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Synthesis and transformation of iron-based layered double hydroxides

C. Ruby [a],*, M. Usman [a], S. Naille [a], K. Hanna [a], C. Carteret [a], M. Mullet [a], M. François [b], M. Abdelmoula [a]

[a] *Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), UMR7564 CNRS-Nancy Université, 405, Rue de Vandœuvre 54600 Villers-Lès-Nancy, France*
[b] *Institut Jean Lamour, Département P2M, Matériaux-Métallurgie-Nanosciences-Plasmas-Surfaces, UMR 7198-CNRS-Nancy-Université-UPV-Metz, Faculté des Sciences, BP 239, 54506 Villers-lès-Nancy, France*

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ABSTRACT

Iron-based layered double hydroxides (LDHs) have the general formula $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]^{x+}\cdot[(x/n)\ A^{n-},\ m\ H_2O]^{x-}$ and contain a molar fraction of iron, i.e. Fe^{II} or Fe^{III} situated in the cationic layers, higher than 50%. LDHs containing Fe^{II} species are interesting materials for several applications such as the reduction of anionic pollutants or the degradation of organic pollutants. They are mostly prepared either by coprecipitation of dissolved species or by oxidation of hydroxylated Fe^{II} species. The synthesis routes were visualised in binary and ternary mass-balance diagrams. The LDH[Fe^{II}–Fe^{III}] particles were well crystallised hexagonal plates, the size of which diminishes rapidly when divalent or trivalent cations substitute ions. The LDH[Fe^{II}–Fe^{III}–CO_3] transformed into a mixture of magnetite Fe_3O_4 and siderite $FeCO_3$ in alkaline conditions, but the adsorption of silicate or phosphate anions on the lateral faces of the crystal prevented this decomposition. In oxic conditions, two mechanism of transformation were identified: (i) a fast *in situ* oxidation within the solid, (ii) dissolution–precipitation of the LDH forming ferric oxyhydroxides such as goethite (α-FeOOH).

1. Introduction

Mixed M^{II}–M^{III} layered double hydroxides (LDHs) are described by the general formula $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]^{x+}\cdot[(x/n)\ A^{n-},\ m\ H_2O]^{x-}$ where M^{II} and M^{III} are metal cations in the brucite-type layers $Mg(OH)_2$, A^{n-} are the intercalated anions and x is the molar fraction of the trivalent cation and also the electrostatic charge of both the brucite-type layers and the anionic interlayers. Most commonly, the values of x are found in the range of 0.2–0.33 (Khan and O'Hare, 2002). Recently, the interest for the synthesis and the characterisation of LDHs increased since these materials can be used for many potential applications. For example, LDHs are well known for their capacity to exchange various types of inorganic anions (Miyata, 1983; Khan and O'Hare, 2002). LDHs can easily incorporate organic and bioorganic molecules such as ascorbic acid (Aisawa et al., 2007), urease (Vial et al., 2008), DNA (Oh et al., 2006) and even ferritin (Clemente-León et al., 2008). A particular type of LDHs which contains only iron as a cation in the brucite-type layers is called Green Rust (GR), i.e. the LDH[Fe^{II}–Fe^{III}]. GR is an intermediate compound that forms during the Fe^{II} species oxidation in solution (Feitknecht and Keller, 1950). For example, carbonated GR was observed as a corrosion product in water drain by Stampfl (1969). In 1996, a natural sample found in a hydromorphic soil in the forest of Fougères (Brittany, France) was identified to be homologous to green rust by using Mössbauer and Raman spectrocopies (Trolard et al. 1997). This mineral was then named fougerite (IMA 2003-057). More recently, three new occurrences were found: one in coal mine drainage sediment in South Wales (Bearcock et al., 2006) and two others in Denmark (Christiansen et al., 2009). In this last study, an X-ray diffraction pattern that corresponds to synthetic carbonated GR was presented for the first time. The properties of GR, i.e. the LDH[Fe^{II}–Fe^{III}], were also studied because of its ability to reduce several anionic pollutants such as nitrate (Hansen, 2001), chromate (Loyaux-Lawniczak et al., 2000; Bond and Fendorf, 2003; Legrand et al., 2004) and seleniate (Refait et al., 2000, 2005a; Hayashi et al., 2009). Finally, GR was shown to promote the reduction/oxidation of an azo dye and therefore its removal from water (Kone et al., 2009) and the Fenton-like oxidation of phenol at neutral pH (Hanna et al., 2010).

