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ORIGINAL CONTRIBUTION

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Study on the hydrothermal reaction of $FeCl_3$ solution in the presence of poly(vinyl alcohol)

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Abstract A 0.5 dm^3 aqueous solution of 0.1 M $FeCl_3$ dissolving 1 wt% poly(vinyl alcohol) (PVA) was treated hydrothermally in a stainless steel autoclave at various temperatures ($T_h = 110$–200 °C). Highly ordered red corpuscle-like hematite particles around 2 μm in diameter were produced after aging the solution at $T_h = 110$ °C for 7 days, though large numbers of spherical PVA microgels around 2–4 μm in diameter were produced together with the red corpuscle-like particles at $T_h \geq 120$ °C. The number of red corpuscle-like hematite particles decreased but that of spherical PVA microgels increased with increasing T_h, leading to the proposal that the method carried out in the present study will become a new synthetic method of polymer microgels. The ferric ions acted as a cross-linking agent to make PVA insoluble in water. The red corpuscle-like hematite particles produced at $T_h = 110$ °C had high specific surface areas and showed high mesoporosity. The mesoporosity appeared to be more pronounced after evacuating the particles above 300 °C. The diameter of the mesopores after evacuation above 300 °C ranged from 2 to 20 nm, with a maximum at around 5–6 nm. The H_2O and N_2 adsorption experiments revealed that there are no ultramicropores in the particles. The H_2O and CCl_4 adsorption experiments further disclosed that the surface hydrophobicity of the particles is low even though PVA molecules remain after evacuation of the particles at 100–400 °C. Furthermore, the micropores produced after evacuation of the particles at 400 °C exhibited a high size restriction effect, i.e., the micropores produced were accessible to H_2O (diameter 0.253 nm) and N_2 (diameter 0.318 nm) molecules but not to CCl_4 (diameter 0.514 nm).

Keywords Hydrothermal reaction · Hematite · $FeCl_3$ solution · Corpuscle-like particle · Mesoporosity

Introduction

So far, many studies have been done on the preparation of monodispersed hematite particles from a forced hydrolysis reaction of acidic Fe^{3+} ions at 100 °C [1, 2, 3, 4, 5, 6]. These studies revealed that the monodispersity and morphology of the hematite particles strongly depend on different factors, such as the concentration of Fe^{3+} ions, the kinds of vessels and additives, pH, temperature, and aging time. In the last decade, our research group has also extended the investigation on the forced hydrolysis reaction of acidic $FeCl_3$ solutions [7, 8, 9]. Efforts are still continuing to produce monodispersed iron oxide particles as ideal constituents for varieties of advanced materials. Nowadays, the hydrothermal precipitation method receives much attention because this technique represents the most promising route for low-cost production of advanced ceramic materials with characteristics suitable for the final application; i.e., either in batch reactors or in continuous reactors [10, 11, 12].

In a previous study, we reported the hydrothermal reaction of a 0.1 M $FeCl_3$ aqueous solution at hydrothermal temperatures between 110 and 200 °C. Highly ordered cubic particles around 2 μm in edge length and uniform micropores of 0.8 nm in diameter were produced at low T_h, though the cubic particles became less uniform in both shape and pore size by raising T_h [13]. The effects of polymers on the formation of spherical hematite particles produced by a forced hydrolysis reaction at 100 °C were recently reported [14]. Poly(ethylene glycol) (PEG) inhibited the phase transformation from β-FeOOH, first precipitates of the reaction, to hematite by adsorbing onto both β-FeOOH and the primary polynuclear particles formed when β-FeOOH was dissolved. The hematite produced with PEG consisted of micronmeter-sized spherical particles and changed to a highly nanoporous material by evacuation at 200 °C, i.e., PEG acts as a prominent templating agent for providing nanopores. In the case of poly(vinyl alcohol) (PVA), the hematite particles were disklike and consisted of cluster particles with a diameter of around 5–10 nm formed by aggregation of the primary polynuclear particles [15]. These particles drastically changed from microporous to mesoporous by elimination of residual PVA molecules adsorbing on cluster particles on raising the evacuation temperature above 300 °C. To our knowledge, however, no study has been done on the preparation of hematite from the hydrothermal reaction of Fe^{3+} ions with polymers. The hydrothermal conditions of an aqueous medium correspond to temperature and pressure higher than 100 °C and 100 kPa. Such conditions allow considerable modifications of the chemistry of cations and polymers in solution. Therefore, new hematite particles different in morphology and microstructure are expected to be formed by the hydrothermal technique in the presence of polymers. From this point of view, we investigated in this study the hydrothermal reaction of a 0.1 M $FeCl_3$ aqueous solution at various hydrothermal temperatures in the presence of 1 wt% PVA.

