

Synthesis of Copper(II)-Containing Nickel(II) Hydroxide Particles as Precursors of Copper(II)-Substituted Nickel(II) Oxides

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Copper(II)-containing nickel(II) hydroxide particles, i.e., $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ ($0 < x \leq 0.4$), have been prepared by aging 0.5 mol dm⁻³ urea, Ni(NO₃)₂, and Cu(NO₃)₂ solutions at 363 K. After 3 h, coprecipitation is almost complete. The formed solids, characterized by powder X-ray diffraction, scanning electron microscopy, energy dispersion X-ray spectroscopy, and Fourier transform infrared spectroscopy, preserve the typical characteristics of $\alpha\text{-Ni}(\text{OH})_2$. Still, their chemical composition, i.e., the copper-to-nickel ratio, is nearly that of the initial solutions. The analysis of the processes that take place during the formation of $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ indicates that, although Cu(II) and Ni(II) precipitation are separate events, the simultaneity of *am*-Cu(OH)₂ (amorphous copper(II) hydroxide) redissolution and $\alpha\text{-Ni}(\text{OH})_2$ growth provides the appropriate conditions for the intercalation of aqueous Cu(II) species within the interlayer space of the growing $\alpha\text{-Ni}(\text{OH})_2$ particles. Upon mild thermal treatment, i.e., $T \geq 523$ K, $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ powders are readily converted in Ni_{1-x}Cu_xO (bunsenite), provided $x \leq 0.33$; when x is larger than 0.33, the thermodynamically expected segregation of tenorite is realized. The ease of Ni_{1-x}Cu_xO (bunsenite) formation is rationalized in terms of the topotatic relationship between the layered structure of the precursors and the rock salt structure of the mixed oxide.

Introduction

Mixed metal oxides constitute a wide class of inorganic compounds that range from solid solutions to stoichiometric solids of precise composition. Substitution of a metal, M, for another, M', in the framework of MO₂ results in altered, or even new, properties that are of practical interest in many fields of application. Currently, the most common preparative methods of these materials are based on solid-state reactions that involve precursor phases synthesized by sol-gel procedures.¹⁻⁵ The clear advantages of these novel methods, over the traditional heat treatment of mixtures of individual metal oxides or metal salts, stem from the less stringent kinetic barriers set by the higher degree of metal intermixing that coprecipitation of precursor phases allows for. All procedures, however, share in common the constraints imposed by the ther-

modynamic stability of the mixed oxides to be synthesized. Thus, any attempt to improve preparation procedures resorts to the synthesis of better precursors, which, in turn, requires sound knowledge of the processes involved in this preparative stage.

Coprecipitation from aqueous solutions is a very useful route to prepare mixed metal hydroxides, or basic salts, as precursor phases. Different strategies of synthesis have been explored: coprecipitation at large supersaturation degrees (usually fixed by the dosing of reagents),⁶⁻⁹ forced hydrolysis by thermal decomposition of aqueous metal complexes,¹⁰⁻¹³ and homogeneous alkalization by urea hydrolysis.¹⁴⁻¹⁸ The latter pro-

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cedure, which allows for the gradual increase of supersaturation, is perhaps one of the most suitable methods to explore the processes leading to the formation of the mixed precursors.^{19,20}

In this work, we investigate the mechanism of formation of Cu(II)-containing α -Ni(OH)₂ particles during the coprecipitation of Cu(II) and Ni(II) from solutions that become alkaline, homogeneously, by the hydrolysis products of urea, and we report the synthesis of Ni_{1-x}Cu_xO (bunsenite), $x \leq 0.33$, by subsequent thermal treatment.

The studied system is not only challenging, for the different hydrolytic and complexation chemistries of Cu(II) and Ni(II) would restrict the synthesis of the mixed hydroxides via coprecipitation to very narrow conditions, it has also important implications in the realm of the performance of materials. Indeed, both Ni_{1-x}Cu_xO and its precursor, copper(II)-containing nickel(II) hydroxide, have potential applications in different fields of current interest. The mixed oxides provide the active materials of catalysts used in the production of synthesis gas from steam-reforming of ethanol²¹ and in the reduction of NO_x.²² Usually, these catalysts are prepared by traditional impregnation procedures, which may lead to the segregation of the active components. The procedure attempted here, instead, should grant a larger degree of homogeneity and, perhaps, a lesser reduction of the surface area due to the lower temperatures required for oxide formation. Nickel(II) hydroxide, on the other hand, has received considerable attention because of its electrochemical and electrochromic properties. Partial substitution of Ni(II) by metal ions that hinder the α -Ni(OH)₂ \rightarrow β -Ni(OH)₂ transition improves the cycling durability of nickel cathodes.²³⁻²⁵ Similarly, its electrochromic properties can be tailored by substitution of Ni(II) by adequate transition metal cations.^{26,27} Interestingly, partial substitution by Cu(II) should provide intermediate redox levels that must expand the electrochromic response to more cathodic potentials. The properties of copper(II)-containing nickel(II) hydroxide, however, have not yet been characterized, presumably because of the lack of a suitable synthesis procedure.

