

Synthesis of α -cobalt(II) hydroxide using ultrasound radiation

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Cobalt hydroxide with an interlayer spacing of 7.53 Å and needle-like morphology has been synthesized with the aid of ultrasound radiation. Characterization by powder X-ray diffraction, transmission electron microscopy, thermogravimetric analysis, FT-IR spectroscopy, as well as elemental analysis, indicates the formation of α -cobalt hydroxide. Thermal decomposition of the hydroxide at 300 °C under air or argon yields nanometer-sized oxide particles of Co₃O₄ (ca. 9 nm) and CoO (ca. 6 nm), respectively.

1 Introduction

Chemists are increasingly contributing to the synthesis of advanced materials with enhanced or novel properties. The use of the inorganic/organic interface to achieve controlled synthesis of inorganic materials is an emerging soft chemical route to novel solids.¹ Specific molecular interactions at the inorganic/organic interface seem to control nucleation and growth, often stabilizing new modifications.²

Transition metal layered hydroxide materials, such as cobalt hydroxide and nickel hydroxide, have received increasing attention in recent years due to their many important technological applications.³ Hydroxides and oxide-hydroxides of cobalt are of importance on account of their applications in alkaline secondary batteries.⁴ A further very interesting application of these materials is as precursors of heterogeneous catalysts.⁵ The hydroxides of cobalt have a hexagonal layered structure and exist in two polymorphic forms, α and β .⁶ The first form is isostructural with hydrotalcite-like compounds, while the second is brucite-like [Mg(OH)₂] and consists of hexagonally packed hydroxy ions with Co(II) ions occupying alternate rows of octahedral sites. The α -hydroxides have a large interlayer spacing (> 7 Å) compared with the β -form (ca. 4.6 Å) and are isostructural with the layered double hydroxide (LDH) phases. The α -hydroxide is a hydroxy deficient compound and consists of stacks of positively charged layers of composition Co(OH)_{2-x}(H₂O)_x, which intercalate anions and water molecules in the interlayer space to restore charge neutrality.⁷ When some of the hydroxyl groups are missing from their positions in the brucite-like sheets, intercalation of anions occurs to restore charge neutrality. The resultant compounds produced in this way have large interlayer spacings due to the anion occupation between the brucite-like sheets.

There has been a considerable degree of interest in evolving an accelerated chemical route to bulk α -hydroxides of cobalt. In contrast to α -nickel(II) hydroxide, there is little reported work on α -cobalt(II) hydroxide.⁸⁻¹⁰ The α -hydroxides are metastable and are difficult to synthesize, as they age rapidly to the β -form. Synthesis of a stable hydrated form of cobalt(II) hydroxide with a large interlayer spacing similar to α -Ni(OH)₂ holds exciting prospects because such a phase should, in principle, show superior electrochemical performance compared with the β -form.¹¹

Chemical synthesis of cobalt hydroxide in a simple precipitation reaction leads to autooxidation of cobalt(II) under high pH conditions. Cathodic reduction of an aqueous solution of cobalt nitrate at low pH, high Co(II) ion concentration and low current densities leads to the formation

of a novel layered hydroxide of Co(II) with an interlayer spacing of 8.9 Å, which the authors have also assigned as the α -phase.⁸ The α -form of cobalt hydroxide was also synthesised by cathodic reduction of a cobalt(II) nitrate solution containing one weight percent of fructose as additive.¹⁰ Homogeneous precipitation using urea as a precipitating agent in a domestic pressure cooker was also used to synthesize α -cobalt hydroxide.⁹

In this paper, we have investigated the synthesis of an α -modification of cobalt(II) hydroxide using ultrasound radiation. We call this phase α -cobalt hydroxide, in keeping with the nomenclature used for the hydroxides of Ni(II). We have accounted for all the observed structural, compositional and morphological features of the α -type hydroxides.

Sonic energy has been routinely used in the field of materials science for many years. Its chemical effects have recently come under investigation for the acceleration of chemical reactions and for the synthesis of new materials,¹² as well as for generating novel materials with unusual properties.¹³ The chemical effects of ultrasound radiation arise from acoustic cavitation. The extremely high temperatures (\approx 5000 K), pressures (> 20 MPa) and cooling rates (> 10¹⁰ K s⁻¹) attained during cavitation lead to many unique properties in the irradiated solution and these extreme conditions have been exploited to prepare nanoscale metals, metal oxides, and nanocomposites.^{14,15} It is also believed that the interparticle collisions, which occur at very high speed during high intensity ultrasound radiation, ultimately lead to fusion and agglomeration.¹⁶

Homogeneous precipitation using urea has been increasingly employed to synthesize novel hydroxide phases and fine particulate materials.¹⁷ Urea is a very weak Brønsted base and its hydrolysis rate may be easily controlled by means of the temperature.¹⁸ The objective of the present work is to utilize ultrasound radiation in the process of homogeneous precipitation for the synthesis of α -cobalt hydroxide.

