Adsorption of Phosphate Ions from Aqueous Solution of Nickel Hydroxides Calcined at Different Temperatures

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Nickel hydroxide (Ni100) and nickel hydroxide, including cobalt (NiCo91), were calcined at different temperatures. These materials were investigated by analyzing data obtained from X-ray diffraction (XRD), scanning electron microscopy, specific surface area, thermogravimetric-differential thermal (TG-DTA) technique, and electron-probe microanalysis. The XRD and TG-DTA data obtained indicated that calcination at 250–270°C can promote the conversion of $\text{Ni}(\text{OH})_2$ into NiO, and that cobalt hardly affected the structural changes of nickel hydroxide. The specific surface areas of Ni100 and NiCo91 were determined to be in the range 17.9–148.3 and 21.0–145.1 m^2/g , respectively. The specific surface area increased suddenly at 260°C. The amount of phosphate adsorbed onto Ni100 and NiCo91 was measured to be in the range 29.2–44.7 and 29.7–54.0 mg/g , respectively. The amount adsorbed onto Ni100 or NiCo91 was greater than that onto another adsorbent previously reported. The correlation coefficient relationships between the specific surface areas of Ni100 and NiCo91 and the saturated amount of the adsorbed phosphate ions were found to be 0.935 and 0.960, respectively. These results suggested that adsorption of phosphate ions with Ni100 or NiCo91 is related to the specific surface area. Our study demonstrated that Ni100 and NiCo91 can be considered as promising materials for the adsorption of phosphate ions from aqueous solutions.[DOI: 10.1380/ejsnt.2014.404]

Keywords: Nickel; Cobalt; Adsorption; Phosphate ion

I. INTRODUCTION

Phosphate is an essential macronutrient in aquatic environments; however, when present in excess, it can cause eutrophication of reservoirs, lakes, and coastal areas [1]. Thus, effluent concentration of phosphate from wastewater-treatment facilities and industrial plants must be controlled with chemical and biological techniques to meet the discharge limits [2, 3]. In the past decades, several approaches for phosphorus removal from wastewater have been developed, including precipitation through chemical methods, active sludge, ion exchange, and phosphate crystallization [4–8]. Although highly effective for phosphorus removal, these techniques have serious drawbacks such as high costs, low efficiency, and nontrivial implementation. To solve these problems, adsorption is being increasingly used in research on phosphorus removal because of its high efficiency and relatively simple application. Thus, diverse adsorbents have been used for phosphorus removal, such as Kanuma mud, $\text{Mg}_3\text{-Fe}$ layered double hydroxides, hydrous manganese oxide, and graphene-nanosheet-supported lanthanum hydroxide nanoparticles [4, 9–11]. Nickel hydroxide and nickel oxide materials have received much attention in recent years for application in alkaline secondary batteries, fuel cells, electrochemical capacitors, electrolyzers, electrosynthetic cells, and electrochromic devices [12–16]. Rechargeable alkaline nickel batteries (e.g., Ni/Cd, Ni/Fe, Ni/Zn, Ni/ H_2 , and Ni/MH) are usually positive limited, i.e., the capacity and cycle life of the cells are mainly determined by the

properties of nickel electrodes [17]. Driven by a high commercial demand, several methods have been developed to improve the preparation and discharge of the active materials of nickel hydroxide electrodes for rechargeable nickel batteries [18]. Despite these efforts, nickel hydroxide and nickel oxide are not extensively used. Moreover, purification of wastewater (adsorption of phosphate ions from aqueous solutions) by nickel hydroxide or nickel oxide has never been reported. Thus, if methods for purification of wastewater based on nickel hydroxide and nickel oxide could be developed, the value and the application range of these materials would drastically increase. In this study, the properties of nickel hydroxide (Ni100) and nickel hydroxide, including cobalt (NiCo91), calcined at different temperatures were investigated and their adsorption capability of phosphate ions evaluated.

II. EXPERIMENTAL METHODS

A. Materials

Ni100 and NiCo91, obtained from Kansai Catalyst Co., Ltd. (Japan), were calcined at 200, 250, 260, 270, 280, 290, and 300°C. The morphology and crystallinity of the studied samples were investigated using a JSM-6380LA system (JEOL, Japan) and a MultiFlex (Rigaku, Japan), respectively. The thermogravimetric-differential thermal analysis (TG-DTA) was carried out with DTG-60AH (Shimadzu, Japan). The amount of nickel and cobalt on the adsorbent was measured with an electron-probe microanalyzer (EPMA, JXA-8530F, JEOL, Japan), with an accelerating voltage of 45.0 kV and a beam di-

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FIG. 1. SEM images of Ni100 at different temperatures. Scale bar is 10 μm .

ameter of 5 μm . The specific surface areas were measured with a specific surface analyzer (NOVA4200e, Yuasa Ionic, Japan).

