The Structural Transformation of Ferric Oxyhydroxides and Their Activity to Sulfur Dioxide

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α-, β-, and γ-FeOOH calcined at various temperatures up to 500°C have been examined by determining adsorption isotherms in order to relate the reactivity to SO_2 with the structural transformation. For each ferric oxyhydroxide, the amount of chemisorbed SO_2 per unit surface area (A_c), a measure of reactivity to SO_2, decreases with the progress of transformation into α-Fe_2O_3. At temperatures of calcination below 200°C the A_c value of β-FeOOH is larger than that of α-FeOOH or γ-FeOOH. It is shown by thermogravimetric analysis that the weight loss of β-FeOOH caused by heating is larger than the theoretical value corresponding to the dehydration of hydroxyl groups; $2FeOOH \rightarrow Fe_2O_3 + H_2O$. Changes in the X-ray diffraction patterns and Cl content of β-FeOOH with calcination indicate that β-FeOOH is transformed into α-Fe_2O_3 with elimination of inherently contained Cl at a higher temperature than other oxyhydroxides. The high reactivity to SO_2 and large weight loss of β-FeOOH caused by heating have been discussed with respect to the particular crystal structure of β-FeOOH containing Cl and molecular H_2O, in addition to hydroxyl groups.

It is known that SO_2 in the atmosphere and stack gases accelerates the corrosion of iron. Various oxides and oxyhydroxides of iron, composing the corrosion products of iron, play important roles in the corrosion process and consequently determine the physical and chemical properties of corroded metal surfaces. It seems significant to clarify the mechanism of the acceleration of corrosion by studying the interaction of SO_2 with those oxidized compounds.

Ferric oxyhydroxide is transformed into α-Fe_2O_3 by heating, through courses differing with environmental conditions and the crystal structures of ferric oxyhydroxides in question,[1] although the transformation mechanism has been proposed by several workers.[2,3,4]

The surface activity also changes during the course of transformation. Jurinak[5] reported from water adsorption measurement on α-FeOOH heated at various temperatures that the adsorbability decreases at the temperature range where the conversion occurs from α-FeOOH to α-Fe_2O_3. It is well-known that hydroxyl groups contained in ferric oxyhydroxide are eliminated as H_2O at approximately 300°C according to the reaction; $2FeOOH \rightarrow Fe_2O_3 + H_2O$. Okamoto, Furuichi and Sato[4] have reported that ferric oxyhydroxide releases the "bound" water at approximately 170°C and the "crystallization" water is evolved at approximately 300°C, the former appearing to affect the chemical reactivity of ferric oxyhydroxide.

If we assume that the reactivity of ferric oxyhydroxide to SO_2 mainly depends on hydroxyl groups in ferric oxyhydroxide, it would be interesting to see whether the reactivity changes with the removal of hydroxyl groups in the transformation into α-Fe_2O_3. In the preceding paper,[6] the authors reported on the SO_2 adsorption on ferric oxyhydroxides (α-, β- and γ-FeOOH) to show that each oxyhydroxide chemisorbs a considerable amount of SO_2; the amount of chemisorption is especially larger for β-FeOOH than other oxyhydroxides. Furthermore, by the kinetic treatment of the reaction between SO_2 and ferric oxyhydroxides, it was suggested that β-FeOOH is more reactive to SO_2 than other oxyhydroxides.

The purpose of the present investigation is to study the interaction of SO_2 with α-, β- and γ-FeOOH at various temperatures of calcination and to relate the reactivity to SO_2 with the structural transformation.

Experimental Procedures

Materials. α-FeOOH (α-1) was precipitated by the hydrolysis of 0.1 M ferric oxalate solution at 100°C for 45 minutes and at the initial pH of 6.6, regulated by adding 1 M $NaHCO_3$ solution. The precipitate produced was washed repeatedly and dried at 100°C.[7] More crystalline α-FeOOH (α-2) prepared similarly by the hydrolysis of ferric sulfate solution, the pH being adjusted at 13.6 with 0.1 M KOH solution, was stirred at 50°C for 30 hours. After filtering the suspension, the α-FeOOH precipitates obtained were washed until no sulfate ions were detected. They were then dried at 100°C for 5 hr.[8]

The hydrolysis of 1 liter of 0.1 M ferric chloride solution containing 100 g urea at 100°C for 15 hours gave crystalline β-FeOOH (β-1). The precipitates of β-FeOOH were washed with water and dried at 100°C for 2 hr.[9] Less crystalline β-FeOOH (β-2) was prepared by hydrolysing 0.1 M ferric chloride solution at 75°C for 6 hours. The precipitates were washed with 1 N ammonium chloride until no Fe ions were detected with thiocyanate solution. They were finally washed with methanol and with ether, and dried in an air oven at 100°C for 2 hours.[10].