Experimental Section

Materials. Stock solutions of nickel(II) nitrate and copper(II) nitrate (0.025 mol dm⁻³, each) were prepared by dissolving Ni₂(OH)₂CO₃ in dilute HNO₃ and Cu(NO₃)₂·8H₂O in water, respectively, filtered through 0.2 μ m pore size cellulose nitrate membranes and stored in plastic bottles.

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All solutions were made up using analytical grade reagents and deionized water (18 M Ω cm) obtained from a Milli-Q apparatus. All glassware was washed using a sulfonitric acid solution (10 g of H₂SO₄ and 10 g of HNO₃ in 100 mL) and rinsed thoroughly with water and steam.

Procedures. Precursors were prepared by aging mixed nickel(II)-copper(II) urea containing solutions at 363.0 \pm 0.5 K for different periods. In all cases, the concentrations of urea and total metal (i.e., [Ni(II)]₀ + [Cu(II)]₀) were kept constant at 0.5 mol dm⁻³ and 5.0 \times 10⁻³ mol dm⁻³, respectively, and the initial pH was fixed at 5.0 \pm 0.1 by addition of NH₃; these experimental conditions were found to be adequate for the synthesis of mixed Gd(III)-Cu(II) and Zn(II)-Cu(II) compounds.^{17,18} The ratio Cu(II) to total metal, $X = [Cu(II)]_0 / ([Ni(II)]_0 + [Cu(II)]_0)$, was varied between 0.1 and 0.4.

Typically, precipitation experiments were performed as follows. Starting solutions were prepared by mixing the necessary amounts of the stock solutions, solid urea, and water to yield the desired reactant concentrations. Aliquots (10 mL) of the filtered solutions were poured in 20 mL screw-capped borosilicate test tubes, which were then placed in a thermostated water bath preheated at the working temperature. After prefixed time intervals, the tubes were removed and immersed in an ice-water bath to quench the reaction; the temperature of the systems dropped ca. 60 K in less than 1 min. Precipitated solids were collected by filtration through 0.2 μ m pore size cellulose nitrate membranes, washed three times with cold water, and dried in vacuo at room temperature. Supernatant solutions were stored for chemical analyses; pH was measured (\pm 0.02 units) using a combined glass-electrode, and Cu(II) and Ni(II) were determined, within 1%, by atomic absorption spectrometry.

Cu(II) to Ni(II) ratios in the precipitated samples were assessed by atomic absorption spectrometry, after dissolving the powders in concentrated nitric acid.

Mixed oxides were synthesized by heating precursors coprecipitated after 3 h of aging. The precursors, contained in ceramic crucibles, were placed in a tubular furnace preheated at the working temperature (423 \leq T/K \leq 673) and left standing for different prefixed periods, after which the thermal reaction was quenched. During heating, all powders were kept under nitrogen to avoid Ni(II) oxidation. Simultaneously, differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses were carried out at a 5.0 K min⁻¹ temperature ramp; the nitrogen flow was 50 cm³ min⁻¹.

All synthesized solids were characterized by powder X-ray diffraction (PXRD) using the graphite-filtered Cu K α radiation ($\lambda = 1.5406$ Å), scanning electron microscopy (SEM), energy dispersion X-ray spectroscopy (EDS), and Fourier transform infrared spectroscopy (FTIR).

Results and Discussion

Characterization of Coprecipitated Precursors.