B. Adsorption of phosphate ion

Adsorbent (1.0 g) was added to a solution (300 mL) containing phosphate ions (initial concentration was 500 mg/L). Suspensions were shaken at 100 rpm for 24 h at 25°C. Samples were filtrated through a 0.45 μm membrane filter; the filtrate was then measured by the DR/890 colorimeter (Hach, USA). The amount of phosphate ions adsorbed was calculated with Eq. 1:

$$X = (C_0 - C_e)V/M \quad (1)$$

where X is the amount of phosphate ions adsorbed (mg/g), C_0 is the concentration before adsorption (mg/L), C_e is the concentration after adsorption (mg/L), V is the volume of the solvent (L), and M is the mass of the adsorbent (g).

III. RESULTS AND DISCUSSION

A. Properties of Ni100 and NiCo91 at different temperatures

The SEM images displayed in Figs. 1 and 2 show that Ni100 and NiCo91 consist of spherical particles of various diameters. We observed that the calcination treatment hardly affected the surfaces of Ni100 and NiCo91. Moreover, the particle diameter of Ni100 was larger than that of NiCo91. The XRD patterns of Ni100 and NiCo91 are displayed in Figs. 3 and 4, respectively. The characteristic

diffraction peaks at (001), (100), (101), (102), and (110) show that Ni100 and NiCo91 calcined below 250°C and have a β -type crystal structure [17]. The XRD patterns of the calcined samples at temperatures > 260°C exhibited sharper reflection peaks, indicating that a growth in the crystallite sizes of NiO has occurred. The characteristic diffraction peaks at (111), (200), (220), (311), and (222) suggested that Ni100 and NiCo91 calcined at temperatures > 260°C have a NiO structure. No peaks related to $\text{Ni}(\text{OH})_2$ were found, indicating that $\text{Ni}(\text{OH})_2$ was completely decomposed into NiO at 280°C [19]. The XRD data of NiCo91 showed a similar trend to that of Ni100. Previous studies on heating nickel hydroxide materials have proposed two types of chemical reaction [16, 20]: i) dehydration (Equation 2), which corresponds to the loss of the adsorbed and/or structurally bonded water below 250°C; ii) decomposition of nickel hydroxide to nickel oxide (Equation 3), when $\text{Ni}(\text{OH})_2$ is heated at temperatures > 250°C.

Dehydration reaction:

where X_w is the moles of water. Decomposition reaction:

TG-DTA curves for Ni100 or NiCo91 are shown in Figs. 5 and 6, respectively. An endothermic peak at 270°C on the DTA curve of virgin Ni100 and NiCo91 was observed; the TG curve shows a sharp weight loss with 20 wt%. This corresponds to the decomposition of $\text{Ni}(\text{OH})_2$ into NiO and H_2O . No peaks on the DTA curve of Ni100 and NiCo91 calcined at 300°C were detected. This finding suggested that calcination in the range 250–270°C can promote the conversion of $\text{Ni}(\text{OH})_2$ into NiO, and that cobalt hardly affect the structure of the nickel

FIG. 2. SEM images of NiCo91 at different temperatures. Scale bar is 10 μm .

FIG. 3. XRD of Ni100 at different temperatures.

hydroxides. The relationship between the decomposition temperature and the crystallite size of the nickel hydroxides was also observed by Watanabe *et al.* [18, 21]. In addition, our data confirmed the presence of nickel and cobalt on the adsorbent (Fig. 7). The amount of cobalt onto the NiCo91 surface was larger than that onto Ni100, indicating that cobalt is present onto the NiCo91 surface. From the BET measurements (Table I), the specific surface areas of Ni100 and NiCo91 were determined to be in the range 17.9–148.3 and 21.0–145.1 m^2/g , respectively. Our data showed that the specific surface areas increased suddenly at 260°C. These results indicated

that the presence of the NiO species affects increase the specific surface area of Ni100 or NiCo91 (from Figs. 2-5). Previous studies reported that the specific surface areas of micro-sized spherical $\text{Ni}(\text{OH})_2$, spherical $\text{Ni}(\text{OH})_2$, and nanostructures $\text{Ni}(\text{OH})_2$ are 10.8, 10, and 39.6 m^2/g , respectively [22, 23]. These results suggest that Ni100 and NiCo91 calcined at different temperatures have a larger surface area; this can provide a high density of active sites, which, in turn, can promote the adsorption of materials from the aqueous solution. Therefore, obtaining a larger specific surface area can improve the application of these materials [17]. Addition of cobalt hardly affected

FIG. 4. XRD of NiCo91 at different temperatures.