Crystalline γ-FeOOH (γ-1) was prepared by the method

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[1] A. L. Mackay, "Reactivity of Solids", ed. by J. H. De Boer, Elsevier Publishing Co., Amsterdam, (1961), p. 571.

[2] J. D. Bernal, D. R. Dasgupta and A. L. Mackay, *Nature*, **180**, 645 (1957).

[3] H. B. Weiser and W. O. Milligan, *J. Amer. Chem. Soc.*, **57**, 238 (1935).

[4] G. Okamoto, R. Furuichi and N. Sato, *Electrochim. Acta*, **12**, 1287 (1967).

[5] J. J. Jurinak, *J. Colloid Sci.*, **19**, 477 (1964).

[6] T. Ishikawa and K. Inouye, *Nippon Kagaku Zasshi*, **91**, 935 (1970).

[7] K. J. Gallagher and D. N. Phillips, *Trans. Faraday Soc.*, **64**, 785 (1968).

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[9] E. R. Nightingale Jr. and R. E. Benk, *Anal. Chem.*, **32**, 566 (1960).

[10] I. M. Kolthoff and B. Moskoviz, *J. Amer. Chem. Soc.*, **58**, 777 (1936).

of Baudisch and Albrecht.[11] The ferrous hydroxide suspension, obtained by mixing 1 liter of ferrous chloride aqueous solution containing 40 g $FeCl_2 \cdot 4H_2O$ with 200 m*l* of 2 M hexamethylenetetramine solution, was treated with 27 m*l* of 1 M sodium nitrate, and then kept at 60°C for 45 minutes. γ-FeOOH (γ-1) was collected by filtering the suspension. Amorphous γ-FeOOH (γ-2) was prepared by adding 400 m*l* of 0.25 M potassium iodate to the mixture of 800 m*l* ferrous sulfate aqueous solution containing 56 g $FeSO_4 \cdot 7H_2O$ and 800 m*l* of sodium thiosulfate aqueous solution containing 90 g $Na_2S_2O_3 \cdot 5H_2O$, and then by stirring the resulting suspension at 45°C for 1 hr.[12] Preparation of γ-FeOOH samples was performed in a stream of nitrogen, and the resulting precipitates were thoroughly washed with water and dried at 60°C for 10 hr.

Methods. The amount of adsorbed SO_2 was determined gravimetrically at 30°C by means of a quartz spring balance with an accuracy of 0.20 mg. Before the adsorption measurement, approximately 200 mg of the sample was outgassed under 10^{-5} Torr, heated up to 110, 150, 200, 300, 400, and 500°C at a heating rate of 8°C/min and kept for 5 hours at each temperature under 10^{-5} Torr. Pure SO_2 dried with $CaCl_2$ was then introduced to the adsorption apparatus to measure the elongation of quartz spring by a cathetometer. The adsorption equilibrium was attained within 1 hr for each sample. Desorption was carried out immediately after the adsorption experiment. The desorption equilibrium was attained within 2 hours.

The BET surface area determination was made by a conventional volumetric nitrogen adsorption measurement. The pretreatment of the sample was similar to that in the SO_2 adsorption.

The X-ray diffraction patterns were obtained by the powder method with a diffractometer Geigerflex 2001 (Rigaku Denki Co. Ltd.) by use of Mn-filtered FeK_α (30 kV, 10 mA). The samples, calcined at 110, 150, 200, 300, 400 and 500°C under 10^{-5} Torr for 5 hours, were examined by means of X-ray diffraction.

Differential thermal analysis was carried out in air by Thermoflex 8001 S (Rigaku Denki Co. Ltd.) using α-Al_2O_3 as a reference sample. The enthalpy change in the structural transformation of the sample was measured by a differential scanning calorimeter DSC-1 (Perkin-Elmer Co.), at a heating rate of 8°C/min. The weight loss of the sample by heating was determined gravimetrically with a quartz balance, at a heating rate of 8°C/min.

