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Chemical synthesis of α -cobalt hydroxide

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Abstract

Precipitation reactions using ammonia yield a novel cobalt hydroxide phase that is structurally and compositionally similar to α -nickel hydroxide. The use of other synthetic methods yields the well-known β -Co(OH)₂. The slab composition, mode of anion inclusion, and thermal behavior of the hydroxides obtained by ammonia precipitation are similar to those of α -nickel hydroxide; however, the materials are poorly ordered. A DIFFaX simulation of the powder X-ray diffraction patterns offers the best visual match with the observed patterns for a 50% stacking disorder and a disc radius between 100 and 1000 Å. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Despite the many similarities in the structure and chemistry of the hydroxides of nickel and cobalt, polymorphism in the cobalt hydroxide system is not as well known as it is among the hydroxides of nickel. The hydroxides of Ni(II) are known to crystallize in two polymorphic modifications known as α and β [1]. While the β -form is a stoichiometric phase of the composition Ni(OH)₂, the α -form is an anion containing the hydroxyl-deficient phase of the composition Ni(OH)_{2-x}(Aⁿ⁻)_{x/n}·yH₂O where Aⁿ⁻ = NO₃⁻, Cl⁻, AcO⁻, SO₄²⁻, CO₃²⁻;

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$x = 0.1\text{--}0.2$ and $y = 0.6\text{--}1.0$ [2–4]. Among the hydroxides of Co(II), the only well-known phase is $\beta\text{-Co(OH)}_2$ (PDF 30-443).

The distinguishing feature of α -nickel hydroxide is its larger interlayer spacing (7.6 Å) compared to that of the β -form (4.6 Å), on account of which the α -form has a higher electrochemical activity [1] and an interesting interlayer chemistry [5]. There is therefore considerable interest in synthesizing a hydroxide of Co(II) similar in structure and composition to α -nickel hydroxide.

We have earlier reported the synthesis and characterization of cobalt hydroxides with an enhanced interlayer spacing. Cobalt hydroxide obtained by homogeneous precipitation from solution by urea hydrolysis showed an interlayer spacing of 7.2 Å [6], while the product obtained through electrosynthesis by cathodic reduction of a cobalt nitrate solution using a corrosive electrode showed an interlayer spacing of 9 Å [7].

Genin et al. [8] have used ammonia precipitation to obtain α -nickel hydroxide. As cobalt and nickel exhibit similar chemistry, it should be possible to obtain an α -hydroxide of Co(II) by the ammonia precipitation method. In this paper, we report the synthesis of α -cobalt hydroxide by the use of ammonia as the precipitating agent.

2. Experimental

20 ml of a 0.5 M solution of a suitable cobalt salt, $\text{CoX}^{n-}_{2/n}$ ($\text{X}^{n-} = \text{NO}_3^-, \text{Cl}^-, \text{AcO}^-, \text{SO}_4^{2-}$), was added at once to 100 ml of 0.5 M NH_3 solution containing an excess of Na_nX (0.9/n moles of X^{n-} anion per mole of Co^{2+}) with vigorous stirring. Nearly quantitative precipitation was observed. The product formed was immediately centrifuged, washed free of anions with water and acetone, and dried to constant weight at room temperature (24–26°C).

All the samples were characterized by powder X-ray diffraction (JEOL JDX8P, Co K α radiation, $\lambda = 1.79$ Å), infrared spectroscopy (Nicolet Impact 400D FTIR spectrometer, KBr pellets, 4 cm^{-1} resolution), and thermogravimetry (lab-built system, heating rate, 5°C min^{-1}).