Experimental

Analytical grade reagent $FeCl_3 \cdot 6H_2O$ and PVA (degree of polymerization 577, degree of saponification 90) from Wako Pure Chemical were used as starting materials. The experimental conditions are shown in Table 1 along with the minimal aging time for providing a single hematite phase, *t*, and the pH values of the solutions after the reaction. The synthetic process was as follows. A 0.5 dm^3 aqueous solution containing 0.1 M $FeCl_3$ and 1 wt% PVA was prepared in a 1.0 dm^3 glass beaker and set in a 1.5 dm^3 stainless steel autoclave. The autoclave was tightly sealed and heated in a forced conventional oven at the desired T_h (110–200 °C) for different periods of 1–7 days. After cooling, the solid samples were filtrated and washed several times with distilled water to make the precipitates free from chloride by checking with silver nitrate solution. Finally, the precipitates were dried at 70 °C for 20 h.

The particles produced were characterized by the following complementary means. X-ray powder diffraction (XRD) was measured using a Rigaku RU-200B diffractometer (Cu Kα, 200 mA and 40 kV). IR spectra of these particles in KBr pellets were recorded with a Nicolet Fourier transform (FT) IR spectrometer (Protégé 460). The morphology of the particles was observed using a JEOL scanning electron microscope (SEM: JSM-840A and JSA-5600) and a JEOL transmission electron microscope (TEM: 200B). Thermogravimetry (TG) and differential thermal analysis (DTA) were performed simultaneously using a Seiko thermal analyzer (SSC5200) at a heating rate of 5 °C min^{-1} in an air stream. The N_2 adsorption isotherm was recorded volumetrically step by step at a liquid N_2 temperature by an automatic setup built in our laboratory. The adsorption isotherms of H_2O and CCl_4 were determined gravimetrically at 25 °C with an automatic quartz spring balance designed in our laboratory. Prior to these adsorption experiments, the samples were evacuated at 100–400 °C for 2 h.

Results and discussion

Conditions for hematite precipitation and particle morphology

The *t* values determined by the XRD and TEM experiments and final pH values of the solutions at each T_h employed are shown in Table 1. This table suggests, for example, at $T_h = 110$ °C, that a single hematite phase is obtained after aging the solution at 110 °C for 7 days though aging for less than 6 days gives a mixture of hematite and rodlike β-FeOOH particles. The *t* value is reduced by an increase in T_h and finally it becomes 1 day at $T_h \geq 160$ °C, showing the same trend as the hydrothermal reaction of $FeCl_3$ solution without PVA reported before [13]. This can be regarded as a reasonable result because the precipitation is the result of polycondensation involving the hydrolysis of metal ions in solution and the condensation of hydroxylated complexes:

Table 1 Experimental conditions and results of hydrothermal reaction of a 0.5 dm^3 aqueous solution of 0.1 M $FeCl_3$

Hydrothermal temperature T_h (°C)	Minimal aging time for providing hematite single phase, *t* (days)	pH (at room temperature)
110	7	0.79
115	7	0.73
120	6	0.71
130	4	0.68
140	2	0.61
160	1	0.66
180	1	0.64
200	1	0.56

$$\mathrm{Fe-OH+HO-Fe \rightarrow Fe-O-Fe+H_2O} \tag{1}$$

$$\mathrm{Fe-(OH)-Fe \rightarrow Fe-O-Fe+H^+} \tag{2}$$

Additionally, the basicity of Cl^- ions in aqueous media becomes higher on increasing the solution temperature as expressed by the following reaction [16]:

$$\mathrm{Cl^- + H_2O \rightleftharpoons HCl + OH^-} \tag{3}$$

It has been reported that the equilibrium constant of Eq. (3) at 500 °C and 200 MPa is 9 orders of magnitude higher than at normal conditions in water [16]. Therefore, the hydrolysis reaction could be enhanced under hydrothermal conditions.

Typical SEM pictures of the hematite particles produced at various T_h are shown in Fig. 1. At 110 °C, highly ordered red corpuscle-like particles with large dimples on both sides of the disklike particles are produced. On raising T_h, the number of these unique red corpuscle-like particle decreases, they become thinned and many large spherical particles are produced. The TEM observation clarified that all the red corpuscle-like particles produced consist of cluster particles which were formed by aggregation of the primary polynuclear particles (pictures not shown). All particles produced at $T_h \leq 160$ °C gave the characteristic XRD pattern of pure hematite (JCPDS 33-664) but the XRD patterns are broadened and the diffraction peaks disappear at $T_h \geq 180$ °C (Fig. 2). This change strongly suggests that the number of hematite particles is reduced and the material becomes less crystalline even though the hydrothermal reaction was