The aging of Cu(II) and Ni(II) nitrate solutions ($0 < X \leq 0.4$) containing 0.5 mol dm⁻³ urea for 3 h at 363 K leads to almost complete coprecipitation and produces crystalline mixed copper(II)-nickel(II) hydroxides. The PXRD diagrams of all synthesized powders show well-defined peaks at 7.31, 3.647, 2.669, and 1.555 Å (Figure 1), which correspond, respectively, to the [003], [006], [101], and [110] reflections of the turbostratic structure of α -Ni(OH)₂.²⁸⁻³¹ The term turbostratic indicates the orientational disorder of the successive brucite-like

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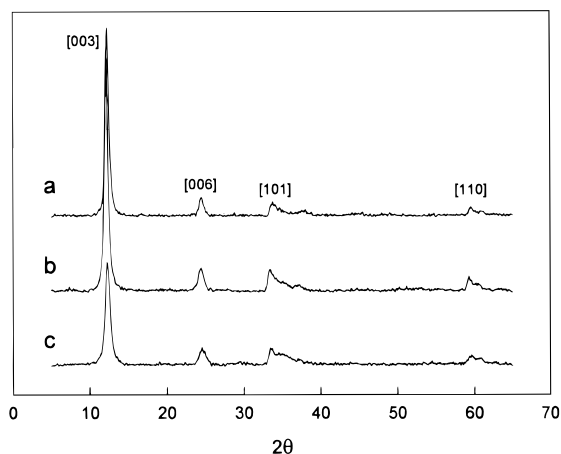


Figure 1. PXRD patterns of $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ particles synthesized after the aging of mixed systems for 180 min at 363 K: (a) $x = 0.14$, (b) $x = 0.22$, (c) $x = 0.40$.

$\text{Ni}(\text{OH})_2$ layers that are spaced along the c -axis by intercalated water molecules. Since no peaks corresponding to any possible crystalline copper solid phase are detected in the PXRD diagrams, the solids can be described as $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$; the values of x , which were assessed both chemically and by EDS analyses, are nearly equal to X .

Although the focus of this work is the synthesis of $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ as $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ precursors (the thermodynamic solubility of CuO in NiO is ca. 34 mol %),^{32,33} the results of a brief exploration of coprecipitation from $X > 0.4$ systems are worth mentioning. The $0.8 \leq X < 1$ systems evolve to yield $\text{Ni}(\text{II})$ -substituted malachites and systems of intermediate compositions ($0.5 < X < 0.8$) yield mixtures of $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ and $\text{Ni}(\text{II})$ -substituted malachites. As judged by the nature of the latter solids, coprecipitation from copper-rich mixed solutions should resemble, with slight differences, that described earlier for mixed $\text{Cu}(\text{II})\text{-Zn}(\text{II})$ systems;¹⁸ a detailed study of the formation of $\text{Ni}(\text{II})$ -substituted malachites is currently in progress.

The morphology of the synthesized $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ particles is illustrated by the SEM micrograph presented in Figure 2. All particles present the expected crystalline habit of $\alpha\text{-Ni}(\text{OH})_2$ and are fairly uniform in size. It is worth noting that they are also uniform in composition, as $\text{Cu}(\text{II}):\text{Ni}(\text{II})$ ratios determined by EDS analyses were constant and independent of the probed spots.

FTIR spectra of different $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ particles are collected in Figure 3. The spectrum of $\alpha\text{-Ni}_{0.86}\text{Cu}_{0.14}(\text{OH})_2$ is very similar to those reported earlier for pure $\alpha\text{-Ni}(\text{OH})_2$.^{28–30} The notable difference, however, is the intense band at ca. 2250 cm^{-1} , which is present in the spectra of all precipitates and becomes weaker as x increases. This band is a characteristic of $\alpha\text{-Ni}(\text{OH})_2$ particles synthesized via the urea method,^{31,34,35} and must be assigned to the $\nu_{\text{C}\equiv\text{N}}$ stretching of OCN^- ions.³⁶ Although the production of cyanate is intrinsic to the urea method, OCN^- ions were not

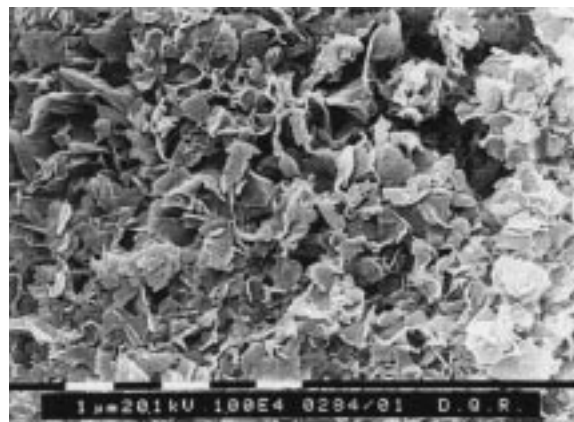


Figure 2. SEM micrograph of $\alpha\text{-Ni}_{0.78}\text{Cu}_{0.22}(\text{OH})_2$ particles synthesized after the aging of the 0.22 systems for 180 min at 363 K.