2.1. Wet chemical analysis

All samples were subjected to wet chemical analysis. A known weight (approx. 200 mg) of each sample was dissolved in a minimum amount of dil. HNO_3 and the Co content was determined gravimetrically. The absence of Co^{3+} was confirmed by dissolving a known amount of the hydroxide in excess of a standard solution of ferrous ammonium sulfate and backtitrating the excess Fe^{2+} with a standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ potentiometrically. The hydroxide content was determined by dissolving a known amount of the sample in excess of standard acid (HCl) and backtitrating the excess acid with a standard base using a pH meter. The hydroxyl content was found to be less than what was expected of a stoichiometric bivalent hydroxide in all the samples, indicating the possible presence of anions to restore charge balance. This was verified by gravimetric estimation of Cl^- and SO_4^{2-} in the corresponding samples as AgCl and BaSO_4 , respectively. The nitrate and acetate contents of

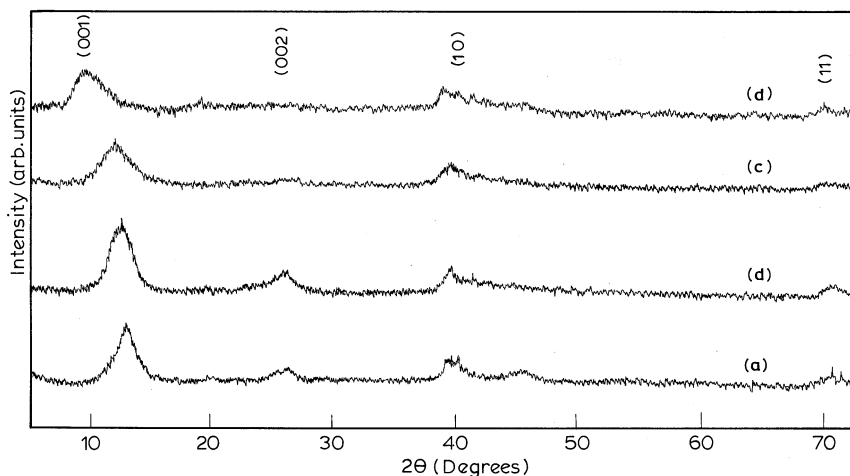


Fig. 1. The powder XRD patterns of α -cobalt hydroxide samples with intercalated chloride (a), nitrate (b), acetate (c), and sulfate (d) anions.

the other samples were assumed equal to the hydroxyl deficiency. The unaccounted weight was attributed to the water content to obtain an approximate formula for each sample. This formula was verified by TG. The end product of thermal decomposition was found to be Co_3O_4 ($a = 8.1 \text{ \AA}$) in all cases except for the sulfate containing sample, where it was assumed to be $\text{Co}_3\text{O}_4 + \text{CoSO}_4$.

3. Results and discussion

The well-known β modification of Co(II) hydroxide is a crystalline compound and exhibits sharp reflections in its powder XRD pattern at 4.65, 2.76, 2.37, 1.778, 1.591 and 1.551 \AA (PDF 30–443; $a = 3.17 \pm 0.01$, $c = 4.61 \pm 0.02 \text{ \AA}$). The powder XRD patterns of the samples prepared by ammonia precipitation are shown in Fig. 1. The prominent reflections are listed in Table 1. The complete absence of a reflection at 4.6 \AA clearly

Table 1
Powder XRD data for the α -cobalt hydroxide samples

hkl^a	d (\AA) of the α -cobalt hydroxide sample containing:			
	Cl^-	NO_3^-	CH_3COO^-	SO_4^{2-}
001	7.85	7.97	8.36	10.1
002	3.92	3.96	—	—
10	2.64	2.65	2.65	2.67
11	1.54	1.56	1.54	1.56
	$a \approx 3.09$	$a \approx 3.12$	$a \approx 3.21$	$a \approx 3.12$
	$c \approx 7.85$	$c \approx 7.97$	$c \approx 8.36$	$c \approx 10.1$

^a Indexing was done assuming a hexagonal unit cell and turbostraticity.

