

Kazuhiko Kandori  
Natsuko Hori  
Tatsuo Ishikawa

## Control on shape, porosity and surface hydrophilicity of hematite particles by using polymers

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K. Kandori (✉) · N. Hori · T. Ishikawa  
School of Chemistry,  
Osaka University of Education,  
Asahigaoka 4-698-1,  
Kashiwara, Osaka 582-8582, Japan  
e-mail: kandori@cc.osaka-kyoiku.ac.jp  
Fax: +81-729-783394

**Abstract** The shape, porosity, and surface hydrophilicity of hematite particles formed from a forced hydrolysis reaction of acidic  $\text{FeCl}_3$  solution were controlled by using a trace of polymers (0.001 and 0.003 wt%). The spherical particles were produced on the systems with polyvinyl alcohol (PVA) and polyaspartic acid (PAS). In the case of polyacrylamide (PAAm), slightly small spherical particles were precipitated at 0.003 wt%. However, polyacrylic acid (PAAc) and poly- $\gamma$ -glutamic acid (PGA) gave ellipsoidal particles. This morphological change on hematite particles depended on the order of functional groups of polymers as  $-\text{OH} < -\text{CONH}_2 < -\text{COOH} < -\text{COOH}$

and  $\text{C}=\text{O}$ , corresponding to the order in extent of polymer molecules for complexation to  $\text{Fe}^{3+}$  ions and adsorption onto particle surface. Accompanying this order, the hematite particles produced were changed from less porous to microporous. On the other hand, only the system with 0.003 wt% of PAAm produced mesoporous hematite particles. Choosing the kinds of polymers also controlled the ultramicroporosity and surface hydrophilicity of the particles.

**Keywords** Hematite · Effects of polymers · Forced hydrolysis reaction · Porosity · Ultramicroporosity · Surface hydrophilicity

### Introduction

Iron oxides represent an important basic material due to their large occurrence on Earth. It is well known that iron oxides are extensively used in the production of pigments, gas sensor, catalysis, and magnetic storage devices. Their thermodynamically stable crystallographic phase is hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), which represents the most important ore of iron. Therefore, designing novel iron oxides materials is of great significance and fundamentally important in basic sciences and of relevance for various fields of industrial applications. Our research group has extended the investigation on the formation of hematite particles from the forced hydrolysis reaction of acidic  $\text{FeCl}_3$  solution in the presence of polymers [1–3]. In the previous study, we found interesting effects of polyethylene glycol (PEG;  $[-\text{CH}_2-\text{CH}_2-\text{O}-]_n$ ) on both the formation and structure of spherical hematite particles [1]. The hematite particles,

precipitated in the presence of PEG up to 20 wt%, were spherical and the diameter of the particles was increased from 400 to 1,500 nm (1.5  $\mu\text{m}$ ) with an increase in the PEG concentration. The spherical particles thus produced, exhibited a high microporosity. In addition, we further found that the addition of polyvinyl alcohol (PVA;  $[-\text{CH}_2-\text{CHOH}-]_n$ ) over 1 wt% varies the shape of hematite particles from spherical to disk-like by reducing their thickness [2]. TEM and SEM observations strongly revealed that the disk-like hematite particles with the average diameters of ca. 500 nm and aspect ratios of about 2 are formed by aggregation of cluster particles with a diameter of ca. 5–10 nm. Therefore, these particles changed from microporous to mesoporous after elimination of residual PVA molecules adsorbing on cluster particles by evacuating the samples above 300 °C. In contrast to their high concentrations of PEG and PVA, we found, recently, that vinyl series polymers (polyacryl-

amide, PAAm, and polyacrylic acid, PAAc) with a high complexity to  $\text{Fe}^{3+}$  ions and a high adsorption affinity on both  $\beta\text{-FeOOH}$  of initial hydrolysis products of  $\text{FeCl}_3$  aqueous solution and polynuclear (PN) primary particles produced after dissolved  $\beta\text{-FeOOH}$  strongly influence morphology and structure of hematite particles even at extremely low concentrations (less than 0.004 wt%) [3]. The shape of the particles produced with PAAc was ellipsoidal though it was spherical for those formed with PAAm. This finding reveals that the particle shape strongly depends on the mode and strength of polymer adsorption onto  $\beta\text{-FeOOH}$  and PN primary particles. Accompanying the change in particle shape, it is expected that the porosity and hydrophilicity, which are important for developing new adsorbents and nanocomposites by hybridization in organic matrix of the particles can be also altered by addition of a trace of PAAc and PAAm. However, this information on hematite particles produced in the presence of polymers with different functional groups is obscure. To compare the effect of polymers not only in shape but also in the porosity and surface hydrophilicity, a fundamental study using many kinds of polymers under the same concentration is desired. Hence, we investigated this subject in this paper. The results of this study will give the fundamental information for producing new inorganic porous materials with various morphologies and surface hydrophilicities.