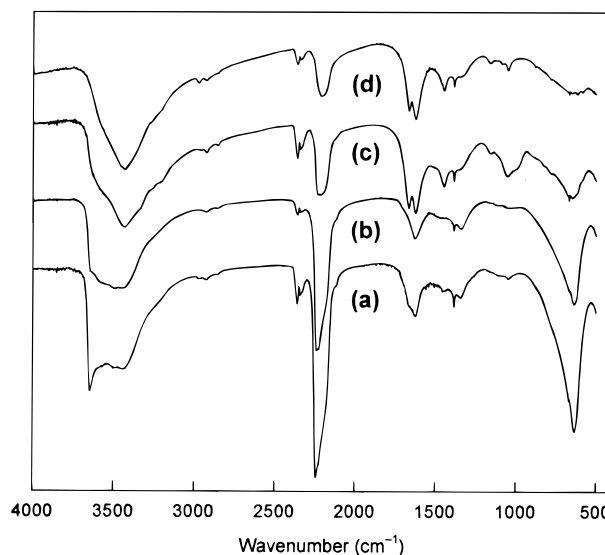


Figure 3. FTIR spectra of $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ particles synthesized after the aging of mixed systems for 180 min at 363 K: (a) $x = 0.14$, (b) $x = 0.22$, (c) $x = 0.30$, (d) $x = 0.40$.

detected in other solids prepared through this procedure (see, e.g., refs 17, 18, and 37). It was speculated that OCN^- ions can be hosted within the interlayer space of the turbostratic structure of $\alpha\text{-Ni}(\text{OH})_2$.³⁵ Anion intercalation, however, is only akin to layered double hydroxides, which bear a fixed positive charge due to isomorphic substitution by a trivalent cation.^{38–40} Since partial substitution of lattice hydroxyls by weakly complexing anions, such as nitrate and carbonate, is known,⁴¹ a more plausible explanation would invoke the formation of inert $\text{nickel}(\text{II})\text{-cyanate}$ complexes that become incorporated into the growing $\text{Ni}(\text{OH})_2$ layers; note that the intensity of the cyanate band increases

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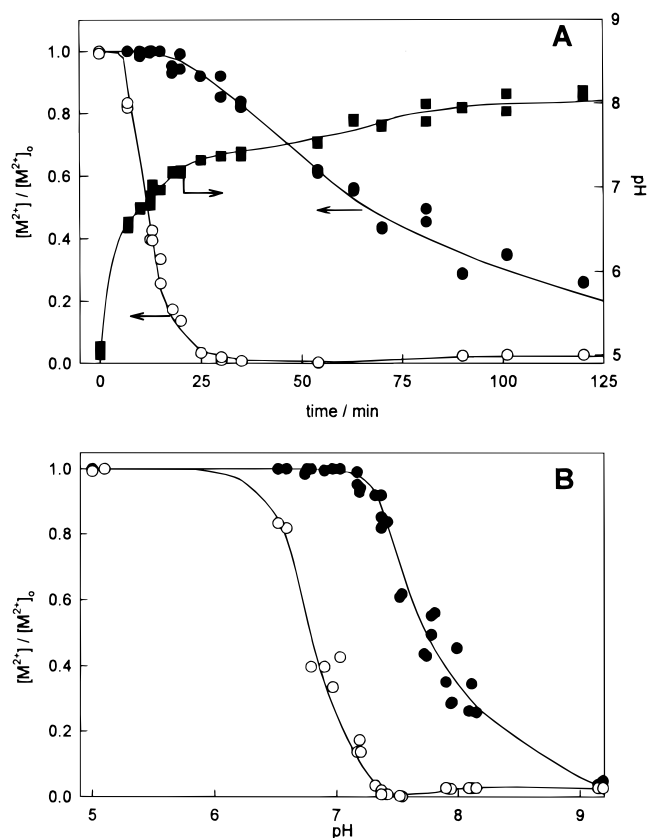


Figure 4. (A) Evolution of pH (■) and copper (○) and nickel (●) concentrations during the aging of the 0.14 system at 363 K. (B) pH dependence of the concentrations of (○) copper and (●) nickel.