2 Experimental

Preparation

The synthesis of α -cobalt hydroxide has been carried out with the aid of ultrasound radiation. Typically, to an aqueous 0.2 M solution of Co(NO₃)₂·6H₂O in a sonication flask (total capacity 80 ml, 26 mm o.d.), 3.5 g of urea (Aldrich) was added. The urea was homogeneously dissolved in the cobalt nitrate solution at room temperature. The solution was purged with argon for 30 min and irradiated with high intensity

ultrasound radiation for 2.5 h by employing a direct immersion titanium horn (20 kHz, 100 W cm⁻²). The titanium horn was inserted to a depth of *ca.* 1 cm into the solution. The temperature during the sonication experiment increased to 80 °C, as measured by an iron–constantan thermocouple. The pH of the solution changed from 5.7 prior to the sonication to 6.1 at the end of the reaction.

After the precipitation process was completed, the precipitates were separated from the solution by centrifugation. The recovered precipitates were washed several times with distilled water and dried under vacuum. For comparison, a sample of cobalt hydroxide was also synthesised under the same conditions, except that ultrasound radiation was not used.

Product characterization

Powder X-ray diffraction patterns were recorded by employing a Rigaku X-ray diffractometer (Model-2028, Cu-K α , $\lambda = 1.5418$ Å). The morphology of the products was determined by transmission electron microscopy (TEM, JEOL-JEM 100SX microscope). Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid coated with carbon film (400 mesh, Electron Microscopy Sciences) and were allowed to dry in air. FT-IR spectra were recorded on a Nicolet Impact 410 infrared spectrophotometer from KBr pellets in the range 400–4000 cm⁻¹. Thermogravimetric analysis was carried out using a Mettler Toledo TGA/SDTA851 instrument attached to a mass spectrometer (Balzers Instruments) in the temperature range 30–900 °C at a rate of 10 °C min⁻¹ under an argon atmosphere. Elemental analysis was carried out using a Eager 200 CHN analyser.

3 Results and discussion

From the elemental analysis, in combination with the results obtained from thermal gravimetric measurements, the stoichiometry of the product was found to be Co(OH)_{1.8}(CO₃)_{0.1}(NH₃)_{0.65}. The cobalt content of the sample was estimated gravimetrically using standard methods. The absence of trivalent cations in the α -hydroxides was checked by reaction with excess ferrous ammonium sulfate and back titrating the excess with standard potassium dichromate. Comparison with a blank titration confirmed the absence of any trivalent ions in the α -hydroxides.

Fig. 1 displays the XRD pattern of cobalt(II) hydroxide synthesized using ultrasound radiation. Table 1 lists the observed *d* values along with the *hkl* indexing. The peak positions observed are consistent with those reported earlier.^{7,9} The α -modifications are characterized by a low-angle reflection at *d* values of 7.5 to 7.8 Å due to the (003) plane, followed by a

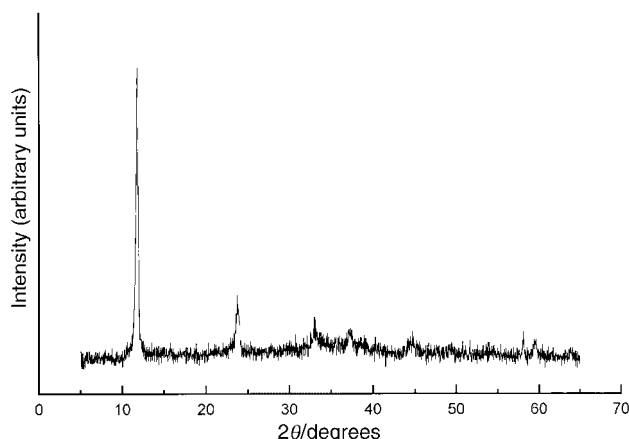


Fig. 1 Powder XRD pattern of cobalt(II) hydroxide obtained with the aid of ultrasound radiation.