The Volhald method was employed to determine the chlorine content of β-FeOOH. A solution of 100 mg of the sample in 30 m*l* concentrated nitric acid was diluted with water to 50 m*l* and an aliquot was titrated with 0.1 N $AgNO_3$ solution.

The iron content in the sample was determined by the following method; Fe^{3+} in hydrochloric acid solution, reduced to Fe^{2+} with $SnCl_2$, was titrated against a standard 0.05 N $K_2Cr_2O_7$ solution in the presence of sodium 4-diphenylammine sulfonate as an indicator.

Results

The thermogravimetric analysis (TGA) curves for α-FeOOH samples (α-1 and α-2) are given in Fig. 1. Both samples show rapid weight losses in the temperature range 200—300°C, but the weight loss of α-1 occurs in a temperature range lower than α-2. However, the total weight loss of each sample is consistently 12%, which is somewhat higher than the theoretical value (10%) corresponding to the change; $2FeOOH \rightarrow Fe_2O_3 + H_2O$. Similar curves were obtained for γ-FeOOH. The TGA curves of β-FeOOH in Fig. 2 differ from those of α-FeOOH in a gradual loss in the temperature range 100—450°C. The total weight loss is 20% for β-1 and 18% for β-2. The sublimed $FeCl_3$ was observed in the inner wall of the TGA apparatus during the course of heating around 400°C, where a stepwise drop of weight also took place for β-1 as shown in Fig. 2.

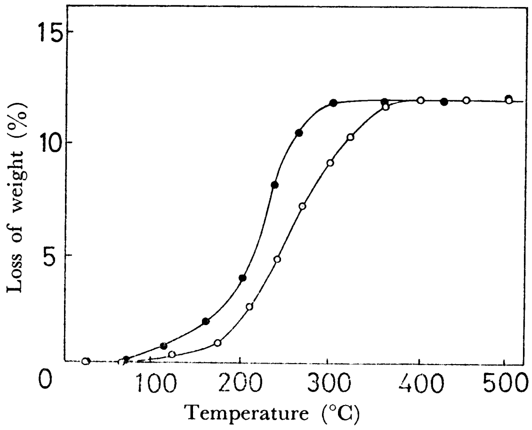

Fig. 1. TGA curves for α-1 and α-2: ●, α-1; ○, α-2.

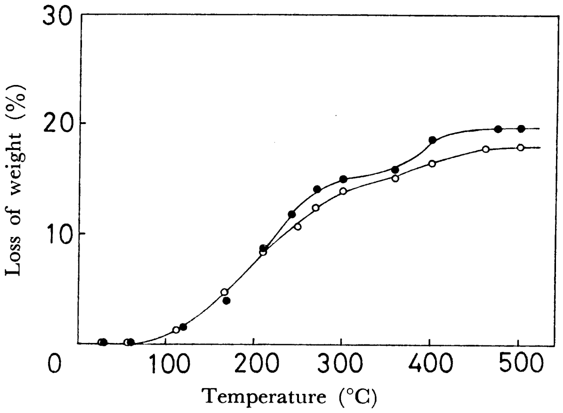

Fig. 2. TGA curves for β-1 and β-2: ●, β-1; ○, β-2.

The differential thermal analysis (DTA) curves of α-2, β-1 and γ-1 are given in Fig. 3. The curves of crystalline α-FeOOH (α-2) involves an endothermic peak at 110°C caused by the desorption of adsorbed water and an endothermic peak at 295°C by the dehydration of "crystallization" water.[13] For β-FeOOH, endothermic and exothermic peaks overlap each other at nearly 300°C. The endothermic peak of the sublimation of $FeCl_3$ appears at 400°C as found in the TGA curves. An endothermic peak at 170°C is probably caused by the elimination of molecular water embraced in β-FeOOH crystal. γ-FeOOH shows the exothermic peak at 430°C, which is considered to be due to the transformation of γ-Fe_2O_3 to α-Fe_2O_3.[13]

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[11] O. Baudich and W. H. Albrecht, *J. Amer. Chem, Soc.*, **54**, 943 (1932).

[12] E. B. Seidman, *Anal. Chem.*, **30**, 1680 (1958).

[13] W. Lodding and L. Hammel, *ibid.*, **32**, 657 (1960).

