

SYNTHESIS AND STRUCTURAL FEATURES OF A NOVEL Ba(II)-Fe(III)-LAYERED DOUBLE HYDROXIDE

D. Srankó^a, A. Pallagi^{a,b}, I. Pálinkó^b, E. Kuzmann^c, S. E. Canton^d, M. Walczak^d, and P. Sipos^{a,*}

^aDepartment of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary

^bDepartment of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary

^cLaboratory of Nuclear Chemistry, Chemical Research Center, HAS, Roland Eötvös University, Pázmány Péter sétány 1/A, Budapest, H-1117, Hungary

^dChemical Physics Department, Chemical Centre, Lund University, PO Box 124, Lund, SE-221 00, Sweden

(*email: sipos@chem.u-szeged.hu)

ABSTRACT

Double hydroxides containing Ba(II) and Fe(III) have been prepared by the co-precipitation of a solution containing Ba(ClO₄)₂ and Fe(ClO₄)₃ in an extremely concentrated (up to 20 M) aqueous NaOH solution. The white to pale yellow compounds formed at [NaOH]_T ≥ 10 M proved to have layered structure by powder XRD. To the best of our knowledge, this is the first report of layered double hydroxide (LDH) preparation from such highly concentrated base solutions.

The interlayer distances of our Ba-Fe-LDHs proved to vary with the base concentration and aging. Ba-Fe-hydroxo-complex salts obtained by others under identical experimental conditions were claimed to consist of [Fe(OH)₆]³⁻ structural units at [NaOH]_T = 10 M and [Fe(OH)₇]⁴⁻ ones at [NaOH]_T = 20 M. EXAFS and XANES data indicated that the local environment of Fe(III) is independent of [NaOH]_T. From ⁵⁷Fe Mössbauer spectroscopy, the local structure of Fe(III) in our Ba-Fe-LDHs is identical to that obtained for Na₃Fe(OH)₆.xNaOH, *i.e.*, the Fe(III) is in octahedral environment, which is typical for the cationic components incorporated in the LDH structure.

INTRODUCTION

Layered double hydroxides (LDHs) can generally be described by the following formula: [M(II)_{1-x}M(III)_x(OH)₂]^{x+}[X^{m-}_{x/m}.nH₂O]^{x-} (1 > x > 0). The positively charged layers are often comprised of metal hydroxides of divalent metal cations (*e.g.*, Mg²⁺, Ca²⁺, Zn²⁺, Mn²⁺, Co²⁺, Ni²⁺, Sr²⁺, Ba²⁺ and Cu²⁺) and trivalent metal cations (*e.g.*, Al³⁺, Mn³⁺, Fe³⁺, Co³⁺, Ni³⁺, Cr³⁺, Ga³⁺, B³⁺, La³⁺ and Gl³⁺). The interstitial anions X^{m-} are usually NO₃⁻, OH⁻, Cl⁻, I⁻, CO₃²⁻,

SO_4^{2-} , SO_3^{2-} , HPO_3^{2-} , MnO_4^- , ClO_4^- , mono- or dicarboxylates, alkyl sulphonates, etc. [1]. The fundamental crystal structure is mostly of brucite ($\text{Mg}(\text{OH})_2$, wherein the magnesium cations are octahedrally surrounded by hydroxyl groups), and the divalent metal ions are partially and isomorphously substituted for the trivalent ones. Minerals with this structure do exist in nature (e.g., pyroaurite, sjogrenite, hydrotalcite, stichtite, reevesite, eardleyite, mannaseite, barbertonite, hydrocalumite, etc.), for applications, however, they are usually synthesized. The generally applied preparation methods have been reviewed [2]. For hydrotalcite-like compounds, the most commonly used production method usually involves the use of concentrated solutions of magnesium and aluminium salts reacting with each other in the presence of strong reagents such as sodium hydroxide, and various acetates and carbonates. Co-precipitation produces hydrotalcite or hydrotalcite-like compounds which are then filtered, washed, and dried. The resulting substances have been used in many ways like hydrocarbon cracking catalysts, sorbents, binder materials for catalysts, water softener agents, etc.