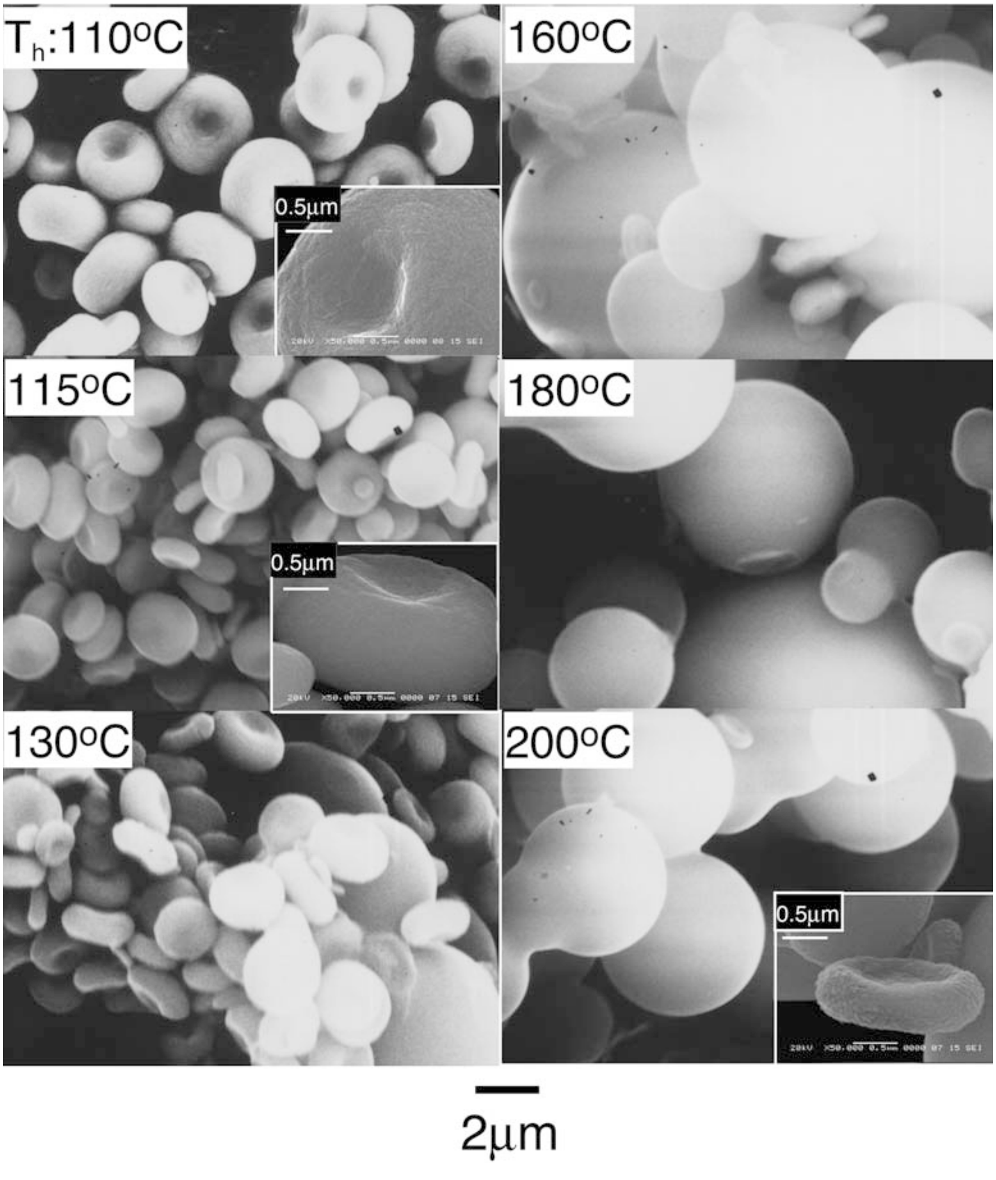


Fig. 1 Scanning electron microscope pictures of particles precipitated at various hydrothermal temperatures