In this paper, we will focus on the description of the synthesis routes and transformation of LDHs that contain a minimum of 50 % of iron atoms in the brucite-like layers, i.e. compound for which the ratio $n(Fe)/\{n(M^{II})+n(M^{III})\}$ is >50%. Similar to the terminology commonly used for metallic alloys, these compounds are called iron-based LDHs. The partial substitution of the Fe^{II} or Fe^{III} cations by other divalent or trivalent species lead to ternary systems such as LDH[{Fe^{II}–M^{II}}–Fe^{III}] or LDH[Fe^{II}–{Fe^{III}–M^{III}}. To our knowledge, three types of partial substitutions were studied: Fe^{II} by Ni^{II} (Refait and Génin, 1993; Refait et al., 2005b), Fe^{II} by Mg^{II} (Refait et al., 2001) and more recently Fe^{III} by Al^{III} (Ruby et al., 2008). Fully substituted compounds that correspond to the minerals pyroaurite $Mg_6Fe_2(OH)_{16}CO_3,4H_2O$ (Allmann, 1968) and reevesite $Ni_{18}Fe_6(OH)_{48}(CO_3)_3,12H_2O$, (De Waal and Viljoen, 1971) are not *strico sensu* iron-based LDHs, and the synthesis of such compounds will not be considered here. We will

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* Corresponding author. Tel.: +33 3 83 68 52 53.
E-mail address: christian.ruby@lcpme.cnrs-nancy.fr (C. Ruby).

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report synthesis routes of iron-based LDH and transformation modes at both oxic and anoxic conditions.

2. Synthesis and characterisation

2.1. Formation paths: General description

2.1.1. M^{II}–M^{III} mass-balance diagram

The synthesis routes of iron-based LDHs can be illustrated in the mass-balance diagram presented in Fig. 1. Initially, this diagram was devised for interpreting pH titration curves obtained during the coprecipitation of Fe^{II} and Fe^{III} soluble species in sulphate solutions (Ruby et al., 2003) but it can easily be generalised to any type of divalent and trivalent cations. The ordinate $R = n(OH^-)/[n(M^{II}) + n(M^{III})]$ represents the number of hydroxyl species per mole of iron that are consumed during the precipitation of a given compound. The abscissa $x = n(M^{III})/[n(M^{II}) + n(M^{III})]$ indicates the molar fraction of trivalent cations. The position of the aqueous species $M^{II}{}_{aq}$, $M^{III}{}_{aq}$ and solid compounds $M^{II}(OH)_2$, the LDH[M^{II}–M^{III}], the spinel $M^{II}M^{III}{}_2O_4$ and the oxyhydroxide $M^{III}OOH$ are indicated. The synthesis of LDHs is most commonly achieved by the addition of a basic solution to a solution of {$M^{II}{}_{aq}$, $M^{III}{}_{aq}$}. It corresponds to the vertical path [AD]. The major advantage of this method is that the value of x of the initial solution can be adjusted accurately in order to determine the flexibility of the M^{III} molar fraction.

LDHs may also contain a metal cation in two oxidation states M^{II} and M^{III} such as the 3d transition metals, i.e. Ti, V, Cr, Mn, Fe, Co and Ni. Such LDHs can be prepared by a precipitation/oxidation route (Fig. 1) in two steps: (i) A basic solution is added to a solution of M^{II} that precipitates to form either a suspension of solid $M^{II}(OH)_2$ or a {$M^{II}(OH)_2$, $M^{II}{}_{aq}$} mixture (path [BC]), (ii) the divalent species are then oxidised to form the LDH[M^{II}–M^{III}] (path CD). As it will be discussed in Section 2.2.2., the slope of line CD depends on the nature of the oxidant. The easiest way of oxidation is agitating the $M^{II}(OH)_2$ suspension in contact with air and controlling the redox potential E_h of the suspension to follow the oxidation steps. Other oxidants such as hydrogen peroxide H_2O_2, iodine I_2 or persulphate $S_2O_8^{2-}$ can also be used. The advantage is to know the oxidation state of the product by controlling the amount of added oxidant. The precipitation/oxidation pathway was used for the preparation of LDH[Fe^{II}–Fe^{III}] (Hansen, 2001; Génin et al., 2006a) and LDH[Co^{II}–Co^{III}] (Ma et al., 2008).

