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The Control of the Particles of Magnetite

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Synopsis. Fine particles of magnetite were prepared by the hydrolysis of urea.[1] The effects of the amount of urea on the particles were investigated. The expected particles were prepared in the range 0.8 to 2.2 μm in size by controlling the amount of urea. Fine particles of magnetite of 0.8 μm in size were prepared from a solution with $R=60$ (R=urea/iron(III) mol ratio).

For the synthesis of magnetite by the wet method, there are four methods: (1) The coprecipitation method adding a strong alkalline solution to a solution containing Fe^{2+} and Fe^{3+} ions;[2] (2) the air-oxidation method bubbling air into a suspension solution of green rust;[3] (3) the reaction of iron(III) hydroxide sol and Fe metal;[4] and (4) the method adding the non-ion surface active agent to mixed iron(III) hydroxide sol and Fe metal.[5]

In the first three methods, the obtained particles were ultrafine particles under 0.06 μm and the particles in the latter were 5 μm. It was clear that magnetite was prepared by the hydrolysis of urea from the solution containing Fe^{2+} and Fe^{3+} ions,[1] or from the aqueous suspension of β-FeOOH containing Fe^{2+} ions.[6] The fine particles of the crystalline magnetite were obtained by these methods. The pH of the solution dissolved Fe^{2+}, Fe^{3+}, ions and urea increased with the hydrolysis of urea. It increased rapidly by the hydrolysis of a great amount of urea; then, the particles of obtained magnetite became small. The change of the pH of each solution with various R values and the particle size of magnetite precipitated from each solution were measured. From these results, the relation between the distribution of particle sizes of magnetite and amount of urea (R=6—60) was discussed.

Experimental

Magnetite was synthesized by heating a solution containing urea, iron(II) chloride, and iron(III) chloride at 98 °C. A reaction apparatus, already described,[6] was used. Zero point zero five mol of iron(III) chloride and the prescribed amount of urea (the range of R=6 to 60) were dissolved in 0.3 dm^3 of distilled water; and the solution was transfered into three neck flask of 1 dm^3. Iron(II) chloride of 0.025 mol was dissolved with bubbling N_2 gas in the solution at the rate of 1 $dm^3\,min^{-1}$. The time required to raise the temperature up to 98 °C from temperature was 5 min and the reaction time was measured from the time when up to 98 °C was reached. After the programed reaction time, the products were filtered, washed with a large amount of boiling water until iron(II) ion could not be detected. They were then dried in a vacuum desiccator on P_2O_5 powder and were stored. In measurement of particle size of magnetite, centrifugal particles size analyzer (Shimazu CP-50) were used. Sodium hexametaphosphate (0.3%) was used as disparse medium.

Results and Discussion

The change of the pH of each solution with R=6, 10, 20, and 60 with reaction time are shown in Fig. 1. The rate of the pH rise increased rapidly with an increase in R and the final pH of the solution became high. The rate of the pH rise slowed down at pH 4—5 in the solution with R=6 and 10. These phenomena were not observed in the solutions with R=20 and 60.

On the other hand, the changes of the intensities of X-ray diffraction patterns of the products obtained from the solution with R=6 with reaction time are shown in Fig. 2. From the results of measurements of pH and X-ray diffraction patterns of products, β-FeOOH was produced at pH 1—2 and magnetite was produced at pH 4—5. α-FeOOH was recognized from the solutions with R=6 and 10. Magnetite and α-FeOOH were produced at the same time; after that, α-FeOOH gradually decreased and α-FeOOH was finally transformed into magnetite.[6] α-FeOOH was not observed from the solutions with R=20 and 60. The relation between the intensities of the X-ray diffraction (311) plane of magnetite produced from solutions R=6, 10, and 20 and the reaction time is shown in Fig. 2. Magnetite precipitated rapidly, since the rate of the rise of pH was quick with an increase in R.

The average particle sizes of magnetite produced from the solutions with R=6—60 were determined by a centrifugal particle size analyzer. The relation between the average particle sizes and R is shown in Fig. 3. The average particle sizes of magnetite became small with the increase in R. The average particle sizes

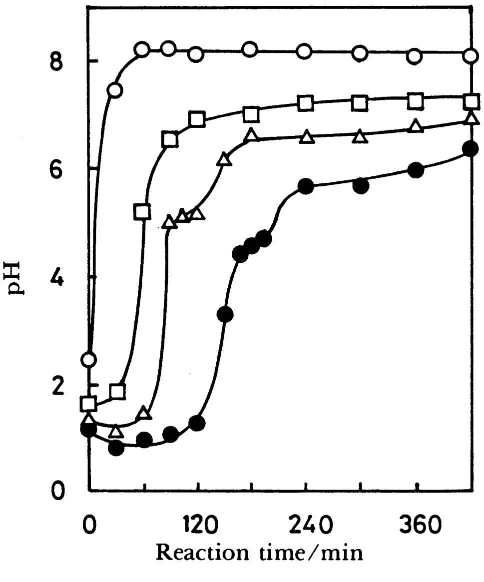

Fig. 1. Relation between change of pH and reaction time. Conditions: R=Urea/iron(III) ion mole ratio. ○–○: R=60, □–□: R=20, △–△: R=10, ●–●: R=6.