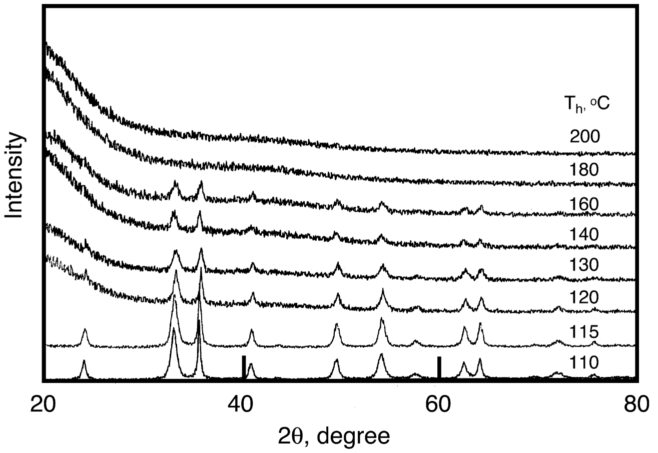


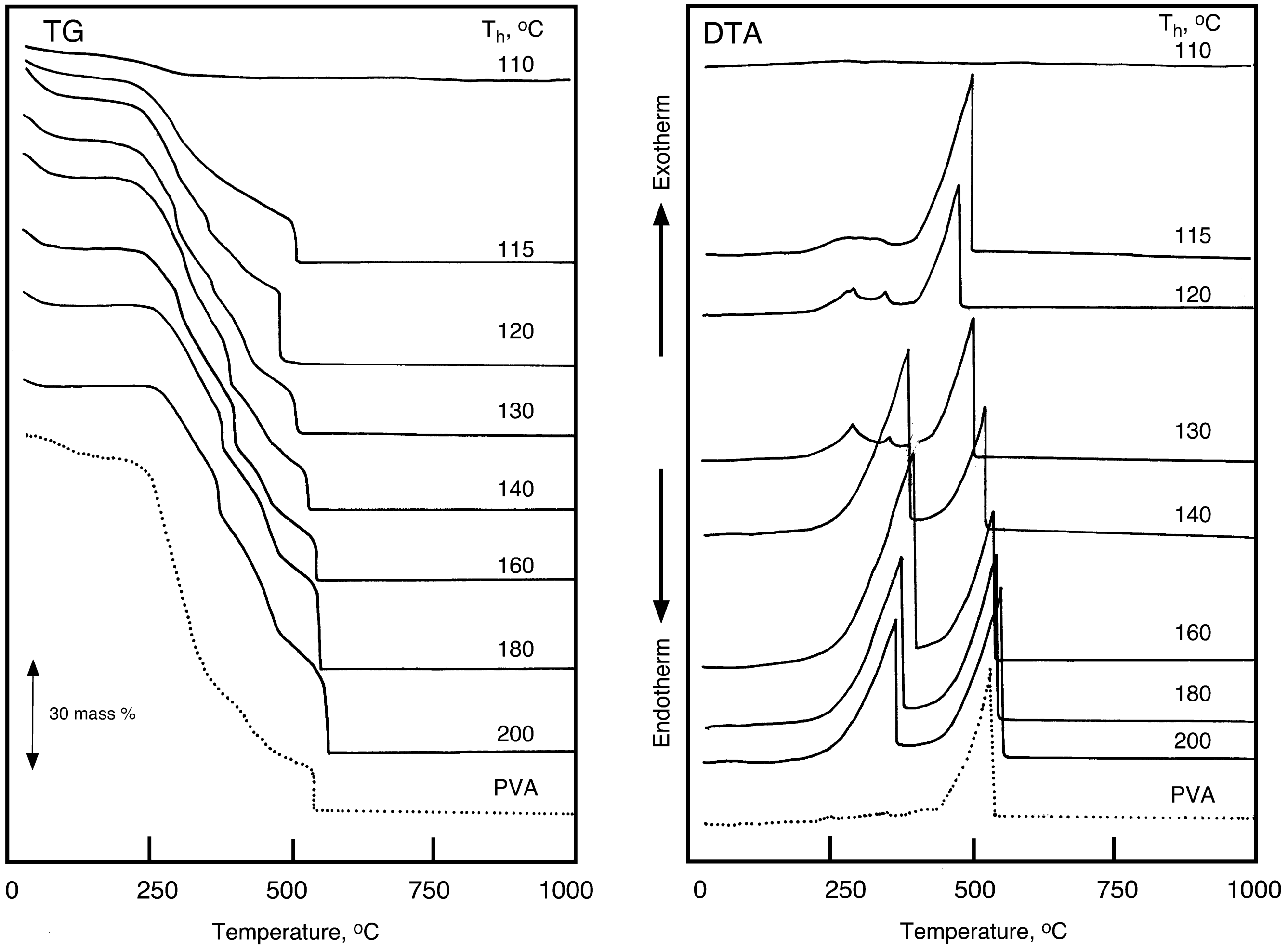
Fig. 2 X-ray diffraction patterns of particles precipitated at various hydrothermal temperatures

carried out at high T_h. Then large spherical particles detected by the SEM at $T_h \geq 120$°C (Fig. 1) are amorphous.

Thermogravimetry–differential thermal analysis

TG–DTA curves of the particles are displayed in Fig. 3. The hematite produced at 110 °C has two small weight loss steps at 100–300 and 700–1,000 °C. The DTA curve has endothermic peaks at corresponding steps though it is hard to recognize these TG steps and DTA peaks in Fig. 3 because of its large scale fitting for other materials including PVA. On raising T_h, the TG curves exhibit three distinct steps, at 25–200 °C, from 200 to around 500 °C and at around 500 °C. There are many small steps in the second step. The DTA curves exhibit a few exothermic peaks at 250–350 and 480–520 °C, corresponding to the second and third steps in the TG curves. These three steps agree fairly well with those observed for pure PVA, implying that the first step in the TG curves is due to the elimination of H_2O adsorbed on hematite particles and PVA molecules. The second and