with Ni(II). The actual cyanate content in the α -Ni_{1-x}Cu_x(OH)₂ particles should, nevertheless, be small, for $\nu_{C=N}$ bands are known to be very strong.³⁶

The other important bands present in the FTIR spectra (Figure 3) are the sharp band at 3650 cm⁻¹ assigned to the ν_{O-H} stretching of geminal hydroxyls in the brucite-like structure,²⁸⁻³⁰ the doublets at ca. 1600 and 1430 cm⁻¹ due to the $\nu_{C=O}$ stretching of bidentate and monodentate carbonate ions in the C_{2v} symmetry,³⁶ respectively, and the band at 680 cm⁻¹ assigned to the δ_{O-H} wagging vibration.²⁸⁻³⁰ Furthermore, all of them are sensitive to x ; while the intensities of the bands due to OH vibrations modes decrease with increasing Cu(II), those assigned to carbonate modes increase.

Formation of α -Ni_{1-x}Cu_x(OH)₂. To identify the processes that lead to the formation of α -Ni_{1-x}Cu_x(OH)₂, the evolution of the systems was monitored as a function of time. Figure 4a, which presents a typical case, illustrates how the composition of the aqueous phase changes during aging. The data, replotted in Figure 4b in the form of a concentration vs pH graph, demonstrate that precipitation of copper and nickel are separate events. The observed trend is in line with the higher absolute solubility of nickel hydroxide at any pH less than 11.⁴² Inasmuch as the overall rate of pH drift (Figure 4a, squares) is determined by the interplay of urea hydrolysis and the base consumption processes leading to precipitation, the slower removal of nickel

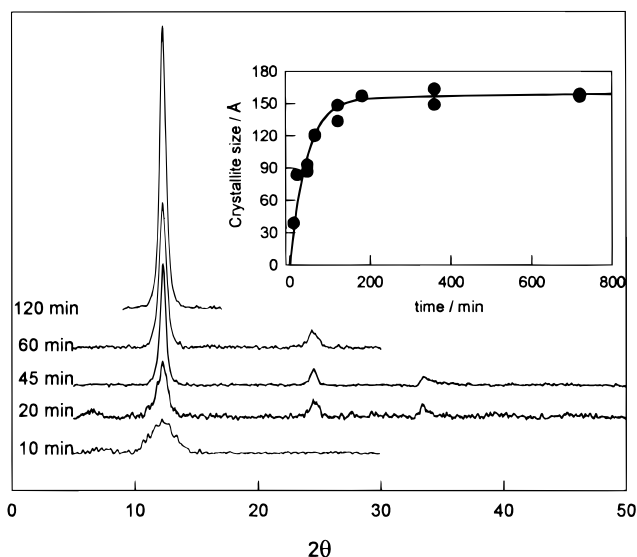


Figure 5. PXRD patterns of the solids formed during the aging of the 0.14 system at 363 K. The inset shows the growth of the crystallite size along the c -axis estimated according to the Scherrer equation.

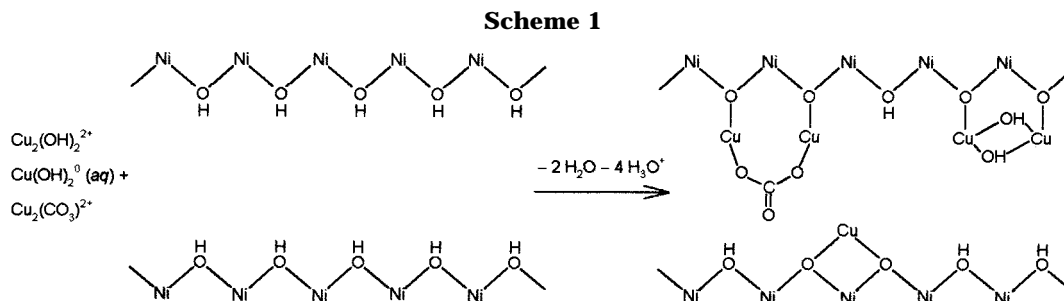
(Figure 4a, circles) reflects the lower rate of urea hydrolysis at the higher pH values.²⁰ As a result, the net composition of the solids varies until coprecipitation becomes complete.