## Experimental

Hematite particles were prepared from the forced hydrolysis of mixed solution of  $\text{FeCl}_3$  and  $\text{HCl}$  dissolving various amounts of polymers. This procedure was almost the same as that which was employed in our previous paper using vinyl series polymers [1]. The total concentrations of  $\text{FeCl}_3$  and  $\text{HCl}$  in a solution were fixed at  $3.12 \times 10^{-2}$  and  $9.60 \times 10^{-3} \text{ mol dm}^{-3}$ , respectively. Five kinds of polymers with various functional groups as listed in Table 1 were used in this study. Polyamino acid sodium salts (PAS and PGA) were supplied kindly by Ajinomoto (Tokyo, Japan). It can be anticipated from their functional groups and molecular weight that the polymers' effect on the hematite formation is in the order of  $\text{PVA} < \text{PAS} < \text{PAAm} < \text{PAAc} < \text{PGA}$  because the formation reaction is strongly related both to the complexation to  $\text{Fe}^{3+}$  ions and adsorption of polymer molecules onto particle surface. As pure hematite phase was only obtained at  $< 0.004 \text{ wt}\%$  on PAAc and PGA systems, two different concentrations (0.001 and 0.003 wt%) were examined. A Pyrex glass vial each containing  $30 \text{ cm}^3$  of reacting solution was tightly closed with a Teflon-lined screw cap and stood in a conventional forced-air oven at  $100 \text{ }^\circ\text{C}$  for 7 days. The morphology and crystal structure of particles filtrated, thoroughly rinsed and dried

**Table 1** Properties of five kinds of polymers used

Polymers	Average molecular weight
Polyvinyl alcohol (PVA) <sup>a</sup>	25,000
Polyaspartic acid sodium salt (PAS) <sup>b</sup>	2,000
Polyacryl amide (PAAm) <sup>c</sup>	10,000
Polyacrylic acid (PAAc) <sup>d</sup>	2,000
Poly- $\gamma$ -glutamic acid sodium salt (PGA) <sup>b</sup>	30,000

a From Wako Pure Chemicals Co. Ltd., Lot 163-03045  
 b From Ajinomoto Co. Ltd.  
 c From Aldric Chemical Co. Ltd., Lot 43,494-9  
 d From Aldric Chemical Co. Ltd., Lot 52,366-7

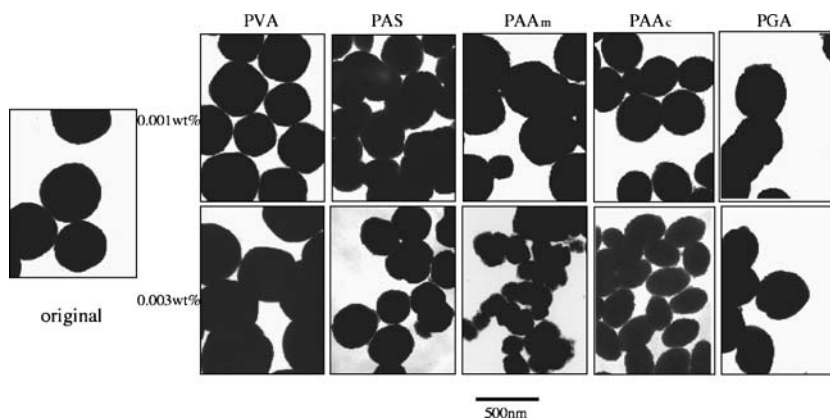
in air at  $70 \text{ }^\circ\text{C}$  were investigated by TEM, TG-DTA and XRD techniques. All of the chemicals used were guaranteed reagent grade and were used without further purification. The porosity and surface hydrophilicity of the hematite particles produced with polymers were investigated by adsorption of  $\text{N}_2$  and  $\text{H}_2\text{O}$  at a liquid- $\text{N}_2$  temperature and  $25 \text{ }^\circ\text{C}$ , respectively.