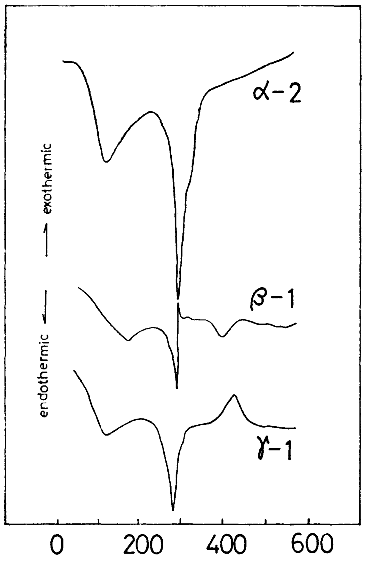


Fig. 3. DTA curves for α-2, β-1 and γ-1.

The endothermic peaks in the differential scanning calorimeter (DSC) curves in Fig. 4 correspond to dehydration. However, the samples used for DSC determinations kept in a desiccator for a long time adsorb less water than the samples used for DTA. No endothermic peaks caused by the desorption of physically adsorbed water are observed in DTA curves. The heat of dehydration obtained from the endothermic DSC peaks is 49, 75, 45 and 36 cal/g for α-1, α-2, γ-1 and γ-2, respectively. These results indicate that the more crystalline oxyhydroxide has a higher heat of dehydration than the less crystalline oxyhydroxide.

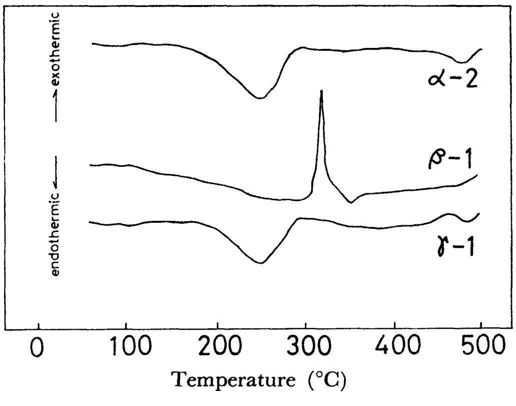


Fig. 4. DSC curves for α-2, β-1 and γ-1.

As demonstrated by the change of X-ray diffraction patterns in Fig. 5, α-2 is transformed into α-Fe_2O_3 at 200°C. The crystallinity of resulting α-Fe_2O_3 is seen to be gradually improved with further appearance of additional diffraction peaks of α-Fe_2O_3 at 400°C. On the other hand, β-1 (Fig. 6) changes to an amorphous mixture, composed of β-FeOOH and α-Fe_2O_3, in the temperature range 200—300°C. At 400°C, however, the amorphous mixture is suddenly transformed into the crystalline α-Fe_2O_3. γ-1 (Fig. 7) is transformed into amorphous γ-Fe_2O_3 at 200°C and is suddenly converted to crystalline α-Fe_2O_3 at 400°C. However, the TGA, DTA and DSC curves

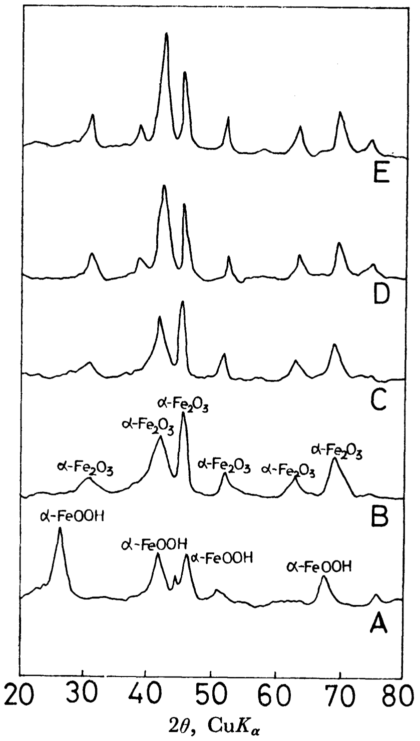
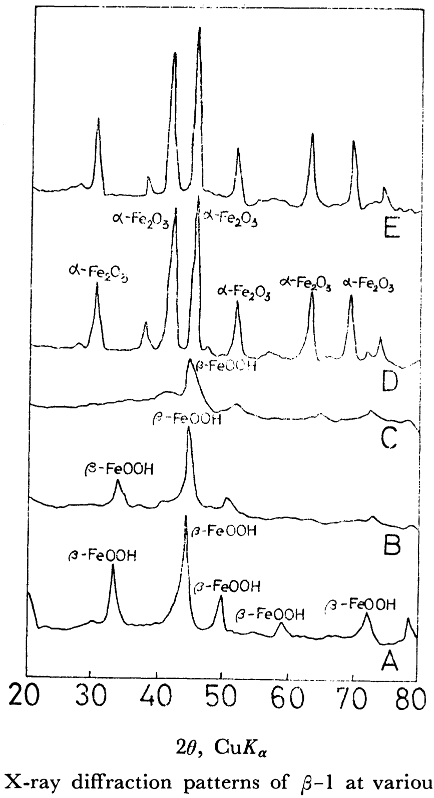