The precipitation behavior of copper and nickel depicted in Figure 4 parallels that observed in the equivalent single-metal systems. The main difference is the disappearance of the pH overshoot that reveals the onset of nickel precipitation in Ni(II) single-metal systems.²⁰ This seems to be the only effect that copper exerts on the overall precipitation behavior of nickel. In fact, Figure 5 shows that, as in the case of Ni(II) single-metal systems, α -Ni(OH)₂ forms as soon as nickel precipitation starts; note that the peak at $d = 7.31$ Å is clearly evident at 10 min, an aging time at which less than ca. 2% Ni(II) has been removed from solution. The increasing definition of the peak reflects the growth of the crystallites during aging (see the inset in Figure 5).

While the presence of Ni²⁺ ions does not influence the early stages of copper precipitation, formation of the turbostratic nickel hydroxide affects strongly the subsequent evolution of precipitated copper. In the equivalent Cu(II) single-metal systems, amorphous copper hydroxide (am -Cu(OH)₂) precipitates first (the actual nature of this precipitate has been discussed in refs 18 and 43) and transforms, upon aging, in tenorite via a dissolution–reprecipitation mechanism;^{18,43} at copper concentrations larger than 2.5×10^{-3} mol dm⁻³, the am -Cu(OH)₂ evolves to malachite, which later yields tenorite. In the mixed $X \leq 0.4$ systems, instead, no crystalline Cu(II) solid phases are detected during the entire aging (Figure 5); under the present experimental conditions, the transition am -Cu(OH)₂ \rightarrow CuO was expected to occur at about 40–50 min of aging, once pH ca. 7.6 is surpassed (cf. ref 18). Importantly, the SEM micrographs of the final solids (cf. Figure 2) do not show any particle morphology that could reveal the presence

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of segregated *am*-Cu(OH)₂ particles. Moreover, the uniformity of the samples (assessed by EDS analyses) indicates that single-phase α -Ni_{1-x}Cu_x(OH)₂ powders are finally obtained.

The notably different evolution of the solids precipitated from the individual single-metal systems may be traced back to the dissimilar labilities of the d⁸ Ni²⁺ and the d⁹ Cu²⁺ ions, the former being much more inert.⁴⁴

On the basis of the advanced evidence, the formation of α -Ni_{1-x}Cu_x(OH)₂ particles under our experimental conditions should involve the following steps: (i) early nucleation and growth of *am*-Cu(OH)₂, (ii) heterogeneous nucleation of α -Ni(OH)₂ followed by slow crystal growth, and (iii) intercalation of Cu(II) aqueous species (probably monomers, dimers, or small polymers, produced by the dissolving *am*-Cu(OH)₂ particles) into the interlayer space of the turbostratic structure of the growing α -Ni(OH)₂ platelets. The latter step is sketched in the Scheme 1, where interlayer water molecules have been omitted for clarity.

Scheme 1 accounts for the disappearance of the band due to geminal hydroxyls and for the increase of those due to carbonate (Figure 3). The above description does not take into account the possible incorporation of Cu(II) monomers in the growing Ni(OH)₂ sheets (i.e., occupying lattice positions), which, owing to the distorted coordination octahedra of Cu(II), should be minor.

The key of the formation of α -Ni_{1-x}Cu_x(OH)₂ is the simultaneity of *am*-Cu(OH)₂ dissolution and α -Ni(OH)₂ growth (cf. ref 18). The former process is driven by the thermodynamic instability of *am*-Cu(OH)₂ and is assisted by the increasing concentration of carbonate anions. This supplies, steadily, small quantities of dissolved Cu(II) species, which become incorporated within the interlayer channels of the turbostratic nickel hydroxide, in a process that competes favorably with the heterogeneous nucleation of tenorite (or eventually malachite). The constant growth of α -Ni(OH)₂ in both the *a* and *c* directions should avoid the saturation of the channels. At larger Cu(II) concentrations, i.e., *X* > 0.4, Ni(II)-substituted malachites also form, either because the excess copper leads to segregation or because malachite recrystallization becomes faster.

