A novel and easy chemical-clock synthesis of nanocrystalline iron–cobalt bearing layered double hydroxides

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ABSTRACT

A novel synthesis of cobalt–iron layered double hydroxide (LDH) with interlayer chlorides was investigated. The method consists in mixing concentrated solutions of hexaamminecobalt(III) trichloride with ferrous chloride at room temperature and in anoxic conditions. Four initial Fe/Co atomic ratios have been tried out (0.12, 0.6, 1.2 and 1.8). Neither heating nor addition of alkali was employed for adjusting the pH and precipitating the metal hydroxides. Still, each mixture led to the spontaneous precipitation of a LDH-rich solid having a crystal-chemistry that depended on the initial solution Fe/Co. These LDHs phases were carefully characterized by mean of X-ray diffraction, ^{57}Fe Mössbauer spectrometry, transmission electron microscopy and chemical analysis (total dissolution and phenanthroline method). Solution Eh and pH were also monitored during the synthesis. Increasing initial Fe/Co ratio impacted the dynamic of the observed stepwise reaction and the composition of the resulting product. Once the two solutions are mixed, a spontaneous and abrupt color change occurs after an induction time which depends on the starting Fe/Co ratio. This makes the overall process acting as a chemical clock. This spontaneous generation of CoFe-LDH arises from the interplay between redox chemistries of iron and cobalt–ammonium complexes.

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0. Introduction

A constantly growing set of studies focuses on layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays. In these structures, the elementary blocks are layers, built of cations in octahedral coordination and sharing their edges. Each adjacent layer is separated by a hydrated interlayer space. From a chemical point of view, those species are represented by a general formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-}\cdot mH_2O$ and consist of octahedral host layers (M^{2+}/M^{3+} are divalent and trivalent metal cations, respectively, located in the layers and x usually ranges between 0.2 and 0.33), charge-balancing anions (A^{n-}, n^- being the valence of the anion), and interlayer water molecules, both being located in the interlayer space. For example, hydrotalcite has for structural formula $[Mg^{2+}_{0.75}Al^{3+}_{0.25}(OH)_2]^{0.25+}[(CO_3)^{2-}_{0.125}]^{0.25-}\cdot 0.5(H_2O)$. Additional complexity comes from layer hydroxyl vacancies and from isomorphic substitution of layer cations and/or interlayer anion, provided that the ionic radii of the former approach that of

Mg^{2+}. As a result, a large variety of multifunctional LDH materials have been synthesized and have found potential applications as anion exchangers, adsorbents, catalysts, solid-state nano-reactors, molecular sieves, polymer composites, and bioactive materials. Furthermore, when exfoliated, their ultrathin lamellar shape should provide building units for designing diverse nano-architectures [1]. In this area, transition metal (e.g., Fe, Co, Ni, Cu or Zn) based LDHs attract much intention as they might exhibit interesting magnetic and redox properties.

Iron-based LDH, such as Co–Fe LDH, may exhibit interesting electronic and magnetic properties. Those compounds could be for instance used as precursors of magnetic materials such as spinel ferrites [2–4]. Various methods have been set up for synthesizing Co–Fe LDH. The most conventional and first discovered routines consist in co-precipitating controlled amounts of M^{2+} and M^{3+} (here, M represents Co and/or Fe) in alkaline conditions [2–6], or precipitating brucite-like $M^{2+}(OH)_2$ phase followed by air oxidation [7,8]. Resulting LDHs are however generally gel-like and of low crystalline quality. Homogeneous precipitation has thus been developed as an alternative method, using progressive hydrolysis of urea [9–11] or hexamethylenetetramine (HMT) [12] to induce progressive formation and growth of larger crystals. Initially, only Al-bearing LDHs were available through this procedure.

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Recent improvement in the crystalline quality has been observed by using topochemical [1,13–15] and laser-ablation [16] techniques, which were successfully applied to the synthesis of micrometer sized Co–Fe LDH. Indeed, large (>2 μm) brucite-like crystals are first precipitated through an hydrothermal treatment of divalent metal containing solution under refluxing conditions, followed by their subsequent oxidation with I_2 or Br_2. Lately, a one-step mechanochemical method has been proposed as well [17], consisting of steel ball milling of a $CoCl_2$ solution. This later technique overcomes some of the drawbacks of the previous existing processes, by lowering the number of steps, avoiding pH control and subsequent heating to shorten the reaction times, therefore greatly simplifying the synthesis routine. However, the crystallinity of the product (0.2 μm average lateral size), is lower than the one synthesised by the topochemical method.

In this paper, we present an alternative one-step synthesis method which produces Co–Fe-LDHs of various compositions and morphologies, depending on the initial conditions. In this method, an aqueous solution of ferrous chloride is mixed with an aqueous solution of hexaamminecobalt (III) trichloride at room temperature and in anoxic environment, without neither pH control nor heating. Once the two solutions mixed, the reaction is spontaneous. Four initial conditions have been tried out by varying the starting dissolved Fe/Co ratio. The present study focuses on the description of the synthesis and the characterization of the obtained Co–Fe LDHs (chemical analysis, powder X-ray diffraction, ^{57}Fe Mössbauer spectrometry, and transmission electron microscopy). Resulting compounds are highly redox sensitive and care had to be taken in order to prevent air oxidation during subsequent analysis.