Fig. 5. X-ray diffraction patterns of α-2 at various temperatures of calcination: A, 150°C; B, 200°C; C, 300°C; D, 400°C; E, 500°C.



2θ, CuK_α

Fig. 6. X-ray diffraction patterns of β-1 at various temperatures of calcination: A, 150°C; B, 200°C; C, 300°C; D, 400°C; E, 500°C.

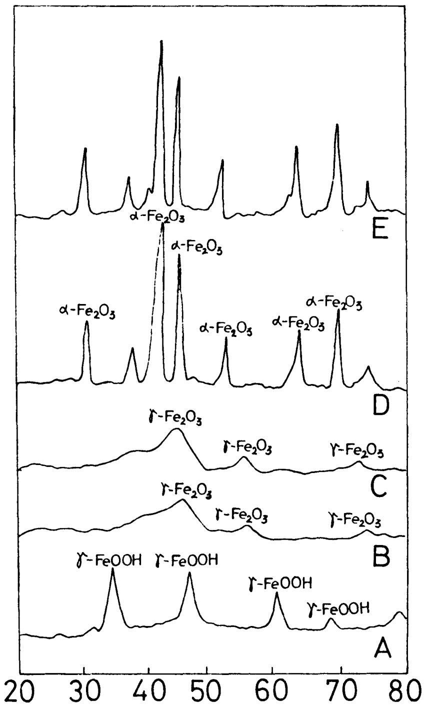


Fig. 7. X-ray diffraction patterns of γ-1 at various temperatures of calcination: A, 150°C; B, 200°C; C, 300°C; D, 400°C; E, 500°C.

shown in Figs. 1, 3 and 4 indicate that α-2 and γ-1 are transformed into α-Fe_2O_3 and γ-Fe_2O_3 at temperatures higher than the transformation temperatures obtained by X-ray diffraction. The discrepancy in transformation temperature is considered to be due to different heat treatments; the X-ray samples were outgassed for 5 hours at various temperatures under 10^{-5} Torr, whereas the DTA, TGA and DSC curves were obtained in air at a fixed rate of heating.

The variation of specific surface area with the temperature of calcination given in Fig. 8 shows a maximum between 200 and 300°C for each sample.

The SO_2 adsorption isotherm obtained at 30°C is of the BET-II type for each sample. Figure 9 shows the isotherm for α-2. The monolayer capacity of the SO_2 adsorption per unit surface area (A_m), calculated by the BET method, is illustrated in Fig. 10 as a function of the outgassing temperature. Below 150°C, the A_m values are almost constant and no differences in A_m are observed between ferric oxyhydroxides examined. The adsorbed SO_2, remaining on the surface after desorption under 10^{-5} Torr at 30°C for 24 hr, is regarded as the chemisorbed SO_2.[6] The relationship between the amount of the chemisorbed SO_2 per unit surface area (A_c) and the temperature of calcination is given

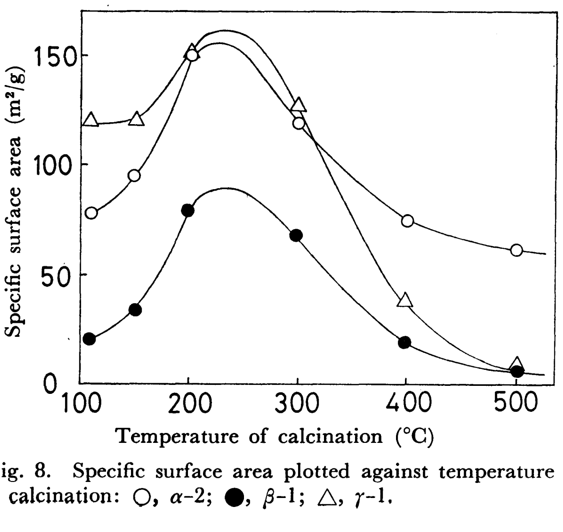


Fig. 8. Specific surface area plotted against temperature of calcination: ○, α-2; ●, β-1; △, γ-1.