Fig. 3 Thermogravimetry (*TG*)–differential thermal analysis (*DTA*) curves of particles precipitated at various hydrothermal temperatures



third steps are caused by the combustion of PVA molecules in the materials. A sharp DTA peak at around 360–380 °C, which is absent for pure PVA, may be due to the combustion of PVA molecules included in the red corpuscle-like particles because the disklike hematite particles (average diameter around 600 nm) with residual PVA molecules produced by the forced hydrolysis at 100 °C had a similar exothermic peak in the same temperature region [15]. The large weight losses at the second and third steps (45–100%) suggest that the large spherical particles in the SEM pictures are microgel particles of PVA. Insolubility of PVA in water by complexation with Cu, Al, Ti, Zn, Sr, and Cr ions has been reported [17, 18]. The Fe ions may act as a similar inorganic cross-linking agent. Since the hematite particles can be dissolved in hydrochloric acid aqueous solution, this result suggests that the hydrothermal technique will become a new preparation technique of PVA microgel particles with fairly uniform particle sizes.

FTIR spectra

The PVA molecules in the materials can be further identified by IR spectra (Fig. 4). The fundamental Fe–O stretching bands of hematite at 457 and 553 cm^{-1} are weakened by increasing T_h, suggesting that the number of hematite particles is decreased. Furthermore, a very strong and broad band at 3,300–3,400 cm^{-1} is ascribed to stretching modes of surface water molecules or to the hydrogen-bonded surface OH groups of hematite and PVA. A C–H stretching mode of PVA molecules can be seen at 2,800–2,900 cm^{-1}. Actually, the intensity of this peak increases with T_h, suggesting that the number of PVA microgels is enhanced. The absorption peaks of the C–O stretching vibration and O–H bending vibration of the PVA molecules appear at 1,104 cm^{-1} and at 1330, 1375, and 1432 cm^{-1}, respectively. Another peak of the C=O stretching vibration appears at 1,701 cm^{-1}. Since this mode of vinyl acetate gives a peak not lower than 1,720 cm^{-1}, the 1,701-cm^{-1} band cannot have originated from vinyl acetate. Probably, this peak can be assigned to aldehyde groups produced by dehydration of dihydroxyl groups, followed by hydrolysis of PVA at high T_h.

$$\begin{aligned}&-CH_2-CH(OH)-CH_2-CH(OH)-CH_2-\\&\quad\rightarrow -CH_2-CH(OH)-CH_3+(HO)_2CH-CH_2\\&\quad\rightarrow -CH_2-CH(OH)-CH_3+CHO-CH_2-\end{aligned} \tag{4}$$

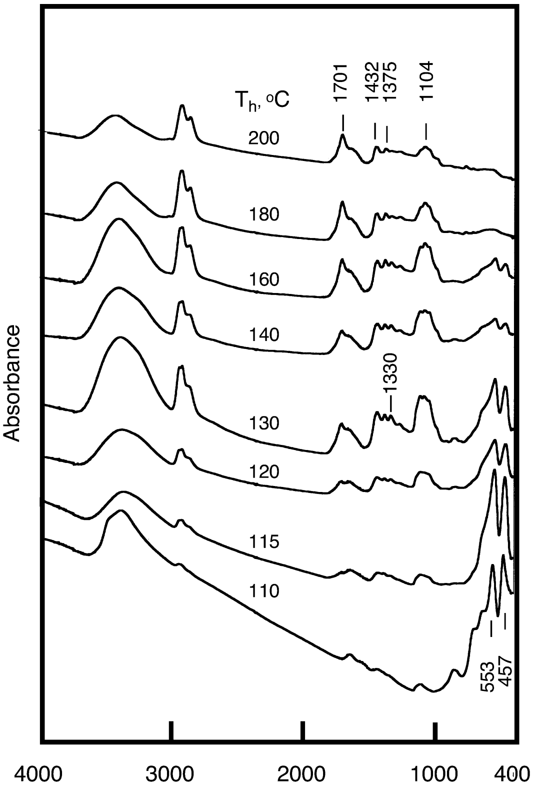


Fig. 4 Fourier transform IR spectrum of particles precipitated at various hydrothermal temperatures

X-ray diffraction

The unit cell dimensions of the particles are plotted in Fig. 5 as a function of T_h. The lattice parameter *a* of the particles fits the literature value of the unit cell dimension of hematite(dotted line in Fig. 5) [19]. In contrast, the lattice parameter *c* increases with increasing T_h,