## Results and discussion

### Morphology

Figure 1 displays the TEM pictures of hematite particles precipitated by aging for 7 days at two concentrations of five kinds of polymers together with those produced without polymers (original). The pure hematite crystal structure of these particles was identified by XRD measurement. Clearly seen in the TEM pictures, no large change of particle shape can be seen on the PVA and PAS systems, though the latter system provides slightly small spherical particles, i.e., the spherical particles similar to the original ones are produced for both systems. This result indicates that the influence of these two polymers on the particle formation is weak. Similarly, PAAm provides spherical particles though their sizes are smaller than PVA and PAS systems when the concentration was increased to 0.003 wt%. Furthermore, PAAc and PGA give ellipsoidal particles. The above results indicate that the effect of a trace

**Fig. 1** TEM images of hematite particles produced with 0.001 and 0.003 wt% polymers

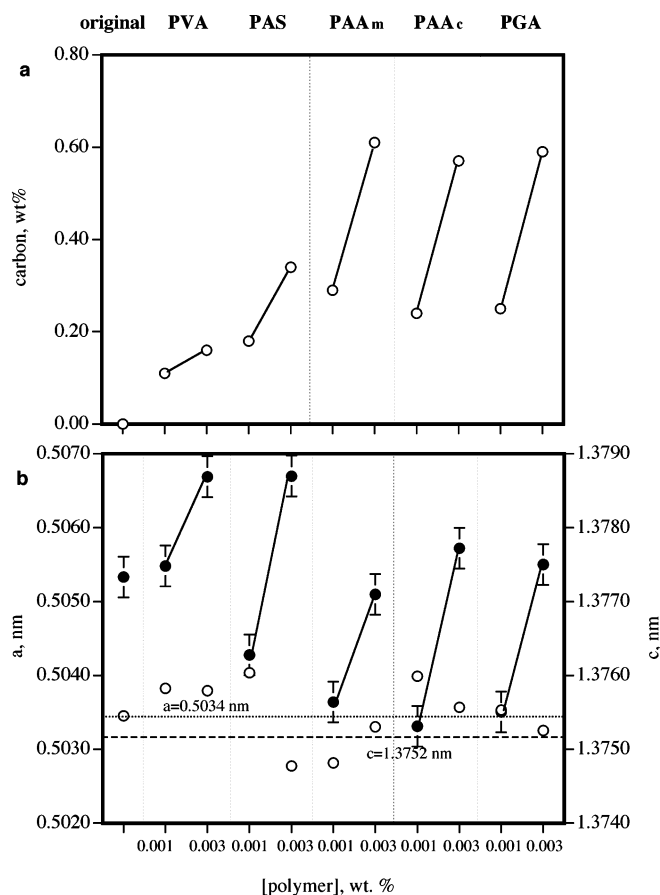


of polymers on the hematite formation is exhibited in the following order PVA<PAS<PAAm<PAAc~PGA (A), corresponding to the order of functional groups of  $-\text{OH}$ < $-\text{COOH}$  and  $\text{C}=\text{O}$ < $-\text{CONH}_2$ < $-\text{COOH}$ ~ $-\text{COOH}$  and  $\text{C}=\text{O}$ . This order is fairly correlated with the order as we expected in a previous section, supporting that particle formation is strongly related to both the complexation to  $\text{Fe}^{3+}$  ions and adsorption of polymer molecules onto particle surfaces. The effect of PAS, rather less than PAAm, may be due to its low molecular weight even though it contains both  $-\text{COOH}$  and  $\text{C}=\text{O}$  groups.

The effect of polymers was further compared by the residual carbon contents and unit cell dimensions of the synthetic hematite particles measured by a CHN elemental analysis and an X-ray diffractometer as shown in Fig. 2a, b), respectively. The carbon contents in the particles produced at 0.003 wt% are, of course, higher than those produced at 0.001 wt% in each system. Furthermore, they are increased in the order of PVA<PAS<PAAc<PGA<PAAm, coinciding with the order of (A) except for the PAAm. This correspondence supports the principle of polymers' effect as mentioned above. The  $a$  edge lengths of all the particles ( $\circ$ ) are almost constant at  $0.5034 \pm 0.0006$  nm, well corresponding to the literature  $a$  value (0.5034 nm) [4]. On the other hand, the  $c$  edge lengths ( $\bullet$ ) of original particles and those produced with 0.001 wt% of PVA are much larger than the literature value (1.3752 nm) [4], though those produced with other polymers are close to the literature. This enlarged  $c$  edge length observed for the original particle was already explained by considering the protonation of  $\text{O}^{2-}$  ions to compensate the charge imbalance by  $\text{Fe}^{3+}$  vacancies with the general chemical formula of  $\alpha\text{-Fe}_{(2-x)/3}(\text{OH})_x\text{O}_{3-x}$  [5]. As PVA possesses hydroxyl groups, the similar mechanism can be expected for PVA molecules, though the detailed mechanism is unclear. However, all the particles produced with 0.003 wt% of polymers exhibit the enlarged  $c$  edge length. This fact signifies that large amounts of polymer molecules distort the crystal structure of hematite particles by adsorption and/or incorporation to the PN primary particles.