Synthesis of Ni_{1-x}Cu_xO (Bunsenite). In principle, α -Ni_{1-x}Cu_x(OH)₂ powders should be excellent precursors of Ni_{1-x}Cu_xO (bunsenite). In fact, not only do they grant a high degree of metal ion intermixing (almost to an atomic level) but they also preserve the layered structure of α -Ni(OH)₂, which is topotactically related to the rock salt structure of NiO (cf. refs 45 and 46). To set

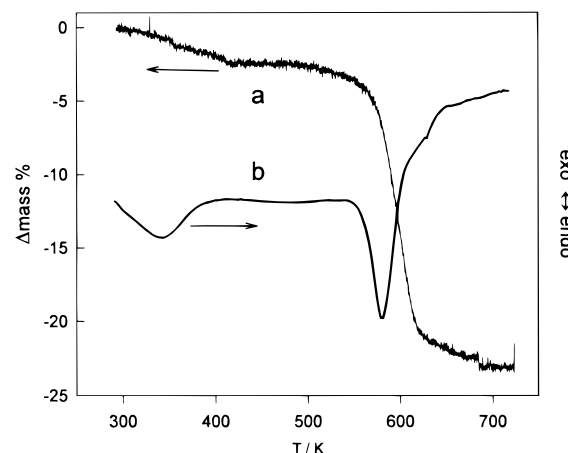
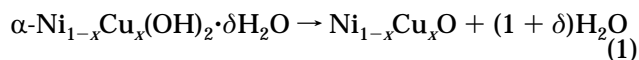


Figure 6. TG (a) and DSC (b) profiles of α -Ni_{0.78}Cu_{0.22}(OH)₂; temperature ramp, 5 K min⁻¹; nitrogen flow, 50 cm³ min⁻¹.

the best synthesis conditions, the thermal behavior of different α -Ni_{1-x}Cu_x(OH)₂ samples was analyzed by TG and DSC. Figure 6, which presents the results of typical runs, shows two successive weight losses that correspond to endothermic processes. The first one ranges from ambient temperature to 383 K and is due to the removal of weakly adsorbed water molecules. The second, centered at 578 K, corresponds to the one-stage dehydration:^{28,31}



In eq 1, δ is the stoichiometric coefficient of interlayer water. The temperature at which this process occurs is slightly, albeit randomly, influenced by the precursor composition and lies within the range where dehydration of pure α -Ni(OH)₂ has been reported.^{34,46,47} No peaks attributable to the loss of carbonate and cyanate ions could be detected in the DSC profile, either because they are present in modest amounts or, more likely, because the loss of CO₂ and NH₃ is masked by the massive water loss that spans ca. 50 K (Figure 6).

Isothermal analyses carried out at different temperatures show that bunsenite forms above ca. 500 K. At 523 K, the transformation α -Ni_{0.78}Cu_{0.22}(OH)₂ → Ni_{0.78}Cu_{0.22}O takes place directly, as shown in Figure 7a. As the reaction proceeds, the $\nu_{\text{O-H}}$ (3650 cm⁻¹) and $\delta_{\text{O-H}}$ (680 cm⁻¹) bands disappear, and the Ni-O-Ni lattice band located at 420 cm⁻¹ becomes apparent (see Figure 7b). Concomitantly with the loss of interlayer water, both cyanate and carbonate decompose (Figure

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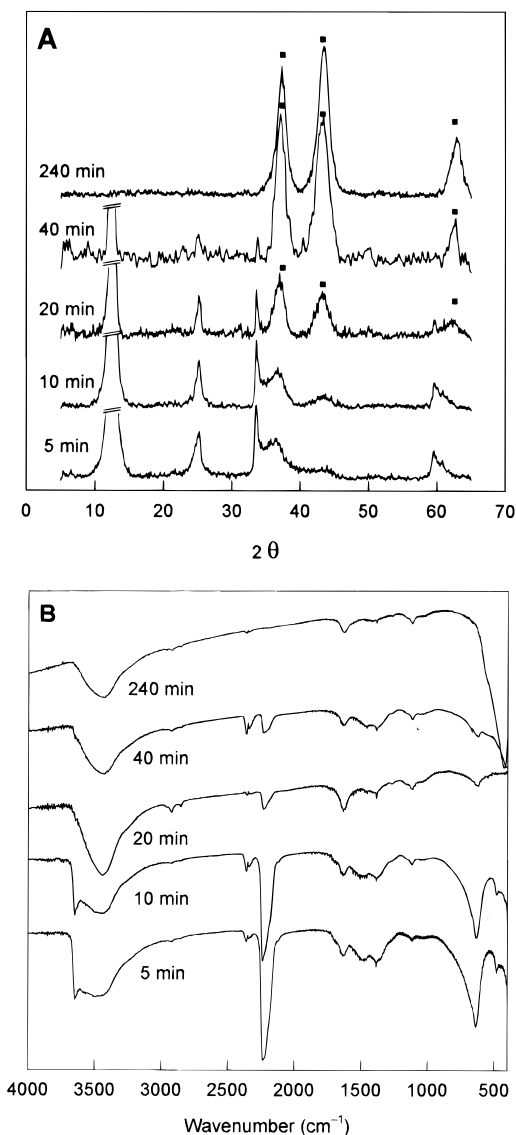