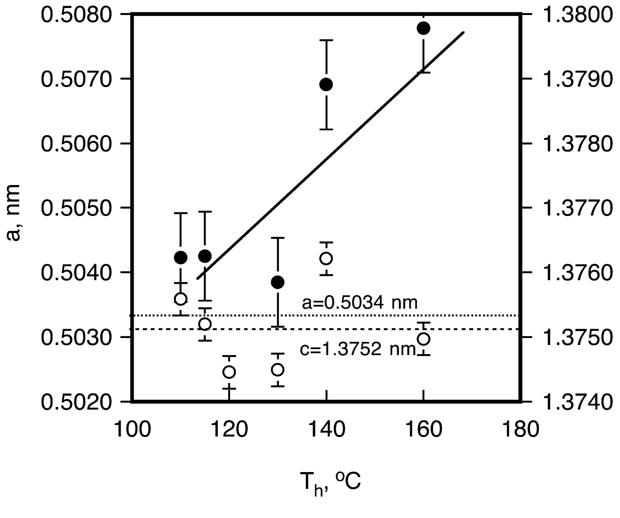


Fig. 5 Changes in *a* and *c* unit cell parameters of hematite particles precipitated at various hydrothermal temperatures, T_h, from 110 to 160 °C. *a* (*open circles*)and *c* (*filled circles*) unit parameters

indicating that the enlargement of lattice parameter *c* occurs by the hydrothermal method. The enlarged lattice parameter *c* is explained by the formation of hydrohematite and considering the replacement of O^{2-} ions with OH^- ions to compensate the charge imbalance resulting from Fe^{3+} vacancies [20]. The presence of OH^- ions in the particles was also verified by a broad adsorption band centered at around 3,400 cm^{-1} in the IR spectra (Fig. 4).

Gas adsorption

The microstructure of the particles was evaluated by gas adsorption using N_2, H_2O, and CCl_4 as adsorptives. Since the single hematite phase was obtained only at $T_h = 110$ °C, these measurements were only performed for this sample. The adsorption isotherms of N_2 on the red corpuscle-like particles after evacuation at 100–400 °C for 2 h are shown in Fig. 6a. All adsorption isotherms exhibit type IV (in the IUPAC classification), especially for the particles evacuated above 300 °C, indicating that the particles are mesoporous. The pore size distribution histograms obtained by applying the Cranston-Inkley method [21] to the N_2 adsorption isotherms are shown in Fig. 6b. This figure strongly reveals that the particles contain mesopores with diameters ranging from 2 to 20 nm with a maximum of around 5–6 nm after outgassing above 300 °C (filled symbols), while the particles possess mesopores with a maximum diameter of around 2 nm at 100 and 200 °C (open symbols) [22]. The disklike particles produced by the forced hydrolysis reaction with PVA at 100 °C drastically changed from microporous to mesoporous by increasing the outgassing temperature [15]. This different porosity between disklike and red corpuscle-like particles can be due to the different reaction temperature and particle size. The hematite particles produced in the present work are aggregates of cluster particles as was confirmed by TEM observation described before. The large voids between the cluster particles filled with PVA molecules within the red corpuscle-like particles may produce mesopores. The adsorption isotherms of H_2O and CCl_4 are displayed in Figs. 7 and 8. The H_2O adsorption isotherms in Fig. 7a are of type II and the amount of H_2O adsorbed decreases on raising the evacuation temperature. Since the affinity of adsorptive molecules to the particle surface is great in the initial adsorption step, the isotherms at very low relative pressure up to $p/p^0 = 0.01$ are shown in Fig. 7b. The adsorption of H_2O is reduced by raising the evacuation temperature, suggesting that the particles become hydrophobic (the number of adsorption sites of H_2O molecules is reduced) or the number of ultramicropores that are accessible to H_2O but not to N_2 molecules decreases. To evaluate the ultramicroporosity of the particles, the specific surface area ratio, S_w/S_N, was evaluated from the H_2O and N_2 adsorption experiments by fitting the isotherms to the Brunauer–Emmett–Teller equation (Fig. 9). Here, 0.108 and 0.162 nm^2 were used for the cross-sectional areas of H_2O and N_2, respectively [22]. The S_N values thus obtained were 67, 79, 69, and 60 $m^2\ g^{-1}$ after outgassing at 100, 200, 300, and 400 °C, respectively. These S_N values are much larger than the specific surface area of 0.6 $m^2\ g^{-1}$ estimated from the size of the particles by assuming the disklike particles are rigid with a density of 5.2 g cm^{-3}. This fact suggests that the red corpuscle-like particles are highly porous. The S_w/S_N ratios (Fig. 9) are less than unity and decrease with increasing T_h. This indicates that there are no ultramicropores in the particles. This fact may be due to the less crystallized, loosely packed hematite particles