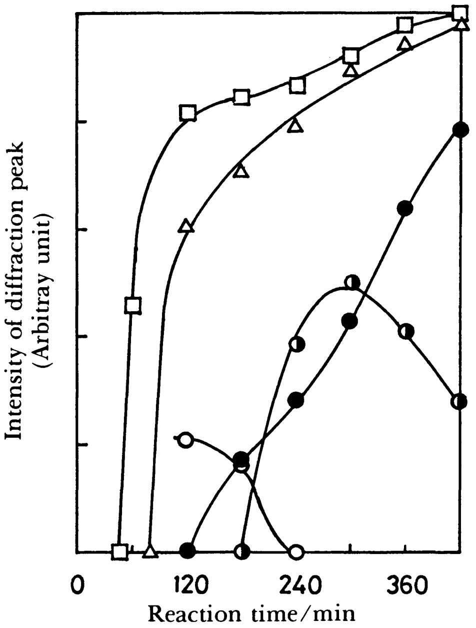

Fig. 2. The relative intensities of X-ray diffraction of magnetite, β-FeOOH and α-FeOOH vs. reaction time after the solution temperature of 98 °C reached. Conditions: R=Urea/iron(III) ion mole ratio. □–□: Magnetite (311)plane, R=20. △–△: Magnetite (311)plane, R=10. ●–●: Magnetite (311)plane, R=6. ○–○: β-FeOOH (310)plane, R=6. ◐–◐: α-FeOOH (110)plane, R=6.

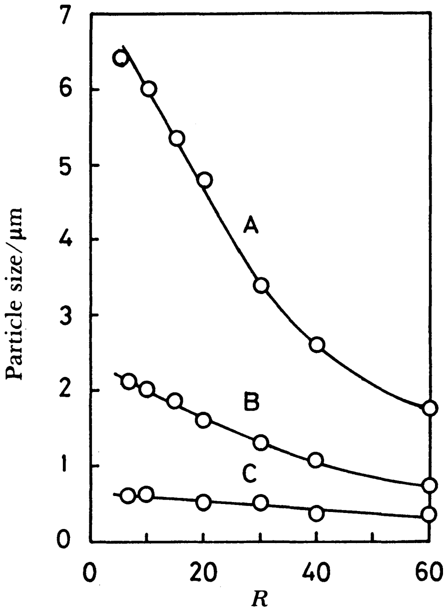

Fig. 3. Plots of average particle size of magnetite and width of distribution of particles. Conditions: A: Upper limit of distribution of particles. B: Average particles. C: Lower limit of distribution of particles.

of magnetite produced from the solutions R=6 and 60 were 2.2 and 0.8 μm, respectively. The widths of the distribution of particle size of magnetite prepared under the various conditions are shown in Fig. 3. The width of distribution was small with the increase of R.

When R value (as R=6) was small, the rate of the rise of pH was slow and the hydrolysis of urea was a rate-determining step in the formation of magnetite, and the pH of the solution was kept at constant of pH about 4.6 during precipitation magnetite. Therefore, nucleation of magnetite took place slightly compared with R=60; the particles precipitated in the first stage were aged for longer periods and the particles became large; however, the particles precipitated in the latter stage were small because of no aging. It was considered that the particle size of β-FeOOH formed in the initial stage of the reaction became large, when R value was small,[7] and that effected the particle size of magnetite. The average size, as a whole, was large. The distribution of particle size was widespread.

When the R value was large, the rate of the rise of pH was rapid and the pH value quickly reached 7—8. Therefore, a high nucleation of magnetite also quickly took place (at a breath). The particles of magnetite produced were small, the width of distribution in particle size narrowed.

It was clear that the R value was large, the average particle size was smaller and that the distribution of particle size was uniformed. When the R value was small, the particles of magnetite precipitated in the initial stage were aged and became large; however, the particles precipitated in the latter stage increased with increasing pH, and were small. Therefore, it was considered that this distribution was not normal; the large particles were a little but the distribution was widespread. When R value was large, the particles precipitated in the first stage were small and amount of particles was much. Therefore, it was considered that the particles were not aged and the particles were small, and that the distribution of particle size was uniformed.

On the ground of these facts, it was elucidated that the magnetite particles of the expected size in the range of 0.8 to 2.2 μm were prepared by hydrolysis of urea easily. The average particle size of 0.8 μm was obtained from the solution with R=60, and the particles were distribution in the range of 0.3—1.75 μm.

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