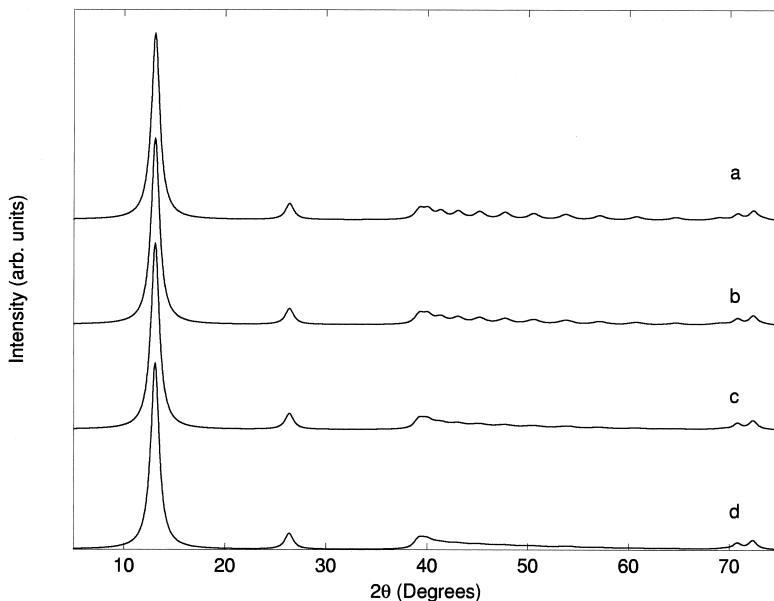


Fig. 2. Simulated powder XRD patterns of α -cobalt hydroxide calculated assuming infinite disc radius, 1.0° Lorentzian line-width with 5% (a), 10% (b), 20% (c), and 25% (d) each of A on B and A on C stacking disorders.

indicates that the hydroxides reported here are not the same as the β -hydroxide. The reflections are fewer in number and are broadly indicative of poorly ordered samples. The patterns are characterized by the appearance of a low angle reflection at $8\text{--}10\text{ \AA}$ followed, in some cases, by another reflection at one-half this spacing. A third reflection appears at $\sim 2.7\text{ \AA}$ and exhibits a pronounced asymmetry on the higher angle side. This feature is characteristic of turbostratic materials in which the layers, which are stacked one upon another, are randomly oriented about the principal (c) crystallographic axis [1]. Another reflection of a similar line shape appears at $\sim 1.56\text{ \AA}$. All these features match with the fingerprint XRD pattern of α -nickel hydroxide [1], leading us to conclude that the cobalt hydroxide samples reported here are of the α modification. Accordingly, we assign the peaks in these XRD patterns to the (001), (002), and the two-dimensional (10) and (11) reflections, respectively.

In an attempt to understand the nature of the X-ray diffraction patterns, we have used the computer code DIFFaX [9], which permits the simulation of X-ray patterns from layered crystalline materials containing coherent planar defects including stacking faults. From the crystal coordinates of a slab in the structure, DIFFaX calculates the scattering contributions for that slab. The slabs are then stacked, either in some deterministic manner or at random, one on top of the other and the scattering from the entire crystal at hkl is determined. Convolution with some suitable profile function then yields plots of the simulated diffraction pattern, which can be compared visually with the experimental diffraction pattern.

In the present case, slabs with the composition CoO_2 were considered, the protons not contributing to the diffraction pattern. The lattice parameters used were chosen to be those of the sample of Cl^- intercalated cobalt hydroxide, given in Table 1. To describe the