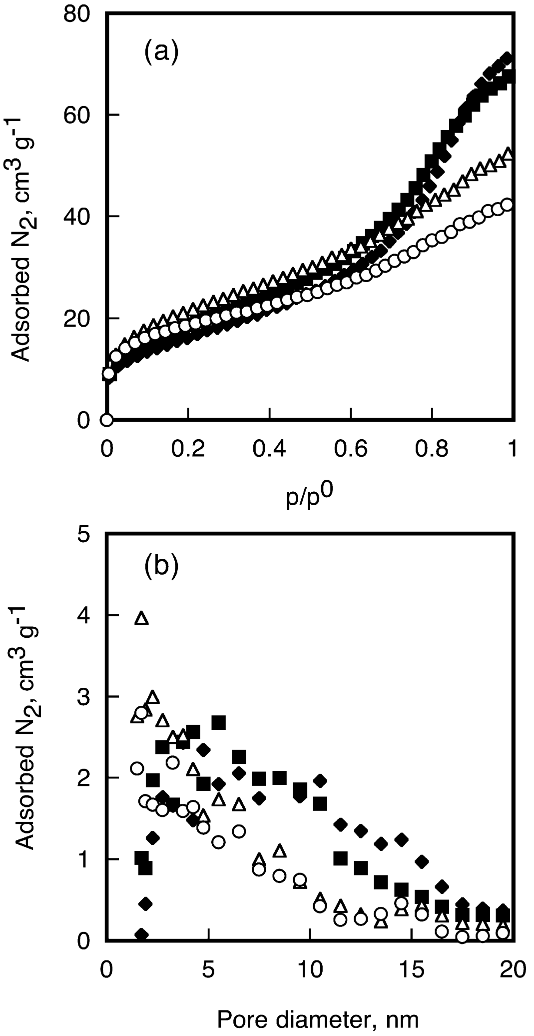


Fig. 6 **a** Adsorption isotherms of N_2 and **b** their pore-size distribution histograms on red corpuscle-like hematite particles precipitated at 110 °C. T_h (°C): 100(*circles*), 200 (*triangles*), 300 (*squares*), 400 (*diamonds*)

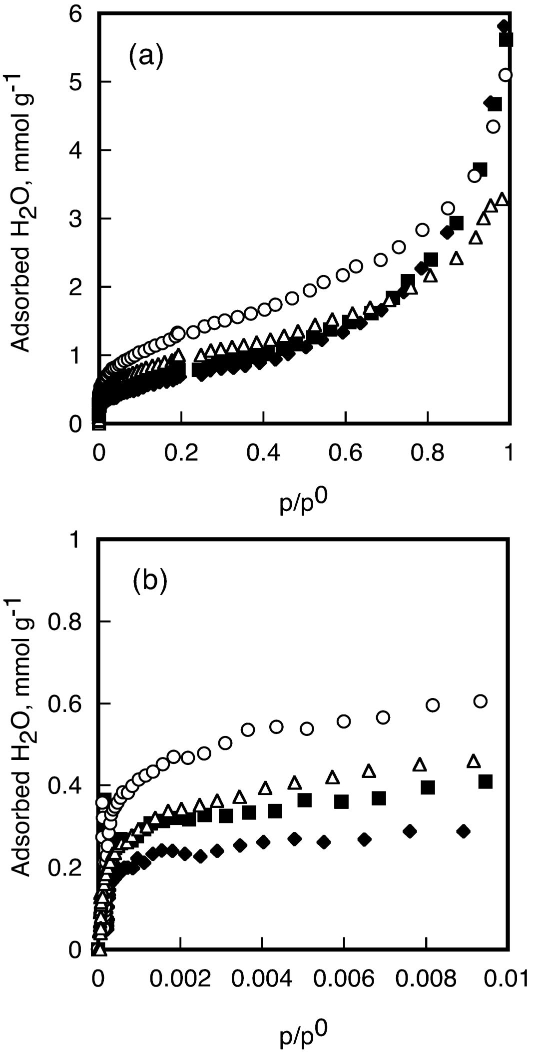


Fig. 7a,b Adsorption isotherms of H_2O on red corpuscle-like hematite particles precipitated at 110 °C. The isotherms at low relative pressure are shown in **b**. T_h (°C): 100 (*circles*), 200 (*triangles*), 300 (*squares*), 400 (*diamonds*)

