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The Structure and Reactivity of Nickel Hydroxide

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This paper examines the correlation between the structure and the reactivity of nickel hydroxide, using X-ray diffraction, DTA, IR spectroscopy, and gravimetry during dehydration. The degree of crystallization of β-nickel hydroxide depends on the preparation conditions of the hydroxide. Highly-crystallized β-nickel hydroxide has "free" hydroxyl groups, as is to be expected from its brucite structure. Poorly-crystallized β-hydroxide, however, has "hydrogen-bonded" hydroxyl groups, this finding is in disagreement with a previous result that "hydrogen-bonded" hydroxyl groups were found to exist only in α-form nickel hydroxide. The dehydration of the hydroxide is shown to take place in first-order kinetics with an activation energy which increases as the crystallization extends.

Nickel hydroxide and nickel oxide are produced during the corrosion of nickel and constitute surface-oxide film.[1] Nickel hydroxide is also used as an active material for the positive electrode of a nickel-cadmium battery. Many attempts have been made to determine the structure of nickel hydroxide,[2–6] and it has been proposed that nickel hydroxide exists in the α-form and the β-form. The α-nickel hydroxide contains crystallized water with "hydrogen-bonded" hydroxyl groups, while the β-form hydroxide contains no excess water and has "free" hydroxyl groups with no hydrogen-bond. McEwen,[7] however, found, by using electron microscopy and diffraction, that the α-form nickel hydroxide proposed by Bode can not exist. In

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[1] N. Sato, K. Kudo, and M. Miki, *Kinzoku Gakkaishi*, **35**, 1007 (1971).

[2] W. Feitknecht, H. R. Christen, and H. Studer, *Z. Anorg. Allgem. Chem.*, **283**, 88 (1956).

[3] H. Bode, K. Dehmelt, and J. Witte, *Chem-Ingr-Techn.*, **36**, 671 (1964); *Electrochim. Acta*, **11**, 1079 (1966).

[4] F. P. Kober, *J. Electrochem. Soc.*, **112**, 1064 (1965); *ibid.*, **114**, 215 (1967).

[5] M. A. Aia, *ibid.*, **114**, 418 (1967).

[6] W. Dennsted and W. Loser, *Electrochim. Acta*, **16**, 429 (1971).

[7] R. S. McEwen, *J. Phys. Chem.*, **75**, 1782 (1971).

spite of the many results reported, the structures and the reactivities have not been established exactly.

This paper will examine the correlation between the structures of nickel hydroxide prepared under several conditions and the dehydration kinetics by using the X-ray diffraction, DTA, IR, and gravimetry.

Experimental

Materials. Four types of nickel hydroxide powders were prepared from nickel nitrate and ammonia water under the conditions described below.

Sample *a* was a fresh hydroxide prepared by mixing 0.2 M $Ni(NO_3)_2$ with 0.2 M NH_3H_2O at room temperature; it was washed by water immediately after precipitation, Sample *b* was prepared under the same conditions except for the solution being 1.0 M NH_3H_2O and the temperature of preparation being 60~70 °C. Samples *c* and *d* were prepared by aging Sample *b* at 30 °C for 24 hr (Sample *c*) and 35 days (Sample *d*).

All of the precipitated nickel hydroxides were dried in a vacuum of 10^{-2} mmHg at 110 °C for 4 hr after having been dried in a desiccator over silica gel in 20 mmHg for 2 days. The sample was ground (200 to 300 mesh) and calcinated in a vacuum at 110 °C before measurements.

The specific surface area of each sample was determined by the BET method using N_2 gas adsorption; the values are listed in the first column of Table 1.

TABLE 1. CHARACTERISTICS OF NICKEL HYDROXIDE SAMPLES

Sample	Specific surface area m²/g	Mean particle diameter Å	Total weight loss % (w/w)	E_a[a)] kcal/mol
a	59	150	20.2	20
b	45	420	19.5	30
c	31	650	19.0	33
d	30	700	19.2	49

a) Activation energy in dehydration reaction.

X-Ray Diffraction. The samples were examined by the powder method with Cu*K*α radiation. As the diffractometer a Geigerflex 2030/P apparatus (Rigaku Denki Co., Ltd.) was used. The mean particle diameter was calculated approximately by the line-broadening method, referring to highly pure silicon as the standard.