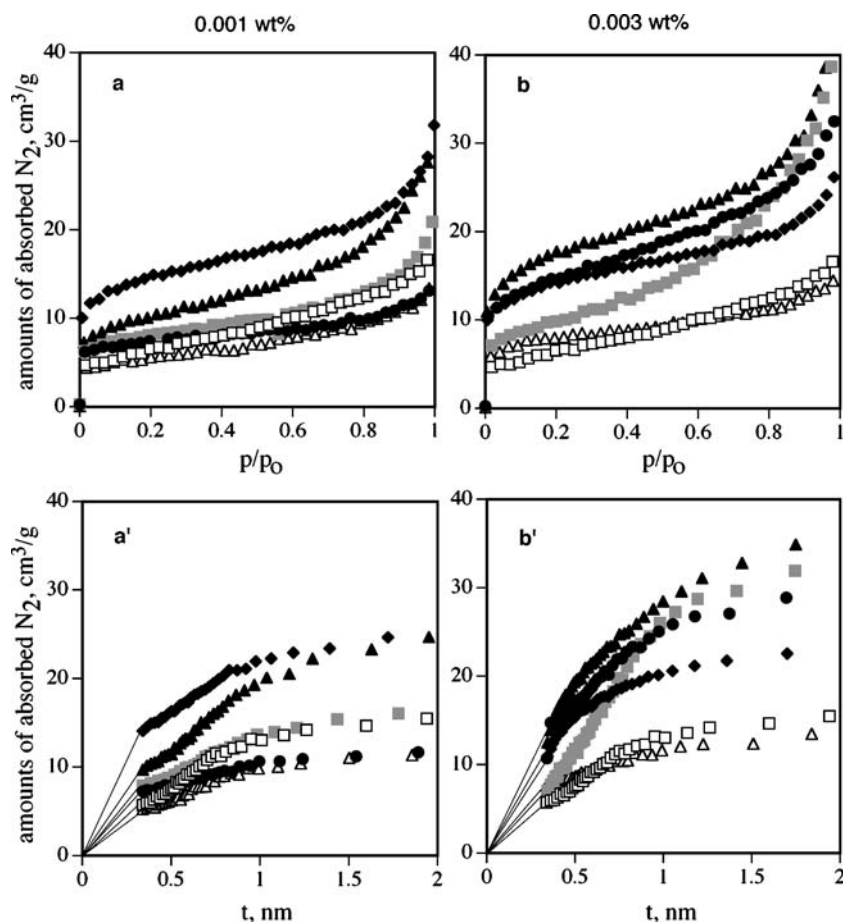
## Porosity

The  $\text{N}_2$  adsorption isotherms for the hematite particles are shown in Fig. 3a,b. The type II isotherms in the International Union of Pure and Applied Chemistry (IUPAC) classification [6] can be recognized for all the particles produced with 0.001 wt% of polymers (Fig. 3a).



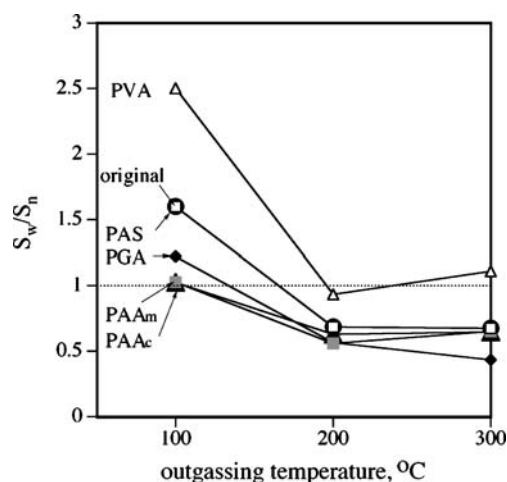
**Fig. 2** Plots of carbon contents **a** and unit cell dimensions **b** of the hematite particles produced with two different concentrations of polymers

**Fig. 3** Adsorption isotherms of  $N_2$  and  $t$ -plot curves of hematite particles produced with (a,a') 0.001 wt.% and (b,b') 0.003 wt.%. Polymers: (□) original, (Δ) PVA, (●) PAS, (◆) PGA, (■) PAAm, (▲) PAAc



