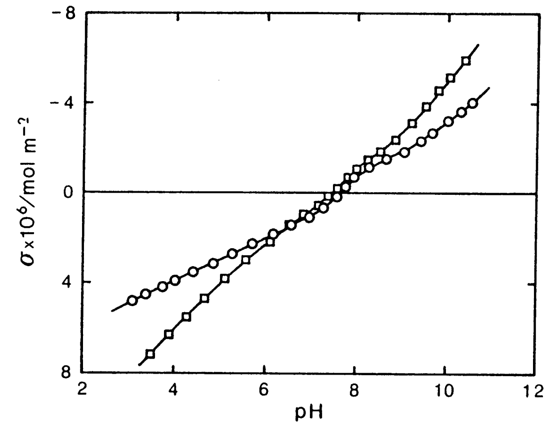

Fig. 8. Surface charge densities of spherical particles at 25 °C and $I=0.1$ mol dm^{-3}. Symbols: ○; hematite particles obtained from iron(II) chloride system, □; mixed particles of hematite and goethite obtained from iron(II) sulfate system.

On the other hand, well-crystallized particles (Fig. 7) were created at rather higher sulfuric acld concentrations (from 5.0×10^{-2} to 7.1×10^{-2} mol dm^{-3}, an initial pH 1.1—1.2), independently of the [bpy]/[FeSO$_4$] ratio. They were identified as hydronium jarosite, $Fe_3(SO_4)_2(OH)_5\cdot2H_2O$,[21,22] by X-ray powder diffractometry, in analogy with that reported.[1] According to the formation constant and enthalpy change of protonation of 2,2′-bipyridine,[23,24] iron(II) ions would hardly form a complex with this ligand in such a low pH range (1.1—1.2). However, iron(II) ions can easily produce the sulfato complex in the presence of a large amount of sulfate ions due to their affinity.[25] Thus, these complex ions generate hydronium jarosite, independently of the [bpy]/[FeSO$_4$] ratio.

Spherical particles of reasonably narrow size distribution were also obtained at 90±1 °C under the same conditions given in Fig. 6, of which the average size was 2.0 μm with a relative standard deviation of 0.11. The composition of these particles varied depending on the duration of aging. Only goethite precipitated as spherical particles at 90±1 °C, while the particles changed to a mixture of goethite and hematite by prolonged aging for 120 h.

Goethite is irreversibly converted to hematite through topotatic dehydration due to similar oxygen stackings in their crystal structure.[26] However, the goethite scarcely changes to hematite in a solution after the former has been deposited, even though -O- bridge is more stable than -OH- bridge.[27,28] Thus, the hematite that becomes incorporated with the goethite would be directly generated during the prolonged aging at 90 °C and not through the conversion of the previously deposited goethite.

Surface Characterization of Monodispersed Spherical Particles. Surface charge densities of the particles were determined by an ordinary potentiometric titration for those obtained from the iron(II) chloride and sulfate systems. The particles were washed twenty times with doubly distilled water using ultrasonic equipment. Then they were further treated with a 1.0×10^{-4} mol dm^{-3} potassium hydroxide solution, followed by washing again twenty times with doubly distilled water. Figure 8 shows the surface charge densities of the particles as a function of pH.

The points of zero charge (PZC) were estimated as being of almost the identical pH (7.7 and 7.5) for particles prepared from the iron(II) chloride and sulfate systems, respectively. However, the PZC of the particles made from the latter was apparently found to be as low as pH 3.7 if the alkali-treatment had not been carried out, whereas that of the particles prepared from the former was approximately the same pH (7.5).

It has been reported that sulfate ions are strongly adsorbed on the surfaces of goethite particles, depending on the pH.[29] The sulfate ions would be easily replaced by hydroxide ions in an alkaline solution. Actually, the titration on the particles (the sulfate system) indicated much lower pH values, especially during the early stage of titration, as a result of the consumption of hydroxide ions. Thus, the value of PZC was apparently found to be as low as pH 3.7. According to the XPS, sulfur was detected from the surface of these particles, in contrast with those prepared from the iron(II) chloride system. A trace amount of sulfur was still detectable, even after these particles had been alkali-treated, as mentioned above, and by etching them with Ar$^+$ ions for 10 min in the XPS instrument. This result indicated that sulfate ions were also internally included, not only on the surfaces of the particles.

Discussion

Hydroxoiron(III) complexes have been proposed to serve as the precursors of iron(III) oxide.[15] An enthalpy change for the formation of 2,2′-bipyridineiron(II) complex has been determined as −105—−131 kJ mol^{-1}.[23,30,31] Thus, this complex should dissociate at elevated temperatures. Figure 9 shows the absorption spectra of the 2,2′-bipyridineiron(II) complex at different temperatures. The intensity of the spectra markedly decreased with increasing temperature. These facts confirmed the above consideration.