Differential Thermal Analysis (DTA). The DTA of nickel hydroxide which had been preheated in 10^{-3} mmHg at 110 °C was carried out in air, using Al_2O_3 as the standard. A thermoflex 8001 apparatus (Rigaku Denki Co., Ltd.) was used, and the rate of heating was 10 °C/min.

IR Spectroscopy. Disks transparent to infrared radiation were prepared by pressing nickel hydroxide to about 10 ton/cm². Their thicknesses were between 0.03 and 0.05 mm. The disks were then placed in an IR cell with sodium chloride windows and could be connected with a conventional high-vacuum system. The spectra were taken at room temperature after treatment at the desired temperatures using a Hitachi grating spectrometer, IR-G2.

Dehydration of Nickel Hydroxide. The weight loss during the dehydration of the hydroxide, which had been dried in a vacuum at 110 °C for 1 hr, was measured gravimetrically by using a quartz spring balance placed in a quartz tube and a cathetometer (0.01 mm=0.0392 mg) under isothermal and isobaric conditions, with air provided, in 40 mmHg. The weight loss measured was then corrected by taking the buoyancy effect into account; its magnitude was separately measured with anhydrous nickel oxide. In order to reduce the pressure change caused by the water vapour produced during the dehydration, silica gel was placed in a drying tube connected to the spring balance system. The temperature was measured outside a quartz tube placed in a furnace and was controlled within an accuracy of ±1 °C. The total weight loss in the dehydration was checked in a vacuum at 400 °C.

Results and Discussion

Structure of Nickel Hydroxide. It has been reported in the literature[5,8)] that the α-form nickel hydroxide can be prepared by precipitation in a mixture of nickel nitrate and diluted ammonia water at temperatures lower than 25 °C and that the β-form can be formed by mixing nickel nitrate with concentrated ammonia water at temperatures above 60 °C.

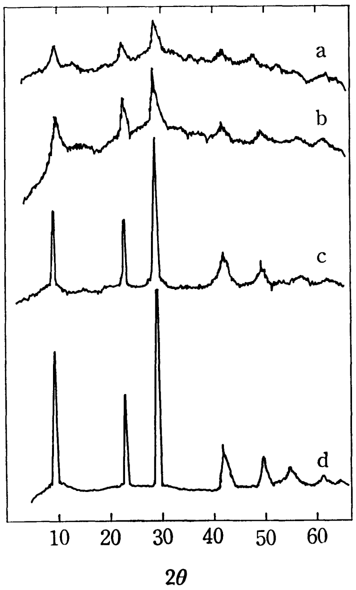

Fig. 1. X-Ray diffraction patterns of nickel hydroxide (sample *a* to *d*)

Since the α-form hydroxide proposed by Bode[3)] is markedly different from the β-form, it is possible how to identify the crystal form. The conditions under which Sample *a* was prepared seem to coincide with the conditions of preparing the α-form given by the literature.[5,8)] All the nickel hydroxide prepared in this work, however, shows the pattern of the β-form in the X-ray diffraction, as is shown in Fig. 1. It may also be seen in Fig. 1 that, as the crystallization extends, the X-ray diffraction pattern becomes sharp for the β-form from Samples *a* to *d*. The crystallization of nickel hydroxide is seen to increase as the concentration of ammonia in the solution for precipitation increases, as the temperature of precipitation rises, and as the aging of the hydroxide extends. The mean particle diameters of the four samples are listed in the second column of Table 1.

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8) H. Bode, K. Dehmelt, and J. Witte, *Z. Anorg. Allg. Chem.*, **366**, 1 (1969).

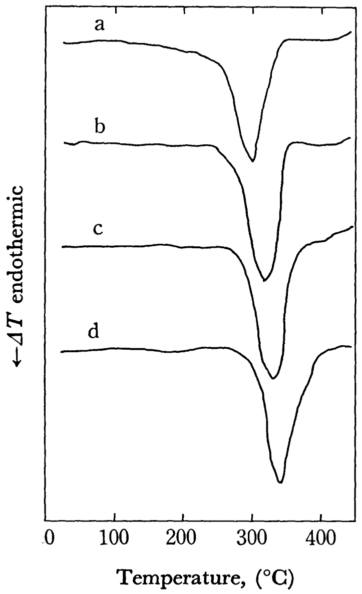

Fig. 2. DTA of nickel hydroxide dried in 10^{-2}mmHg at 110 °C for 4 hr.