Table 1 Observed *d* values, along with indexing, for cobalt(II) hydroxide synthesised with ultrasound

| <i>hkl</i> | <i>d</i> /Å |
|------------|-------------|
| 003 | 7.531 |
| 006 | 3.754 |
| 101 | 2.718 |
| 105 | 2.414 |
| 107 | 2.032 |
| 110 | 1.590 |

reflection at 3.7 to 3.9 Å due to the (006) plane. The β -form, on the other hand, has a more compact cell and its first reflection appears at 4.6 Å, due to the (001) plane. The sample synthesised without the aid of ultrasound radiation showed an interlayer spacing of 7.28 Å. The X-ray diffraction data prove unequivocally that the phases obtained are α -type hydroxides. The larger *d* spacing of the α -form is due to the presence of interlamellar anions, to preserve charge neutrality, and intercalated water molecules. Further evidence for the presence of interlamellar anions and water molecules comes from the IR and TGA studies to be discussed later. The α -hydroxides are poorly ordered phases and exhibit broad bands in their X-ray diffraction patterns. As a result, there is a considerable variation in the interlayer spacing reported by different authors.¹¹ The α -phases obtained by us are reasonably well ordered.

In Fig. 2 the results of electron microscopic investigations of cobalt(II) hydroxide samples synthesised in the present study are shown. The TEM picture of a sample synthesised under the same conditions, except that ultrasound radiation was not used, is also presented. There is a clear morphological difference in particle shape between the two samples. The sample synthesised with the aid of ultrasound radiation consists of scaly particles. The particles have a needle-shaped morphology (length *ca.* 100 nm, width *ca.* 10 nm). The turbostratic morphology in Fig. 2(a) is characteristic of the α -hydroxides,¹¹ whereas the sample prepared without sonication consists of well-defined crystalline platelets, with the hexagonal platelet morphology seen among the β -type hydroxides. However, on the basis of the XRD results, we assign this sample as an α -type cobalt hydroxide with a platelet morphology. The sonication of the solution not only helps in the formation of shaped particles, but also aids in the formation of nanosized particles after the precipitation step. It appears that the formation of nanosized particles is enhanced by the use of sound waves.

Fig. 3 shows the IR spectrum of the sample synthesized using ultrasound. The spectral features are typical of the α -type hydroxides, which are described in detail elsewhere.¹⁹ The broad band at *ca.* 3489 cm⁻¹ can be attributed to the hydroxyl groups, which are extensively hydrogen-bonded. The band at *ca.* 1634 cm⁻¹ is assigned to the bending vibrational mode of the interlayer water molecules. The absorption band at *ca.* 2200 cm⁻¹ has been attributed to the existence of intercalated NH₃ species, as suggested by Kamat *et al.*⁹ The IR spectrum provides evidence for the presence of intercalated carbonate ions. The absorption band at *ca.* 1481 cm⁻¹ has been attributed to the ν_3 mode of CO₃²⁻ ions. The other bands at *ca.* 1071, 830 and 742 cm⁻¹ have been assigned to the ν_1 , ν_2 and ν_4 modes of the carbonate ion, respectively. The interactions existing between the carbonate ions and the water molecules in the interlayer space and/or the cations (or hydroxyl groups) from the layers lead to a decrease in their symmetry (*C*_{2v}) from that existing in the free carbonate ion (*D*_{3h}). The ν_1 mode of carbonate is IR inactive under *D*_{3h} symmetry but becomes active under *C*_{2v} symmetry.²⁰ Therefore, if the band due to this stretching mode is observed, it can be considered as evidence for a change in symmetry of the carbonate (1080 cm⁻¹ for free

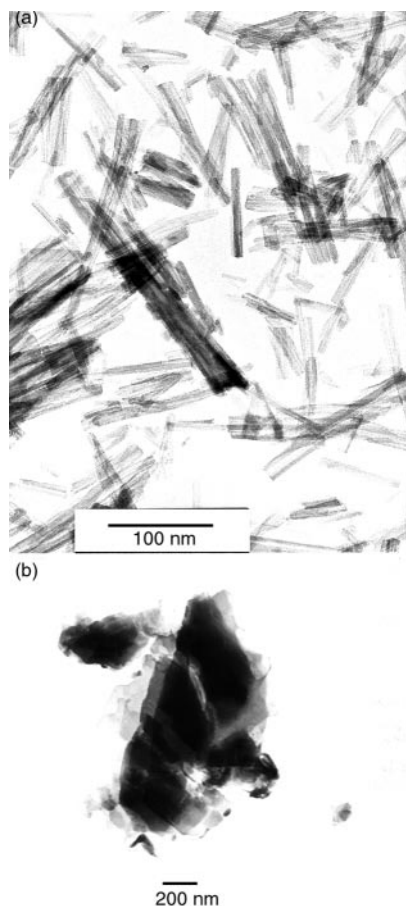


Fig. 2 Transmission electron micrograph of cobalt(II) hydroxide obtained in the presence (a) and in the absence (b) of ultrasound radiation.