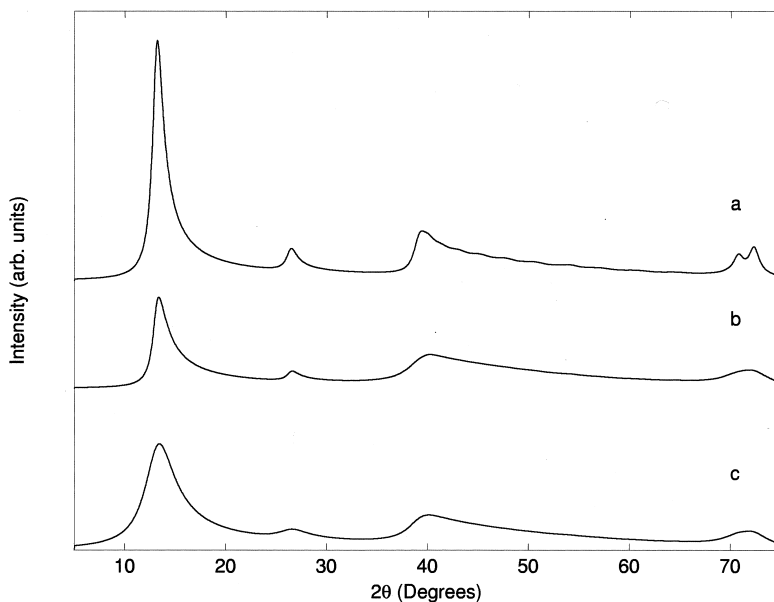


Fig. 3. Simulated powder XRD patterns of α -cobalt hydroxide calculated assuming 25% each of A on B and A on C type stacking disorders with (a) a 1000 Å disc radius, 1.0° Lorentzian; (b) 100 Å disc radius, 1.0° Lorentzian; and (c) 1000 Å disc radius, 3.0° Lorentzian.

individual slabs, Co was placed at the origin and O at $\pm\{2/3, 1/3, u\}$ with u chosen to be 0.135. This choice of u results in chemically reasonable Co–O bond lengths for the chosen lattice parameters. The slabs were stacked upon one another according to different probabilities corresponding to the following different modes. In the first mode, the new slab was stacked directly atop the previous one. This would correspond to the stacking vector **A** $\{0, 0, 1\}$. In the second mode, the new slab was shifted by the vector **B** $\{1/3, 2/3, 1\}$ before stacking it, and in the third, the vector chosen was **C** $\{2/3, 1/3, 1\}$. There is no a priori reason for choosing these vectors, except that they model typical stacking faults in layered materials.

Three parameters were separately adjusted in simulating the X-ray diffraction patterns displayed in Figs. 2 and 3. First, for a fixed Lorentzian width of 1° (used to broaden the calculated diffraction pattern) and assuming infinite slab area, the amount of AB- and AC-type stacking was varied. If only like stacking were permitted, the structure obtained would be crystalline β -Co(OH)₂ with the structure of Mg(OH)₂ [10]. Introducing disorder then meant providing for different probabilities of AB- and AC-type stackings.

We now argue that when the average over the ensemble is considered, even though the stacking vectors chosen are crystalline and permit 1T, 2H, and 3R type structures, their use in random stacking sequences would yield the same result that would be obtained through turbostratic disorder of the individual layers.

From a visual comparison of the trends in Figs. 2 and 3 with the experimental diffraction patterns, it is seen that the degree of stacking disorder is large, being consistent with as much as 50% of the stacking being of disordered (AB and AC) types. Further correspondence with the experimental patterns is achieved by introducing larger Lorentzian linewidths in the

Table 2
Compositions of the α -cobalt hydroxide samples

Intercalated anion (A^{n-})	Weight percentage				Net loss observed in TG (%)	Approximated formula
	Co	OH^-	A^{n-}	H_2O		
Cl	49.80	25.69	5.74	18.77	32.7 (32.1)	$\text{Co}(\text{OH})_{1.79}\text{Cl}_{0.19}\cdot 1.23\text{H}_2\text{O}$
AcO^-	49.22	26.02	8.25	16.51	32.4 (33.0)	$\text{Co}(\text{OH})_{1.83}(\text{AcO})_{0.17}\cdot 1.1\text{H}_2\text{O}$
NO_3^-	48.59	25.19	10.4	15.85	30.7 (34.2)	$\text{Co}(\text{OH})_{1.78}(\text{NO}_3)_{0.22}\cdot 1.07\text{H}_2\text{O}$
SO_4^{2-}	48.19	24.95	7.85	19.01	28.1 (28.2)	$\text{Co}(\text{OH})_{1.79}(\text{SO}_4)_{0.10}\cdot 1.29\text{H}_2\text{O}$

^aExpected weight loss calculated from the approximate formula is given in parentheses.