In this paper the preparation and some structural features of a novel type of layered double hydroxides is described. The samples have been prepared by the co-precipitation of $\text{Ba}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$ in aqueous NaOH solution with varying base concentrations.

EXPERIMENTAL PART

Reagents and solutions

Concentrated NaOH (~20 M) stock solutions were prepared from Millipore MilliQ water and a.r. grade solid NaOH (Spectrum 3D) and their carbonate content was minimised as described previously [3]. The density of the solution was determined picnometrically. The NaOH solution was stored in an airtight, caustic resistant Pyrex bottle.

$\text{Ba}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3/\text{HClO}_4$ solutions were made of solid $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Fluka, p.a. grade), $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich, p.a. grade) and HClO_4cc (ca. 30 m/m%, Merck, p.a. grade). The exact Fe(III) concentration of the $\text{Fe}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$ was determined iodometrically.

Double hydroxides were prepared via dropwise addition of the $\text{Ba}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3/\text{HClO}_4$ solution to hot (ca. 80 °C), vigorously stirred and N_2 -blanketed NaOH solution. The relative decrease of the $[\text{OH}^-]_{\text{T}}$ during the synthesis was less than 10%, therefore the pH of the solution can be considered constant in the course of the LDH formation. The precipitates formed were filtered until air dry with the aid of a caustic resistant vacuum filter unit (Nalgene) equipped with an appropriate membrane (Versapor, 0.45 μm). The solid material was washed with small quantities of pure and hot NaOH, collected in a crystallizing dish. The moisture sensitive crystals were kept at room temperature in a desiccator over dry SiO_2 .

Apparatus and equipment

Powder X-ray diffraction (XRD) patterns of the solid samples were recorded in the $2\theta = 3 - 70^\circ$ range on a Philips PW1710 instrument, using Cu $K\alpha$ radiation.

^{57}Fe Mössbauer spectra of the samples were recorded with conventional Mössbauer spectrometers (Wissel and Ranger) in transmission geometry at room temperature and at temperature of liquid nitrogen (78K). A $^{57}\text{Co}/\text{Rh}$ γ -radiation source of $3 \cdot 10^9$ Bq activity was used.

Iron K edge (7112 eV) XANES and EXAFS spectra were measured on beamline I811 at the MAXlab facility, Lund, in transmission mode for the crystalline samples. Further details of the ^{57}Fe Mössbauer and EXAFS/XANES experiments have been described elsewhere [4].

RESULTS AND DISCUSSION

Upon addition of a mixture of $\text{Ba}(\text{ClO}_4)_2/\text{Fe}(\text{ClO}_4)_3/\text{HClO}_4$ (0.75 M : 0.25 M : 0.1 M), instantaneously a white to pale yellow precipitate appeared in reaction mixtures with $[\text{NaOH}]_{\text{T}} \geq 10$ M, indicating that (otherwise expected) formation of various Fe(III)-oxy-hydroxides (FeOOH) did not take place under these experimental conditions. At lower concentration of the base (5 M and 2 M), formation of FeOOH was observed.

The XRD patterns of the products (Ba-Fe-LDH-*X* in the followings, where *X* represents $[\text{NaOH}]_{\text{T}}$ in M) are shown in Fig. 1. The white to pale yellow products' patterns are characteristic to LDHs and are clearly seen on the patterns of Ba-Fe-LDH-10 and Ba-Fe-LDH-20; no such patterns are seen on the traces of the products obtained at 5 and 2 M base concentrations. This indicated that the prerequisite of the LDH formation in this systems is a sufficiently high $[\text{NaOH}]_{\text{T}}$, *i.e.*, where the solubility of $\text{Ba}(\text{OH})_2$ is relatively low.

From the XRD patterns, the d-spacings of our LDHs vary between 11.18 and 11.38 Å. Upon aging (ca. 1 year at room temperature in a desiccator over SiO_2) small but significant decrease is seen in the d-spacing, which is most likely to be associated with slow dehydration. It is somewhat surprising, that the d-spacing of Ba-Fe-LDH-10 is smaller than that obtained for Ba-Fe-LDH-20; on the basis of the available water of hydration during their formation, an opposite pattern would be expected. The well defined reflection at 30° on the trace of the freshly prepared Ba-Fe-LDH-20, which is almost completely absent from the patterns of the other two LDH-s, will also need further studies.