CO_3^{2-}). For our sample, a fairly weak band is recorded at *ca.* 1072 cm^{-1} indicating such a change, *i.e.* $D_{3h} \rightarrow C_{2v}$. The band at 682 cm^{-1} has been assigned to δ_{OH} vibrations. The band at 635 cm^{-1} has been ascribed to $\nu_{\text{Co-OH}}$. The IR spectrum of the sample synthesised without the aid of ultrasound radiation showed similar bands to that of the sample synthesised with the aid of ultrasound radiation, except for a difference in the intensities of the bands.

The thermogravimetric pattern of the needle-shaped cobalt hydroxide sample over the temperature range $30\text{--}900\text{ }^\circ\text{C}$ exhibits a single step, with a weight loss of 30.3% around $254\text{ }^\circ\text{C}$. α -Hydroxides of cobalt are known to undergo multi-step and larger mass losses compared with the β -hydroxide phase, which shows a weight loss close to 13.5%.⁸ The samples obtained in the present study undergo a single-step dehydra-

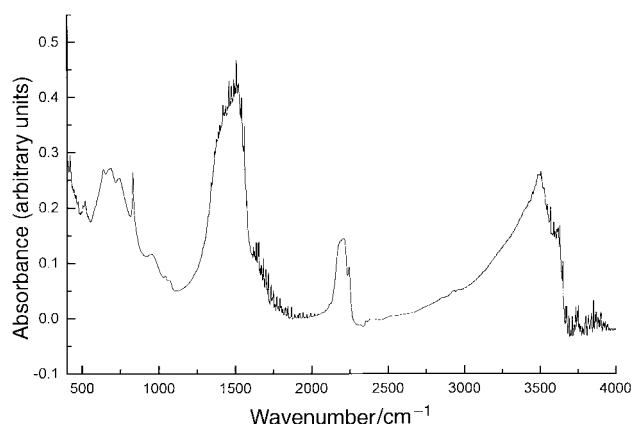


Fig. 3 Infrared spectrum of needle-shaped α -cobalt(II) hydroxide.

tion–decomposition reaction. During the decomposition, a peak at m/z 44 was detected in the mass spectrum which can be ascribed to the evolution of carbon dioxide. The observed mass loss agrees well with what is expected from the formulae obtained from chemical analysis (expected weight loss = 29.6%; observed weight loss = 30.3%). The TGA pattern of the sample synthesised without the aid of ultrasound radiation showed a single step weight loss of 25.3%, corresponding to decomposition. A peak at m/z 44 was also detected in the mass spectrum due to the evolution of CO_2 .

Fig. 4 shows the XRD patterns of the thermal decomposition products of the needle-shaped α -cobalt hydroxide at $300\text{ }^\circ\text{C}$ in air and under an argon atmosphere. From the XRD results, it can be inferred that if the decomposition is carried out under an argon atmosphere, CoO (JCPDS card no. 9-402) is formed, while in air the decomposition product is Co_3O_4 (JCPDS card no. 9-418). The oxides so obtained have a particle size in the nanometer range (*ca.* 6 nm for CoO and *ca.* 9 nm for Co_3O_4), as calculated from powder X-ray patterns using the Debye–Scherrer equation. Particle sizes from TEM results (Fig. 5) also are in accordance with the XRD measurements.

The role of urea in the homogeneous precipitation of α -cobalt hydroxide is to decompose urea homogeneously by hydrolysis in the solution upon heating, producing CO_2 gas and OH^- and NH_4^+ ions in solution. This increases the pH of the medium in a controlled manner, depending on the temperature.¹⁸ A pH measurement before and after the sonication experiment revealed that the pH of the solution increased from 5.7 to 6.1. This increase in pH is favourable for the formation of α -cobalt hydroxide. The use of ultrasound radiation during this homogeneous precipitation process can accelerate the process and can also be beneficial for controlling particle size and shape in the nanoscale range.