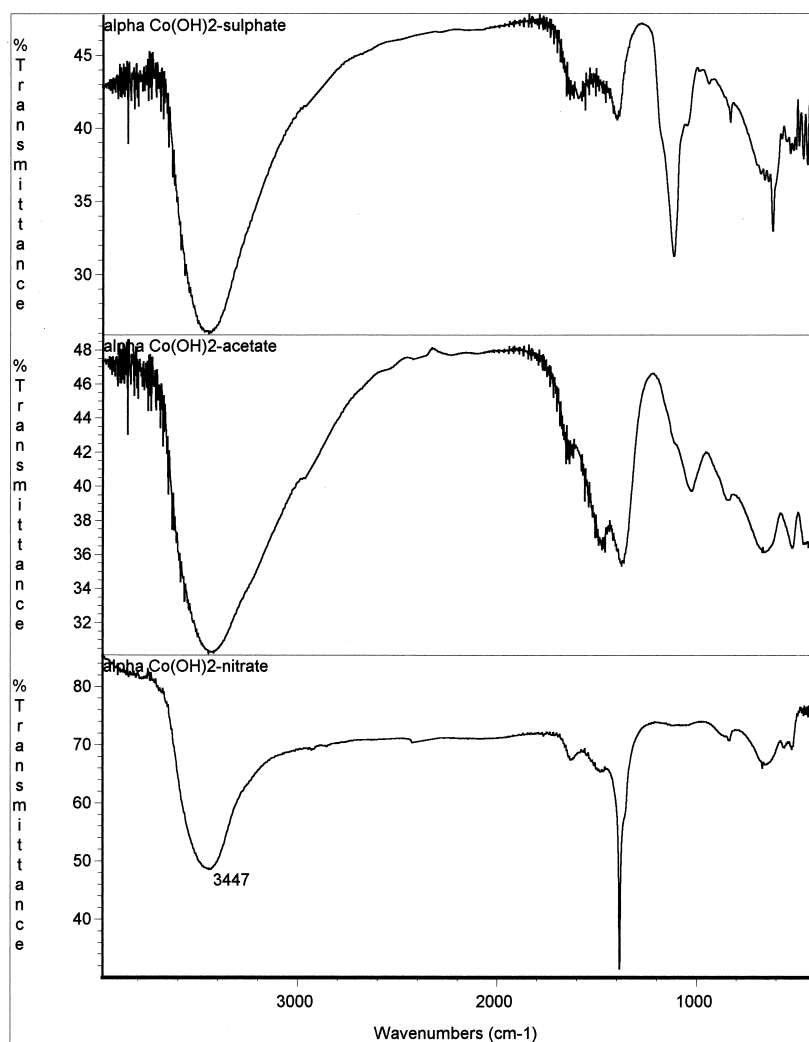


Fig. 4. The IR spectra of α -cobalt hydroxide samples with intercalated nitrate (lower panel), acetate (middle panel) and sulfate (upper panel) anions.