The DTA curves of four samples are shown in Fig. 2. For all samples, one endothermic peak due to the dehydration is observed between 200 and 400 °C. This indicates that the nickel hydroxide, in which physically-adsorbed water is dehydrated in a vacuum at 110 °C, contains only one kind of water species to be dehydrated. The rate of the dehydration of highly-crystallized nickel hydroxide is expected to be small, because the temperature of the peak is shifted to a higher temperature in the order from Samples *a* to *d*, that is, in the order of crystallization.

The dehydration phenomenon shown in the DTA curves in Fig. 2 is coincident with the weight loss of Samples *a* and *c* during the nonisothermal dehydration shown in Fig. 3, in which the weight loss was measured as the temperature rose at the rate of 5 °C/min in air at 40 mmHg. In Fig. 3, α represents the dehydration ratio referred to the total weight loss. Since the total weight loss in reference to the initial weight shown in the third column of Table 1 is 19~20% (w/w) and is nearly equal to 1 mol% of water for all samples, it seems that the excess water or bound water previously observed in ferric oxide[9] is not present in nickel hydroxide.

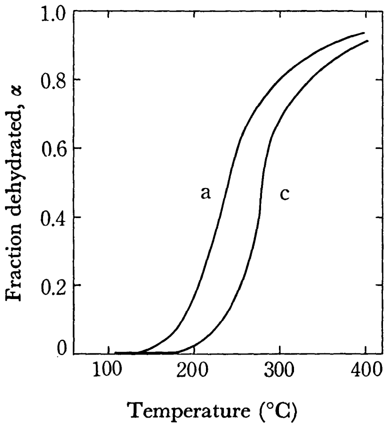

Fig. 3. Weight loss with dehydration of nickel hydroxide (sample a and c)

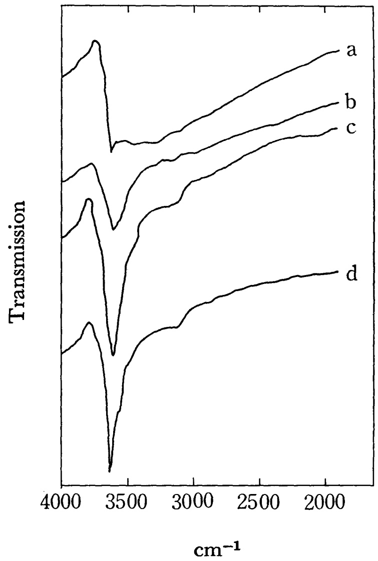

Fig. 4. IR spectra of nickel hydroxide dried in 10^{-5}mmHg at 25 °C.

The IR spectra of four samples in the range between 4000 and 2000 cm^{-1} are shown in Fig. 4. The bands due to the antisymmetric stretching of the hydroxyl group broaden in the order from Samples *d* to *a*. This indicates that Sample *a* has a hydroxyl group "hydrogen-bonded," while Sample d has a nearly "free" hydroxyl group at 3620 cm^{-1}. Samples *b* and *c* have an intermediate hydroxyl group between Samples *a* and *d*.

The variations in the IR spectra of Samples *a* and *d* with the temperature of the heat treatment above 100 °C in 10^{-5} mmHg for 1 hr are shown in Figs. 5 and 6. It may be seen in Fig. 5 that the hydroxyl

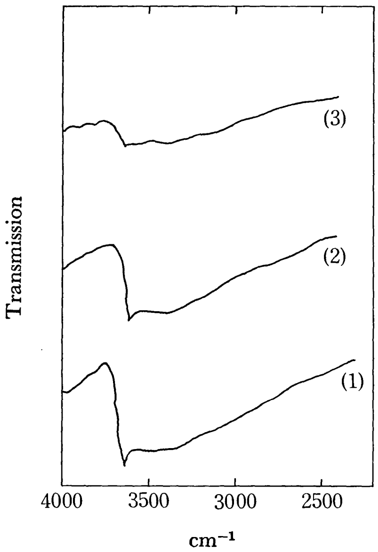

Fig. 5. Variations of IR spectrum of nickel hydroxide (sample a) with calcination in 10^{-5}mm Hg for 1 hr; (1) 110 °C, (2) 150 °C, (3) 200 °C.

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9) R. Furuichi, N. Sato, and G. Okamoto, *Chimia*, **23**, 455 (1969).