Figure 7. PXRD patterns (A) and FTIR spectra (B) of $\alpha\text{-Ni}_{0.78}\text{Cu}_{0.22}(\text{OH})_2$ powders treated at 523 K for different times under nitrogen atmosphere; squared dots in A indicate bunsenite peaks.

7b); cyanate decomposition may involve interlayer water molecules. Once the reaction is completed (ca. 4 h) no traces of carbonate nor cyanate are detected. The influence of temperature on the formation of $\text{Ni}_{0.78}\text{Cu}_{0.22}\text{O}$ is depicted in Figure 8.

Although the best conditions for the synthesis of $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ can be set from Figure 8, different samples were synthesized by calcining the appropriate precursors for 4 h at 673 K under nitrogen. Under these conditions, any possible kinetic effect should be negligible. In principle, all the $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ precursors must evolve to substituted bunsenite, provided $x < 0.35$,^{32,33} at $x = 0.35$ an orthorhombic mixed oxide forms.⁴⁸ Beyond this limit, tenorite segregation is thermodynamically expected. However, tenorite segregates when x is larger than ca. 0.26. The observed segregation must be related to the easy nucleation of CuO , which may be promoted by *copper islands* (i.e., copper(II) hydroxo-carbonate polymeric species) located

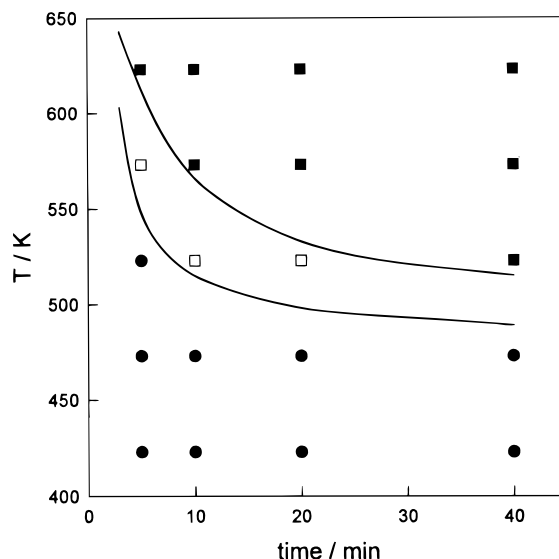


Figure 8. Temperature vs time domains of products formed upon the thermal treatment of $\alpha\text{-Ni}_{0.78}\text{Cu}_{0.22}(\text{OH})_2$ powders under nitrogen atmosphere: (■) $\text{Ni}_{0.78}\text{Cu}_{0.22}\text{O}$; (●) parent solid; (□) mixtures.

within the interlayer space of the precursors. In principle, owing to the dynamic complexation chemistry of Cu(II), the ripening processes that take place upon longer synthesis periods would prevent the development of such intercalated copper islands. Indeed, all $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ ($x \leq 0.33$) samples synthesized after 20 h of aging yield single-phase bunsenite powders.

Conclusions

As compared to other procedures, the method explored here allows for the synthesis of $\text{Ni}_{1-x}\text{Cu}_x\text{O}$ (bunsenite) under unusually mild conditions, both in the temperature and time scales. The success of this method lies on the intrinsic characteristics of the synthesized $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ precursors, which retain the main crystallochemical properties of $\alpha\text{-Ni}(\text{OH})_2$ by accommodating Cu(II) ions within the interlayer space of the structure; as a result, the kinetic barrier for the formation of the mixed oxide is significantly reduced. The synthesis of the $\alpha\text{-Ni}_{1-x}\text{Cu}_x(\text{OH})_2$ precursors is by no means trivial. Due to the unlike hydrolytic and complexation chemistries of Ni(II) and Cu(II), usual coprecipitation procedures should lead to segregated copper and nickel phases. Indeed, the urea method is the only procedure that provides the appropriate conditions that allow for copper intercalation.

Overall, this work provides another illustration of how well-suited mixed-precursors can be prepared by the adequate handling of the intrinsic properties of the involved metal ions.

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