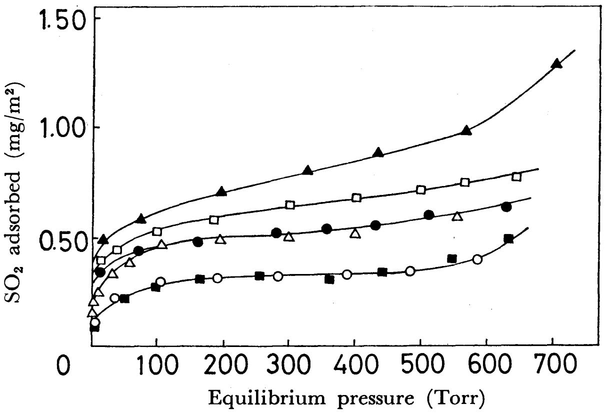


Fig. 9. Adsorption isotherms for α-2 at various outgassing temperatures: △, 110°C; ●, 150°C; □, 200°C; ▲, 300°C; ■, 400°C; ○, 500°C.

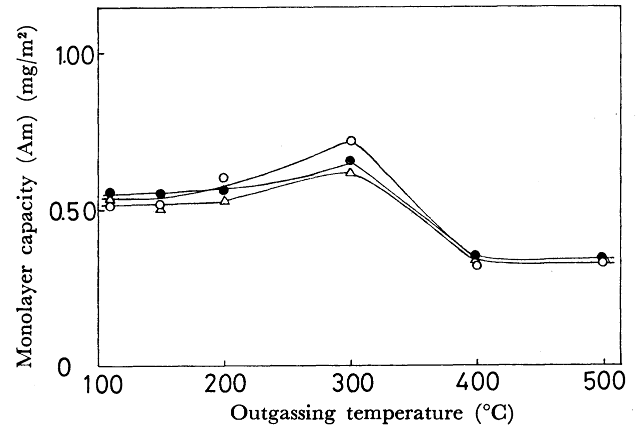


Fig. 10. Effect of outgassing temperatnre on monolayer capacity: ○, α-2; ●, β-1; △, γ-1.

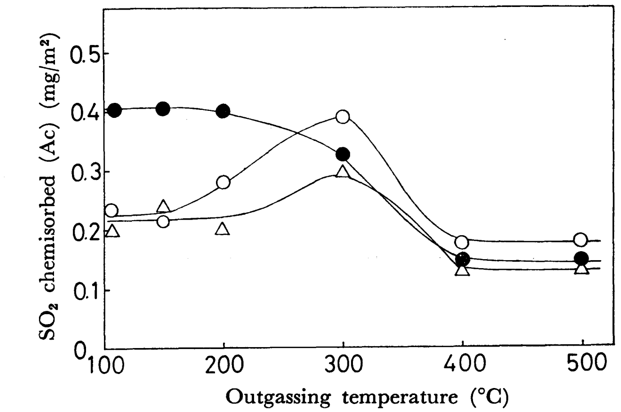


Fig. 11. Effect of outgassing temperature on chemisorption; ○, α-2; ●, β-1; △, γ-1.

in Fig. 11. The A_c value of β-FeOOH is larger than those of other ferric oxyhydroxides below 200°C. However, in the temperature range 200—400°C, the A_c of β-FeOOH drops with the formation of crystalline α-Fe_2O_3 and is nearly equal to the A_c of α-FeOOH and γ-FeOOH above 400°C.

The content of chlorine, which is characteristic of β-FeOOH, was found to be 4.6 wt% for β-1. As illustrated in Fig. 12, the chlorine content of β-FeOOH expressed in the atomic ratio (Cl/Fe) is constant below 200°C and decreases rapidly with increasing temperature in the range 200—400°C.