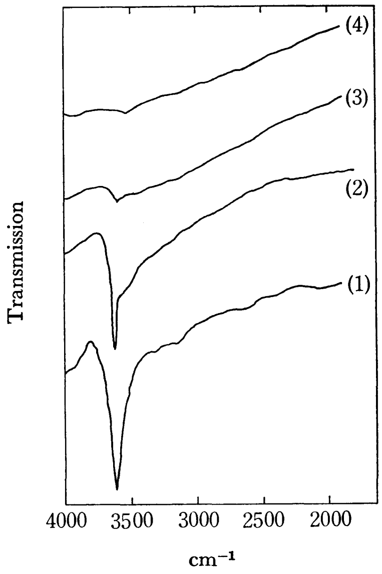

Fig. 6. Variations of IR spectrum of nickel hydroxide (sample d) with calcination in 10^{-5}mmHg for 1 hr; (1) 110 °C, (2) 200 °C, (3) 250 °C, (4) 300 °C.

group in Sample *a* is hydrogen-bonded not only in the initial state, but also in partially-dehydrated states. As Fig. 6 shows, Sample *d* has the "free" hydroxyl group in the partially-dehydrated states as well as in the initial state. As has already been discussed, the samples of nickel hydroxide used in this work were all of the β-form, as is indicated by the X-ray diffraction and by the fact that no excess water was present. In the brucite structure of β-form, it is structually impossible to form a hydrogen bond between hydroxyl groups. The hydrogen bond present in Sample *a* may, therefore, be attributed to the formation of a hydrogen bond between hydroxyl groups on the surface of crystallite.

At any rate, it is a fact that the hydrogen-bonded hydroxyl group exists in poorly-crystallized β-form nickel hydroxide; hence, a hydrogen bond is not always the characteristic of the α-form. It should also be noted that the bonding state of the hydroxyl group in each sample does not change during the dehydration, as is shown in Figs. 5 and 6.

Dehydration Kinetics. The overall dehydration reaction that was measured by the weight loss may be written by:

$$\mathrm{Ni(OH)_{2(solid)}} \longrightarrow \mathrm{NiO_{(solid)}} + \mathrm{H_2O_{(gas)}} \qquad (1)$$

and the normalized rate equation, by:

$$\mathrm{F}(\alpha) = \mathrm{F}(\alpha{=}0.5)t/t_{0.5}, \qquad (2)$$

where α is the fraction of water dehydrated in time t and where $t_{0.5}$ is the time required for 50% dehydration. $F(\alpha)$ can be theoretically derived by assuming the reaction mechanism proposed by many workers for several solid-state reactions.$^{10-12)}$

As is shown in Fig. 7, all the dehydration data for the four types of nickel hydroxide conformed to the same curve of α *vs.* $t/t_{0.5}$. This indicates that the same reaction mechanism operates in all the samples examined.

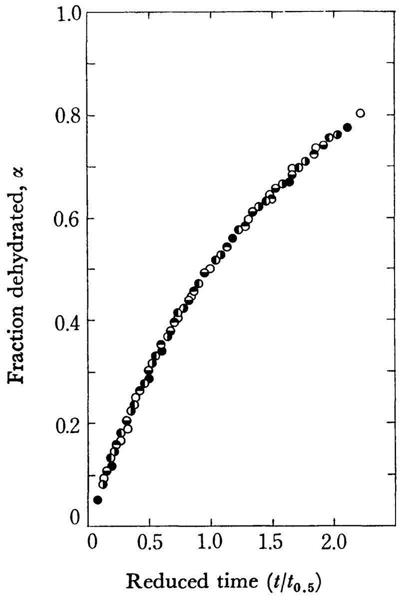

Fig. 7. Fraction dehydrated, α, *versus* reaction time, $t/t_{0.5}$, in reference to the time for 50% dehydration of nickel hydroxide in 40 mmHg air at 225 °C (●) for a sample a, at 242 °C (○) for sample b, at 245 °C (◐) and 268 °C (◑) for sample c, at 243 °C (◒) and 250 °C (◓) for sample d.