A direct oxidation of 2,2′-bipyridineiron(II) complex is unlikely because the formal oxidation-reduction potential, $E^{0\prime}$, of the $[Fe(bpy)_3]^{3+}/[Fe(bpy)_3]^{2+}$ couple (+1.120 V)[32] is much larger than that of the Fe(II)/Fe(III) couple (+0.74 V in 0.2 mol dm^{-3} HNO_3).[33] Furthermore, 2,2′-bipyridineiron(III) species would quickly oxidize iron(II) ions (a rate constant, $k=2.7\times10^4$ l mol^{-1} s^{-1} at 25 °C),[34] even if the direct oxidation of 2,2′-bipyridineiron(II) took place.

The stability of 2,2′-bipyridine, itself, was examined under the conditions given in this work using its own absorption band from 250 to 300 nm. A solution contained 1.5×10^{-2} mol dm^{-3} 2,2′-bipyridine, 5.0×10^{-3} mol dm^{-3} sulfuric acid, and 2.5×10^{-1} mol dm^{-3} potassium nitrate was heat-treated at 100 °C for 24 h. Little change in the intensity of the absorption band indicated that 2,2′-bipyridine scarcely decomposed under these conditions.

These facts clearly indicated that the iron(II) ions were released by only the dissociation of the complex, not by the degradation of the ligand at higher temperatures. Then, iron(II) ions were oxidized to the trivalent state by coexisting nitrate ions, followed by forced hydrolysis. Thus, the 2,2′-bipyridineiron (II) complex acted as a soluble reservoir of hydroxoiron(III) complexes for the iron(III) oxide and hydroxide oxide particles.

Monodispersed spherical particles were obtained at almost the same pH range (2.2—2.4) in both the iron (II) chloride and sulfate systems. Hydroxoiron(III) complexes should be controlled at a suitable supersaturation for making monodispersed oxide particles by adjusting the iron(II) salt concentration and pH of the starting solution. The kind of anions present also affect the shape, size, and chemical composition of the particles.[3,6] As mentioned above, the optimum conditions were limited to within a relatively narrow range.

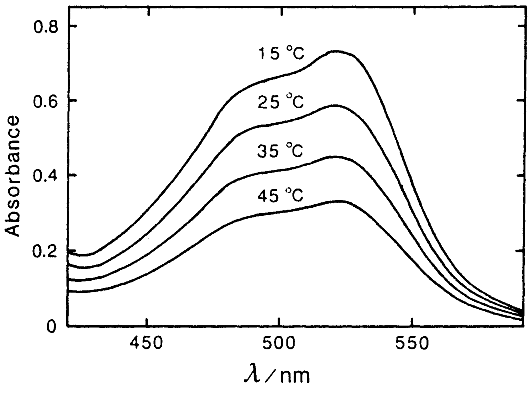

Fig. 9. Spectra of 2,2′-bipyridineiron(II) complex solution at different temperatures. Conditions: $[FeSO_4]=1.6\times10^{-4}$, $[bpy]=4.8\times10^{-4}$, $[H_2SO_4]=5.0\times10^{-3}$ mol dm^{-3}.

Table 1. Effect of Potassium Nitrate Concentration on Formation of Hematite Particles at 100°C[a)]

Sample	$\frac{[KNO_3]}{[FeCl_2]}$	$\frac{d}{\mu m}$	RSD[b)]	Morphology
A	5			Irregular
B	10	1.11	0.21	Spherical
C	25	0.61	0.16	Spherical
D	50	0.39	0.14	Spherical
E	100	0.32	0.17	Spherical

a) $[FeCl_2]=1.0\times10^{-3}$, $[bpy]=3.0\times10^{-3}$, $[HCl]=6.0\times10^{-3}$ mol dm^{-3}; aging time: 94 h (A), 24 h (B—E). b) Relative standard deviation.

The oxidation rate of iron(II) ions is also an important factor for making monodispersed particles. One effect of the oxidant concentration on the morphology and size of the particles was examined by varying the concentration ratio, $[KNO_3]/[FeCl_2]$, from 5 to 100. As shown in Table 1, spherical particles of the narrowest size distribution could be obtained at a concentration ratio of 50 under these experimental conditions, whereas the average size normally decreased from 1.11 to 0.32 μm owing to a rapid oxidation of iron(II) species as the concentration ratio increased from 10 to 100. Thus, this concentration ratio of 50 was taken in the present work.

Nitrate ions, in general, scarcely coordinate with iron(III) ions, so that they hardly affect the nucleation and growth rates by surface complexation but by oxidation. On the other hand, much faster oxidation makes longer nucleation periods, leading to polydispersed particles.

The concentration ratio of 2,2′-bipyridine to iron(II) ions was also sensitive for making monodispersed particles, especially in the iron(II) sulfate system. It is well known that 2,2′-bipyridine coordinates with iron(II) ion at a molar ratio of 3 : 1. Therefore, the stability of this complex would be greatly dependent on the ratio, [bpy]/[Fe(II)], and the pH of the solution.

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