1. Materials and methods

1.1. Chemicals

All solutions were prepared with ultra-pure water (Milli-Q, resistivity = 18 MΩ cm at 25 °C), boiled for 1 h and cooled under N_2 flux overnight prior to its introduction in a N_2 atmosphere glove box (Jacomex GP, $[O_2]$ < 2 ppm, temperature = 22 °C). Dissolution of analytical grade salts was carried out inside the glove box. Only the solutions used in acidic digestions were prepared and used out of the glove box. A complete list of the chemicals used in this study is reported in the supporting information section.

1.2. Synthesis

The two starting solutions consisted in 256.1 mM (50 g L^{-1}) $FeCl_2$ (pH = 3.5) and 37.4 mM (10 g L^{-1}) hexaamminecobalt(III) trichloride (hereafter referred as "Co-Amm$_6$", pH = 4.8). Synthesis has been carried out inside the glove box, in 1 L HDPE pots. Four initial conditions have been tried out, by keeping constant the total volume (1 L) and varying the Fe/Co ratio by changing Fe concentration. Same amount of Co-Amm$_6$ solution was first introduced in each pot, followed by various dilutions of the $FeCl_2$ solution (by first adding pure water in the pot, and then the $FeCl_2$ solution). The pots were then sealed and left for agitation into an orbital shaker (75 rpm). Eh and pH were periodically monitored in synthesis pots (WTV ProfiLine Multi 3320, 1 and 5 min time step in P1 and P3/P4 respectively), and a webcam was used to take a picture of the pots every 30 s. A colored precipitate appeared in each pot after approximately 30–35 min, but shaking was carried out for 5–6 days in order to ensure that equilibrium would be reached. Solids were then collected by filtration (cut-off diameter = 0.1 μm), without any further washing, and were dried overnight at 70 °C in an oven inside the glove box. They were then stored inside the glove box until further analyses. Supernatants were also collected at the end of the experiment and assayed for final Fe (using an inductively-coupled plasma atomic emission spectrometer – ICP–AES) and Co (using an inductively-coupled plasma mass spectrometer – ICP–MS) concentrations, after acidification with 1/10 HCl (30%).

1.3. Sample characterization

1.3.1. Powder X-ray diffraction (XRD)

XRD patterns were acquired in continuous scan mode over the 4–84° 2θ Co Kα range using a Brucker D8 diffractometer equipped with a cobalt anode (λ Kα_1 = 1.78997 Å) and a LynxEye 1D detector. Total counting time was ~8 h, and intensity was integrated every 0.04° 2θ Co Kα. In order to preserve the sample from oxidation, powder was prepared [18] in the glove box using a sample holder equipped with a dome that was under vacuum sealed before taking the samples out of the glove box (placing the closed dome few seconds in the vacuum chamber of the glove box). Thus, the samples were preserved from the atmosphere during XRD measurements.

Calculated LDH XRD patterns were obtained using the structure of fougèrite as a starting model. Fougèrite is a naturally-occurring layered double hydroxide having for structural formula $[Fe^{2+}_{1-x}Fe^{3+}_xMg_y(OH)_{2+2y}]^{+x}[x/nA^{-n}\cdot mH_2O]^{-x}$ (A being the interlayer anion and n its valence, following pioneer work on this structure [19]), here assumed to be $FeO_{2.25}Cl_{0.5}H_{2.75}$. The calculation of LDH XRD patterns is conducted with the software CALCIPOW [20] (based on the mathematical formalism developed by Drits [21]). As a consequence, this software allows the calculation of XRD patterns from layered structure having various density and nature of structural defects, such as layer vacancies, substitutions, well-defined or random stacking faults. In particular, the calculation of layered structures with the systematic occurrence, between adjacent layers, of random translation within the layer plane or random rotation about the normal (known as turbostratic structures) can be performed. This software has been used to successfully model the XRD patterns from phyllosilicates, phyllomanganates and nanocrystalline calcium silicate hydrates [22–26].

Identification of impurities was carried out using ICDD database and constraining the match to minerals having atoms that were known to be present in the initial solution. ICDD records identified were lepidocrocite (00-044-1415), magnetite (01-086-1352) and $Fe_2(OH)_3Cl$ (00-034-0199).

1.3.2. Transmission Electron Microscopy (TEM)

TEM data acquisition was performed using a Philips CM20 operated at 200 kV. Prior to observation, samples were dispersed into ultra-pure ethanol using an ultrasonic bath, and then deposited on a carbon-coated copper grid. In order to avoid as much as possible oxidation, samples were preserved under N_2 atmosphere until quick (<5 min) preparation, and were then directly inserted in the TEM.

1.3.3. ^{57}Fe Mössbauer spectrometry

The Mössbauer spectra were recorded at 77 K using a constant acceleration spectrometer and a ^{57}Co source diffused into an Rh matrix. Velocity calibrations were carried out using α-Fe foil at room temperature (RT, 295 K). The values of the hyperfine parameters were refined using a least-squared fitting procedure using a discrete number of independent quadrupolar doublets and magnetic sextets composed of Lorentzian lines. The values of isomer shift are reported relative to that of the α-Fe spectrum obtained at RT. The proportions of each Fe species were established from the relative spectral area, assuming thus the same values of the f-Lamb-Mössbauer factors characteristic of each phase. Again, in order to protect sample from air oxidation during the analysis, few amounts of sample were embedded in degassed araldite resin, prior to taking them out of the glove box.