We will now consider the mechanism by which the needles of crystalline α -cobalt hydroxide are formed. The effects of ultrasound radiation on chemical reactions are due to the very high temperatures and pressures which develop during the sonochemical cavity collapse, *via* a process called acoustic cavitation. There are two regions of sonochemical activity, as postulated by Suslick *et al.*:^{21,22} the inside of the collapsing bubble and the interface between the bubble and the liquid, which extends to about 200 nm from the bubble surface. If the reaction takes place inside the collapsing bubble, as is the case for transition metal carbonyls in organic solvents, the temperature inside the cavitation bubble can be $5100\text{--}2300\text{ K}$, depending on the vapour pressure of solvent.²¹ If water is used as the solvent, the maximum bubble core temperature that can be attained is close to 4000 K .²³ The product obtained is amorphous as a result of

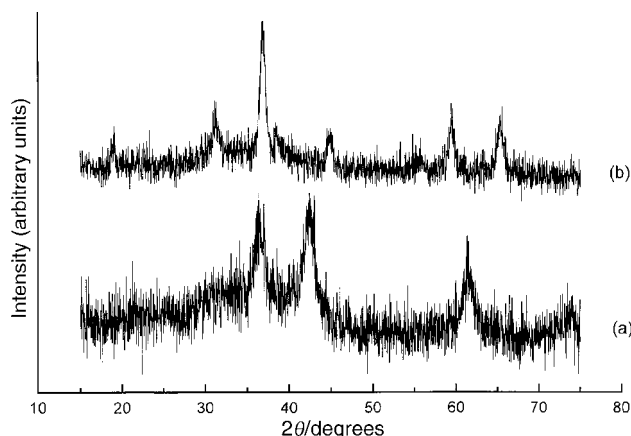


Fig. 4 Powder XRD patterns of the thermal decomposition products of needle-shaped α -cobalt(II) hydroxide (a) under air and (b) under argon.

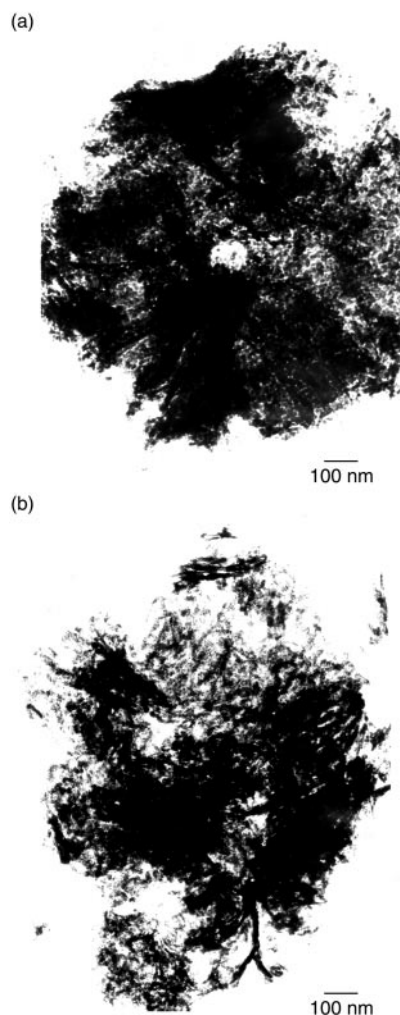


Fig. 5 TEM micrographs of the thermal decomposition products of needle-shaped α -cobalt(II) hydroxide (a) under air and (b) under argon.

the high cooling rates ($>10^{10} \text{ K s}^{-1}$) which occur during the collapse. On the other hand, if the reaction takes place at the interface, the temperature of which has been measured at 1900 K,²¹ one would expect to get nanocrystalline products. If the solute is ionic, and hence has a low vapour pressure, then during sonication the amount of ionic species will be very low inside the bubble and little product can be expected to occur here. Since in the present study the solute is cobalt nitrate, which is ionic, and nanocrystalline α -cobalt hydroxide is formed, we propose that the formation of cobalt hydroxide occurs at the interface between the bubble and the liquid.

4 Conclusions

An easy and convenient approach to the preparation of α -cobalt hydroxide using ultrasound radiation has been described. The compound shows needle-like morphology and has been characterized by a variety of techniques. Cobalt hydroxide synthesised without the use of ultrasound radiation also leads to an α -phase, but with a hexagonal platelet-like morphology. This morphology is significantly different from that of the sonochemically synthesised needle-shaped material. Thermal decomposition of the needle-shaped α -cobalt hydroxide gives rise to nanosized oxides, CoO and Co_3O_4 in argon and air respectively. Synthesis of materials with the aid of ultrasound radiation proves to be a convenient method for the production of materials with new modifications.

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