If the reaction is controlled by a diffusion in the solid, one obtain this equation: $D_1(\alpha)=\alpha^2=0.25\times t/t_{0.5}$, for one-dimensional diffusion and this equation: $D_3(\alpha)=[1-(1-\alpha)^{1/3}]^2=0.0426\times t/t_{0.5}$, for three-dimensional diffusion. In the case of phase-boundary controlled reactions, one has this equation: $R_2(\alpha)=1-(1-\alpha)^{1/2}=0.293\times t/t_{0.5}$, for a two-dimensional reaction and this equation: $R_3(\alpha)=1-(1-\alpha)^{1/3}=0.206\times t/t_{0.5}$, for a three-dimensional reaction. If the dehydration process occurring in the particle is the limiting step, the de-

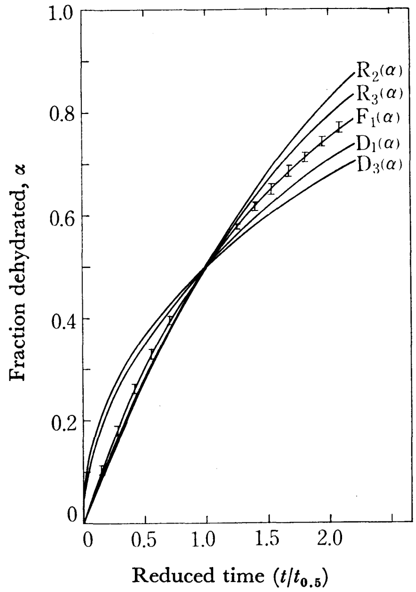

Fig. 8. Comparison of observed values, indicated by vertical line segment, with calculated α versus $t/t_{0.5}$ relation for various dehydration mechanisms.

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10) R. E. Carter, *J. Chem. Phys.*, **34**, 2010 (1961).

11) E. A. Giess, *J. Amer. Ceram. Soc.*, **46**, 374 (1963).

12) J. H. Sharp, G. W. Brindley, and B. N. N. Achar, *ibid.*, **49**, 379 (1966).

hydration is of the first-order kinetics represented by this equation: $F_1(\alpha)=\ln(1-\alpha)=-0.693\times t/t_{0.5}$. The α and $t/t_{0.5}$ for each mechanism calculated are compared with the experimental results in Figs. 7 and 8. All the experimental data are seen to be in good agreement with $F_1(\alpha)$. Accordingly, the first-order reaction mechanism is operative.

Another mechanism has been proposed by Hazell *et al.*,[13] who examined the thermal decomposition of iron(II), cobalt(II), and nickel(II) hydroxides and assumed a phase-boundary reaction mechanism in the range of α less than 0.6. The first-order kinetics, however, is valid not only in the $\alpha<0.6$ range, but also in the $\alpha>0.6$ range.

The first-order kinetics assuming that the dehydration extends in the bulk of crystals is also supported by the electronmicrographical finding[14] which shows the hexagonal crystal form of the original nickel hydroxide to remain in the partially-dehydrated state. If the diffusion mechanism operated, there would be some diffusing water or hydrated hydroxyl groups in the bulk of the crystals and, hence, the IR spectrum would show a broadening peak in the partially-dehydrated state. Since the IR spectrum of Sample *d* shown in Fig. 6, however, has a sharp peak of the "free" hydroxyl groups in the partially-dehydrated state, it seems that the diffusion is unlikely to limit the reaction rate.

The Arrhenius activation energies for the four types of nickel hydroxide are listed in the fourth column in Table 1.

The table indicates that the activation energy also increases with the degree of crystallization. All the activation energies are seen to be larger than the heat of dehydration of nickel hydroxide, $\Delta H^\circ=12.4$ kcal/mol, a finding which is in agreement with the usual conception.

Conclusion

Nickel hydroxide samples prepared from nickel nitrate and ammonia water in the range of concentration from 0.2 to 1.0 M at temperatures between 20 and 60 °C are all β-form, in disagreement with the work of Bode. The more extended crystallization results from the more concentrated ammonia solution, the higher temperature of precipitation, and the more extended time of the aging of the precipitates.

The β-nickel hydroxide contains, in addition to the physically-adsorbed water, only one kind of water which exists in the form of hydroxyl groups corresponding to an endothermic peak in DTA between 200 and 400 °C. The endothermic peak shifts to higher temperatures as the degree of the crystallization rises.

The hydroxyl group of β-nickel hydroxide is "free" in the highly-crystallized particle, but "hydrogen-bonded" in the poorly-crystallized particle.

The dehydration reaction of nickel hydroxide is represented by a first-order reaction mechanism, with an activation energy which increases with the extent of crystallization.

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13) I. F. Hazell and R. J. Irving, *J. Chem. Soc. A*, **669** (1966).

14) F. P. Larkins, P. J. Fensham, and J. V. Sanders, *Trans. Faraday Soc.*, **66**, 1748 (1970).