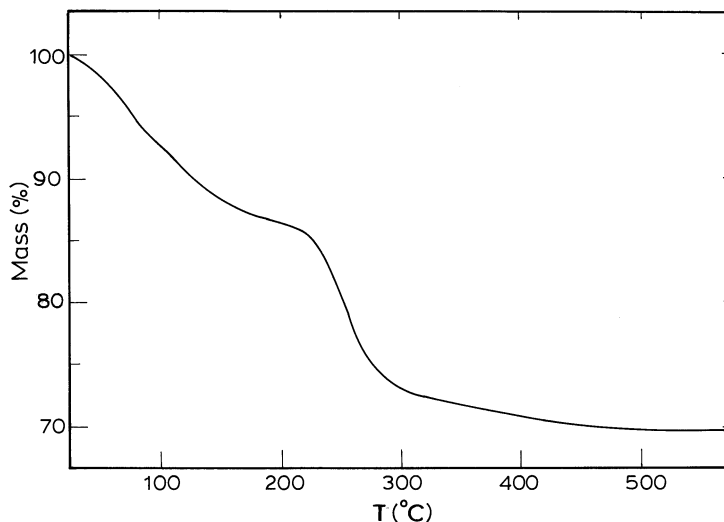


Fig. 5. The thermogram of α -cobalt hydroxide with intercalated nitrate anion.

convolution and limiting the crystalline coherence in the plane of the slab to a diameter between 100 and 1000 Å.

α -Nickel hydroxide is known to be a nonstoichiometric compound with anions intercalated between the layers. Wet chemical analyses reveal that the cobalt hydroxides reported here are also nonstoichiometric (see Table 2) with molecular formulae similar to the α -nickel hydroxides. The anions are intercalated between the hydroxide slabs leading to an increased interlayer spacing compared to the β -hydroxide. The interlayer spacing varies with the anion size in the order $\text{Cl}^- < \text{NO}_3^- < \text{AcO}^- < \text{SO}_4^{2-}$.

The presence of anions is also indicated by the IR spectra. While the β modification shows absorption only in the high ($3600\text{--}3700\text{ cm}^{-1}$) and the low ($600\text{--}400\text{ cm}^{-1}$) wave number regions due to the OH stretching and the M–OH cage vibrations respectively [11], the samples reported here show strong absorptions in the intermediate ($1500\text{--}800\text{ cm}^{-1}$) wave number region as well, due to vibrations of the anions (Fig. 4). These observations are consistent with those of Xu et al. [12]. The nitrate containing sample shows a sharp peak at 1390 cm^{-1} with shoulders at 1490 cm^{-1} (ν_4) and 1370 cm^{-1} (ν_1). The acetate containing sample shows two peaks due to the carbonyl group symmetric and asymmetric stretching vibrations at 1380 and 1480 cm^{-1} , respectively. The sulfate containing sample shows a single intense absorption at 1120 cm^{-1} with a shoulder at 1050 cm^{-1} . The small splittings ($<120\text{ cm}^{-1}$) in the different vibrational modes of the anions indicate that these anions are weakly linked to the slabs by hydrogen bonds. The possibility of the anions being grafted to the layers by direct bonding with the metal ion in the hydroxyl vacancies can be ruled out since such interactions would result in a larger ($>250\text{ cm}^{-1}$) splitting between the vibrational modes of the anions, as is seen in the basic salts [2,13]. The effect of hydrogen bonding is also seen from the broadening and the red shift of the OH stretching vibration.

The hydroxyl vacancies would then be occupied by water molecules to yield slabs of composition $[\text{Co}(\text{OH})_{2-x}(\text{H}_2\text{O})_x]^{x+}$. This so-called structural water would be a fraction of

the total water content, which includes the adsorbed and intercalated water molecules as well [14]. The dehydration is expected to be a multistep process, with the adsorbed and intercalated water loss occurring below the decomposition temperature and the structural water loss taking place along with the dehydroxylation–deanation of the hydroxide during the decomposition step. In the case of the samples reported here the adsorbed and intercalated water species are lost in a single broad step in the range 25–150°C, while decomposition begins at 200°C. Most of the weight loss ends at 300°C, but an extended flanking loss is seen up to 500°C (see Fig. 5). A similar feature observed in the TG of α -nickel hydroxide has been attributed to the loss of structural water and anions from the micropores of the crumbling sheets of the product of decomposition [15].

In conclusion, ammonia precipitation yields α -cobalt hydroxide, which is structurally and compositionally similar to α -nickel hydroxide. The mode of anion inclusion as well as the thermal behavior of α -cobalt hydroxide is similar to that of its nickel counterpart.

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