The amount of adsorbed  $N_2$  is in the order of  $PVA < PAS < PAAm < PAAc < PGA$ , and also in the order of (A). The  $t$ -plot curves shown in Fig. 3a' provide further insight into the pore structure of the particles. The  $t$ -plot curves of original and PVA systems (open symbols) are made up of straight lines passing through the origin, suggesting that these particles are less porous [7]. On the other hand, those of PAS, PGA, PAAm, and PAAc systems (full symbols) are made up of the straight lines at low-pressure branch up to  $t=0.3-1.0$  nm, but the plots curve downward above that point, suggesting that these particles contain micropores with diameters between 0.6 and 2.0 nm [7]. This result suggests that the hematite particles produced with polymers are changed from less porous to porous along with this order. Similar but much larger amount of adsorbed  $N_2$  is observed for the particles produced with 0.003 wt% of polymers (Fig. 3b). In this case, the  $t$ -plot curves (Fig. 3b') exhibit a large radius of curvature, suggesting that the pore diameter within the particles is enlarged. This fact is particularly pronounced on the PAAm system (■), i.e., the adsorption isotherm of this system exhibits the type IV, indicating that the hematite particles are changed to mesoporous. Indeed, the  $t$ -plot curve of this system curve upward above  $t=0.3$  nm. This result may be attributed to a

higher amount of residual PAAm in the particles as shown in Fig. 2a. It is noteworthy, therefore, that the pore size of hematite particles can be simply controlled by introducing



**Fig. 4** Plots of  $S_w/S_n$  for hematite particles produced with polymers as a function of outgassing temperature. Polymers: (□) original, (Δ) PVA, (●) PAS, (◆) PGA, (■) PAAm, (▲) PAAc

extremely low amounts of polymers in the reaction solution.

The authors have also reported that the hematite particles possess ultramicropores that are accessible to H<sub>2</sub>O molecules but not to the N<sub>2</sub> ones [8]. The ultramicropores are formed by dehydration reaction in the less crystalline-aggregated spherical particles. As the polymers possess various functional groups to alter the mode of aggregation of PN particles by their adsorption, it is expected that the ultramicroporosity of the hematite particles can also be altered. To gain the information of hematite particles produced with polymers, H<sub>2</sub>O adsorption measurement was carried out by changing the outgassing temperature of the samples from 100 to 300 °C. The specific surface areas of the particles were estimated by fitting the adsorption isotherms of N<sub>2</sub> and H<sub>2</sub>O to the BET equation. The obtained specific surface areas measured by using N<sub>2</sub> and H<sub>2</sub>O molecules were denoted as  $S_n$  and  $S_w$ , respectively. As  $S_w/S_n$  ratio is a measure of ultramicroporosity, we calculated the  $S_w/S_n$  ratio of hematite particles and was plotted as a function of outgassing temperature in Fig. 4. Indeed, as is seen in Fig. 4, the original particle (□) exhibits a high  $S_w/S_n$  ratio (1.6) after being outgassed at 100°C, indicating that this particle possesses ultramicropores. Furthermore, the highest  $S_w/S_n$  ratio (2.5) of the PVA system (Δ) suggests that the ultramicroporosity of this particle is extremely high. This fact suggests that PVA promotes the formation of ultramicropores. Similar but much less ultramicroporosity can be seen for PAS (●) and

PGA (◆) systems, exhibiting  $S_w/S_n$  ratios of 1.6 and 1.2. On the other hand, the  $S_w/S_n$  ratios of the samples produced with PAAM (■) and PAAc (▲) are unity, indicating that there is no ultramicropore in the particles. This polymer dependence of ultramicropore formation is particularly interesting, though the detailed mechanism is obscure. A detailed understanding of this mechanism must await more experimentation. After the samples were outgassed above 200 °C, however, the  $S_w/S_n$  ratios of all the particles produced with polymers, except for PVA, become less than unity, suggesting that the particle surface changed to hydrophobic by dehydroxylation of surface hydroxyl groups together with the collapsing of the ultramicropores by sintering. As the PVA possess hydroxyl groups, this system only manifests a hydrophilic surface ( $S_w/S_n$  ratios of ca. 1). This possibility of controlling the ultramicroporosity and surface hydrophilicity of hematite particles by using a trace of polymers is of interest along with controlling the particle shape as described before. This procedure will become a new technology for producing inorganic porous materials with controlled morphology and surface hydrophilicity.

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