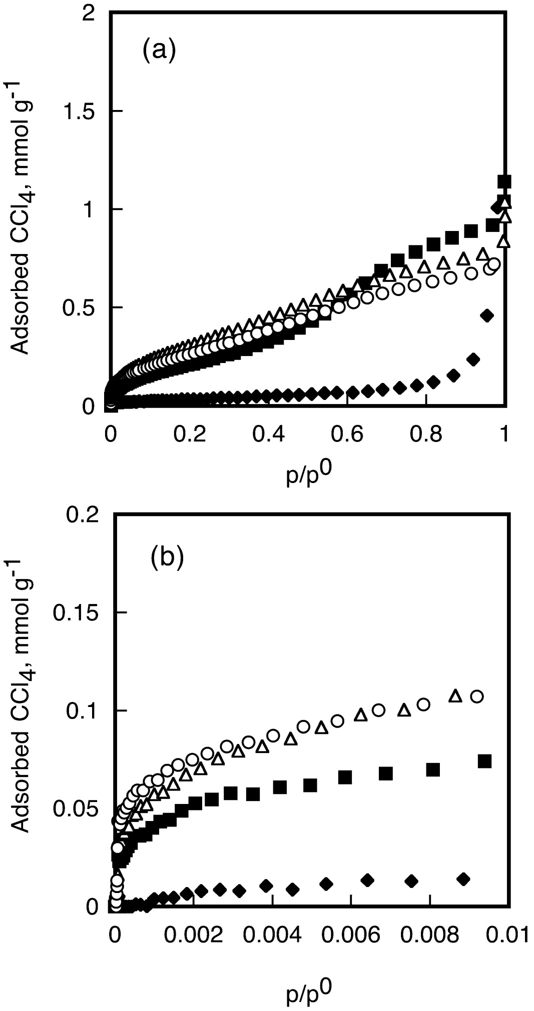


Fig. 8a,b Adsorption isotherms of CCl_4 on red corpuscle-like hematite particles precipitated at 110 °C. The isotherms at low relative pressure are shown in **b**. T_h (°C): 100 (*circles*), 200 (*triangles*), 300 (*squares*), 400 (*diamonds*)

produced with PVA. The ultramicropores formed by dehydration in the cluster particles disappear by sintering at high temperature.

The adsorption isotherms of CCl_4 in Fig. 8 are also type II up to the evacuation temperature of 300 °C, though CCl_4 molecules are merely adsorbed at 400 °C. This figure indicates a drop in an affinity of CCl_4 to hematite particles by raising the evacuation temperature. To estimate the hydrophobicity of the particle surface, we evaluated the specific surface area using the cross-sectional area of CCl_4 as 0.322 nm^2 (S_c). Then, we calculated the S_c/S_w and S_c/S_N ratios at each T_h (Fig. 9). The S_c/S_w and S_c/S_N ratios of the particles evacuated at 100–300 °C range between 0.70–0.95 and 0.54–0.70, respectively. This result suggests that the surface hydrophobicity of the particle is low even though PVA molecules are retained at this temperature owing to the OH groups of PVA molecules in contact with the particles. After evacuation at 400 °C, the S_c/S_w and S_c/S_N ratios decrease to 0.15 and 0.10, though the S_w/S_N ratio remains unchanged. Since the S_w/S_N ratio remains constant at 400 °C, it is hard to consider that the decreases of the S_c/S_w and S_c/S_N ratios result from the lowering of surface hydrophobicity by the elimination of residual PVA molecules. This fact can be explained by a size-restriction effect of the micropores in the particles. Most of the micropores are accessible to H_2O and N_2 molecules but not to CCl_4, i.e., the diameter of the micropores produced ranges from 0.253 nm (diameter of H_2O) to 0.514 nm (diameter of CCl_4). It is noteworthy that no morphological change of the red corpuscle-like hematite particles was observed after evacuating the

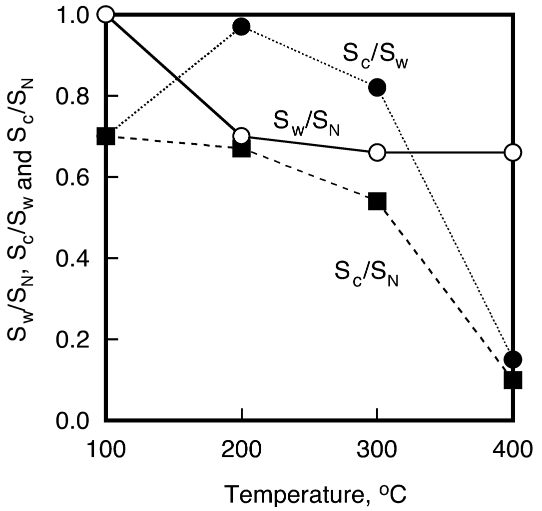


Fig. 9 Changes in S_w/S_N (*open circles*), S_c/S_w (*filled circles*), and S_c/S_N (*squares*) ratios of red corpuscle-like hematite particles precipitated at 110 °C as a function of evacuation temperature

materials up to 400 °C, even though the micropore size is varied by the evacuation treatment.

Conclusion

The hydrothermal reaction of a 0.5 dm^3 aqueous solution of 0.1 M $FeCl_3$ containing 1 wt% PVA at $T_h = 110$ °C for 7 days produced red corpuscle-like hematite particles around 2 μm in diameter. Large numbers of spherical PVA microgel particles around 2–4 μm in diameter were precipitated together with small red corpuscle-like hematite particles on raising T_h. The particles showed mesoporosity, which was more pronounced after outgassing above 300 °C. The particles possess a relatively hydrophilic surface. After evacuation at 400 °C, the micropores were formed with diameters between 0.253 (H_2O) and 0.514 nm (CCl_4).

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