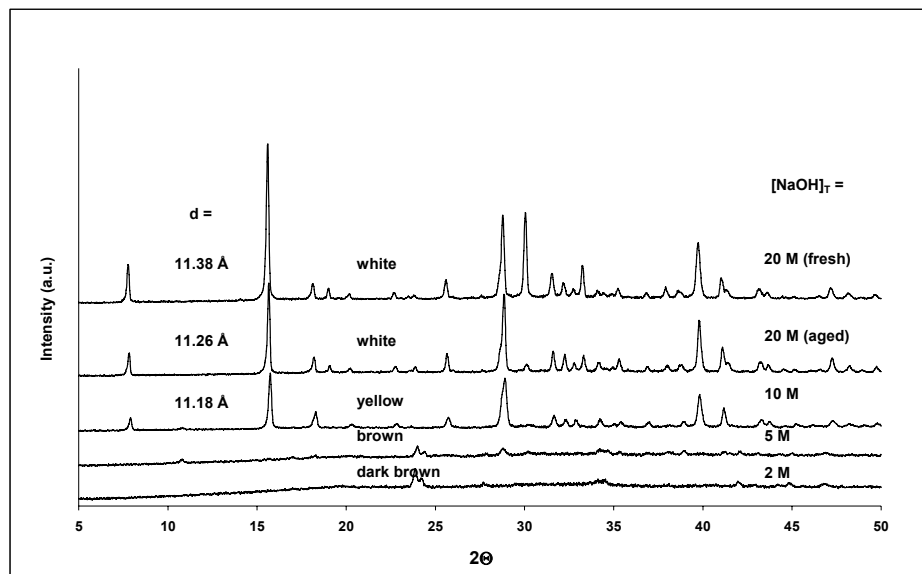


Fig. 1. XRD patterns of the solid products obtained from concentrated NaOH solutions at various $[\text{NaOH}]_T$ -s. The colour of the solid materials and the d interlayer distances for the layered double hydroxides obtained from $[\text{NaOH}]_T \geq 10 \text{ M}$ are also shown.

In an early report of Scholder et al [5-7], the procedure outlined in the Experimental part has already been mentioned and the authors stated that the procedure yielded $\text{Ba}_2[\text{Fe}(\text{OH})_7]$ at $[\text{NaOH}]_T = 20 \text{ M}$ and $\text{Ba}_3[\text{Fe}(\text{OH})_6]_2$ at $[\text{NaOH}]_T = 10 \text{ M}$. On the basis of this assignment, the existence of higher hydroxo complexes, such as $[\text{Fe}(\text{OH})_6]^{3-}$, $[\text{Fe}(\text{OH})_7]^{4-}$ in strongly alkaline solutions has been deduced [8].

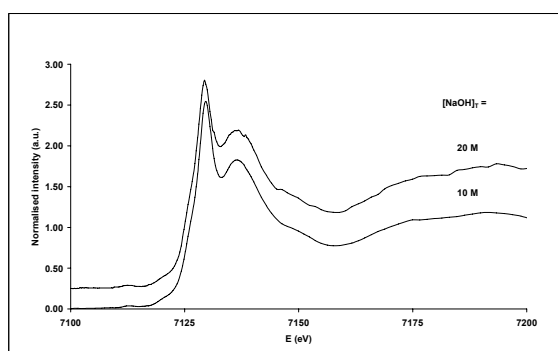


Fig. 2. Fe-K-edge XANES spectra of the layered double hydroxides obtained from solutions with $[\text{NaOH}]_T = 10$ and 20 M , respectively.

LDH layers, is practically insoluble in solutions with $[\text{NaOH}]_{\text{T}} \geq 10 \text{ M}$, the method is suitable for the preparation of carbonate free LDH-s at constant and high pH. It is also expected, that the method is useful for producing LDH-s with bivalent metal ions other than Ba(II). Such preparative efforts are currently in progress.

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