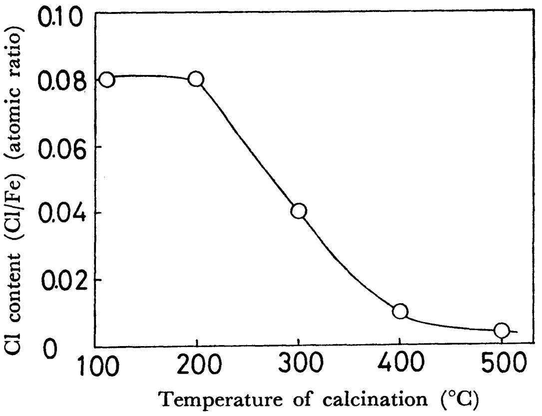


Fig. 12. Cl content in β-1 against temperature of calcination.

Discussion

The weight loss of α-FeOOH and γ-FeOOH by heating, which is larger than the stoichiometric value of water content, indicates that α-FeOOH and γ-FeOOH contain a small amount of "bound" water which is eliminated at a lower temperature range. As shown in Fig. 1, the crystalline sample (α-2) is dehydrated at a higher temperature than the less crystalline sample (α-1). A similar tendency was also observed for γ-FeOOH. Furthermore, the higher heat of dehydration calculated from the DSC curves was obtained for the crystalline sample. These results imply that the crystalline ferric oxyhydroxide is more difficult to be dehydrated as compared with the less crystalline ferric oxyhydroxide.

Dasgupta and Mackay[14,15] suggested that β-FeOOH has the hollandite ($BaMn_8O_{16}$) or α-MnO_2 structure with Cl and H_2O in the Ba^{2+} position. It is known that the Cl content in β-FeOOH varies with the extent of washing, since the Cl can be replaced by H_2O molecule.[3] In our experiments, the DTA curve for β-1 (Fig. 3) shows that H_2O is released from the crystal at approximately 170°C. Chlorine begins to be eliminated at 200°C as shown in Fig. 12, and DTA and TGA curves show that $FeCl_3$ is sublimed at 400°C. Thus the large total weight loss of β-FeOOH is obviously associated with the evolution of Cl_2 and H_2O in the crystal. It is therefore presumed that β-FeOOH contains two kinds of Cl; one which can be easily replaced by H_2O molecule, and the other which is strongly bound to Fe and removed as $FeCl_3$ by heating at 400°C. Figures 6 and 12 show the structural changes of β-FeOOH to α-Fe_2O_3, with elimination of Cl as $FeCl_3$ at approximately 400°C. From our results, the strongly bound Cl seems to stabilize the crystal structure of β-FeOOH with regard to transformation into α-Fe_2O_3. Thus the higher temperature is observed for the transformation of β-FeOOH into α-Fe_2O_3.

The relations between the specific surface area and temperature of calcination (Fig. 8) indicate that each ferric oxyhydroxide becomes amorphous and porous during the course of dehydration. After showing the maximum, the surface area decreases with the rise in temperature owing to crystallization and sintering.

The almost constant value of A_m below 150°C shown in Fig. 10 is referred to the fact that X-ray diffraction patterns are identical up to 150°C. It may be further assumed that the decrease of A_m with transformation is due to the disappearance of hydroxyl groups. On the other hand, the maximum monolayer capacity observed for each sample at 300°C seems to be due to the maximum chemisorption at 300°C as shown in Fig. 11. The maxima of chemisorption observed for α-2 and γ-1 appear to be caused by the higher surface activity in the temperature range, in which the samples undergo transformation into crystalline α-Fe_2O_3 and their crystals are distorted. As illustrated in Fig. 11, β-FeOOH chemisorbs a larger amount of SO_2 than other oxyhydroxides below 200°C. It is considered from the extraordinarily high activity of β-FeOOH to SO_2 that the vacancies formed by the removal of the molecular water by outgassing may be the chemisorption sites for SO_2. The number of such sites decreases with the destruction of the β-FeOOH structure with heating.

These results indicate that the reactivity to SO_2 decreases with the transformation from ferric oxyhydroxide into α-Fe_2O_3, and β-FeOOH in particular has a higher reactivity to SO_2 than other ferric oxyhydroxides at the temperature of calcination below 200°C. The characteristic behavior of β-FeOOH in the transformation process to α-Fe_2O_3 and the higher reactivity to SO_2 would be due to the crystal structure containing molecular water and chlorine which do not exist in other ferric oxyhydroxides.

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[14] D. R. Dasgupta and A. L. Mackay, *J. Phys. Soc. Japan*, **14**, 932 (1959).

[15] A. L. Mackay, *Miner. Mag.*, **32**, 545 (1960).