FIG. 5. TG-DTA of Ni100 at different temperatures.

FIG. 6. TG-DTA of NiCo91 at different temperatures.

FIG. 7. Amount of nickel and cobalt onto adsorbent surface.

TABLE I. Specific surface area of Ni100 and NiCo91 at different temperatures.

Temperature (°C)	Virgin	200	250	260	270	280	290	300
Ni100 (m ² /g)	23.3	17.9	25.7	81.8	142.6	148.3	136.6	116.0
NiCo91 (m ² /g)	21.0	36.8	28.2	74.6	125.1	136.2	138.5	145.1

the specific surface areas.

B. Adsorption of phosphate ions with Ni100 and NiCo91 at different temperatures

As shown in Table II, the amount of phosphate ions adsorbed onto Ni100 and NiCo91 are in the range 29.2–44.7 and 29.7–54.0 mg/g, respectively; these values are relatively large compared to those reported in previous studies (Table III), suggesting that Ni100 and NiCo91 have a significant potential for phosphate removal from aqueous solution [4, 24–26]. We also investigated the relationship between the specific surface area and the saturated amount of phosphate ions adsorbed (Fig. 8). The correlation coefficients of Ni100 and NiCo91 were determined to be 0.935 and 0.960, respectively. A comparison of the adsorption capacities observed in this work and those from other studies is given in Table III [27–29]. The maximum adsorption capacity of the phosphate ions onto Ni100 and NiCo91 at different temperatures is in the range 29.2–44.7 and 29.7–54.0 mg/g, respectively; the maximum adsorption capacities of phosphate ion onto various adsorbents different from those studied here were previously reported to be in the range 2.1–42.0 mg/g. Thus, these data confirmed that Ni100 or NiCo91 can be considered as promising candidates for the adsorption of phosphate ions from aqueous solutions.

FIG. 8. Relationship between specific surface area and saturated amount of phosphate ion adsorbed. ●: Ni100, ○: NiCo91.

TABLE II. Saturated amount of phosphate ion adsorbed onto Ni100 or NiCo91 at different temperatures.

Temperature (°C)	Virgin	200	250	260	270	280	290	300
Ni100 (mg/g)	29.2	30.0	30.7	40.9	42.8	44.3	44.2	44.7
NiCo91 (mg/g)	30.7	29.7	32.1	41.0	54.0	47.6	47.9	47.0

IV. CONCLUSIONS

Nickel hydroxide (Ni100) and nickel hydroxide, including cobalt (NiCo91), at different temperatures were prepared. The particle diameter of Ni100 was larger than that of NiCo91. The results of XRD and TG-DTA indicated that Ni100 and NiCo91 calcined between 250 and 270 °C can promote the conversion of Ni(OH)₂ into NiO.

TABLE III. Comparison of adsorption capacity of various adsorbent for phosphate ion removal.

Adsorbent	Adsorption capacity (mg/g)	Reference
Kanuma	2.1	4
Ferric sludge	25.5	24
Phosphate mine slime	8.7	25
Thermal activated natural palygorskite	42.0	26
Calcined waste egg shell	23.0	27
Red mud granular adsorbent	6.6	28
Granular boehmite	36.9	29
Ni100 at different temperatures	29.2-44.7	This work
NiCo91 at different temperatures	29.7-54.0	This work

Moreover, cobalt hardly affected the structure of nickel hydroxides. The amount of cobalt adsorbed onto NiCo91 was larger than that onto Ni100. The specific surface areas of Ni100 and NiCo91 increased suddenly at 260 °C. The amount of phosphate ions adsorbed onto Ni100 and NiCo91 showed a similar trend. A correlation between the specific surface areas of Ni100 and NiCo91 with the satu-

rated amount of phosphate ions adsorbed was also found, the correlation coefficients being 0.935 and 0.960, respectively. In conclusion, the findings presented in this work strongly indicate that Ni100 and NiCo91 can be considered as promising candidates for the adsorption of phosphate ions from aqueous solutions.

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