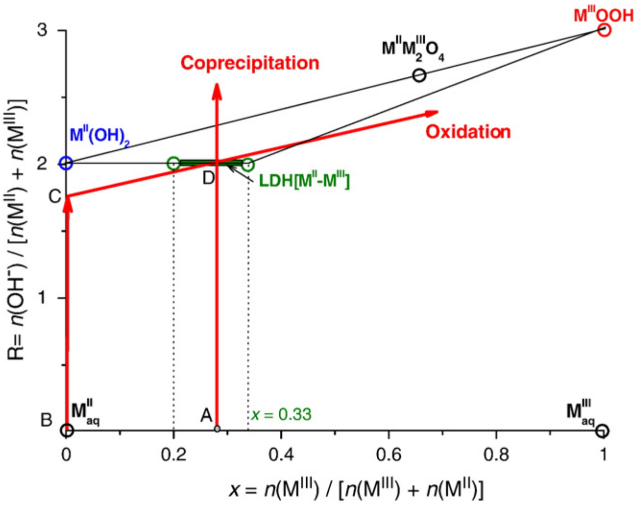

Fig. 1. M^{II}–M^{III} mass-balance diagram showing the coprecipitation and oxidation synthesis routes (adapted from Fig. 1 of Ruby et al., 2006b).

2.1.2. Formation of ternary LDH [Fe^{II}, {Fe^{III}, M^{III}}] and LDH[{Fe^{II}, M^{II}}, Fe^{III}]

Iron-based LDHs, with a partial substitution of the Fe^{III} or Fe^{II} are synthesised like the binary LDH[Fe^{II}–Fe^{III}], i.e. by coprecipitation or oxidation. Such syntheses can be represented in a ternary mass-balance diagram (Fig. 2). This representation was initially proposed to study the coprecipitation of [{Fe^{II}, {Fe^{III}, Al^{III}}] mixtures in sulphate solution (Ruby et al., 2008). The diagram is an equilateral triangle and the composition of any point is easily obtained by plotting the perpendicular to the triangle sides as usually done when studying the phase diagram of ternary alloys (bottom of Fig. 2a). The number of moles of hydroxyl groups per mole of cations $R = n(OH^-)/n(M_{tot})$ necessary to form a given compound is situated on the perpendicular to the triangle base. The formation pathways of the M^{III}-substituted LDHs are presented in Fig. 2a. The domain of the ternary LDH[{Fe^{II}, M^{II}}, Fe^{III}] is situated in between the two segments corresponding to the LDH[Fe^{II}–Fe^{III}] and the LDH[Fe^{II}–M^{III}]. On Fig. 2b, the formation pathways of M^{II}-substituted LDHs are shown. The domain of the LDH [{Fe^{II}, M^{II}} Fe^{III}] is situated in between the segments corresponding to the LDH[Fe^{II}–Fe^{III}] and the LDH[{Fe^{II}, M^{II}}, Fe^{III}] with $x(M^{II}) = 0.5$. In both cases, the most trivial way to prepare such a compound is to prepare a mixture of soluble species, i.e. [{Fe^{II}, {Fe^{III}, M^{III}}] or [{Fe^{II}, M^{II}}, Fe^{III}] with the desired molar fractions, and to add a basic solution at a ratio $R = n(OH^-)/n(M_{tot})$ close to 2. This coprecipitation syntheses route corresponds to a vertical segment that starts into the composition domain of the ternary LDH and is situated perpendicularly to the triangle base. The LDH[{Fe^{II}, {Fe^{III}, M^{III}}] could also be obtained by partial oxidation of LDH[Fe^{II}–M^{III}] (Fig 4a), such a reaction has not yet been tested. In sulphate solution, the coprecipitation of the LDH[Fe^{II}–Al^{III}] leads unfortunately to an amorphous compound (Ruby et al., 2008) that is difficult to use as a starting product for an oxidation experiment. The oxidation path presented in Fig. 2b was used to prepare the LDH[{Fe^{II}, Ni^{II}}, Fe^{III}] (Refait and Génin, 1993). In these experiments, a mixture of soluble species {$Fe^{II}{}_{aq}$, $Ni^{II}{}_{aq}$}, *i.e.* point A, was precipitated to form a mixture of {$Fe(OH)_2$, $Ni(OH)_2$} in point B. In a second step, the Fe^{II} species were oxidised by air to form LDH[{Fe^{II}, Ni^{II}}, Fe^{III}] by following the path BC. During this oxidation, the quantity of Ni^{II} remained constant since Fe^{II} species were much more easily oxidised by dissolved O_2. A similar way of syntheses was used to prepare a fully substituted LDH(Co^{II}–Fe^{III}) by oxidation of LDH(Co^{II}–Fe^{II}) (Ma et al., 2007). Iodine I_2 was chosen as an oxidant because the standard redox potential of the I_2/I^- couple is situated in between the E^o values of the Fe^{II}/Fe^{III} and Co^{II}/Co^{III} couples. By this way, only the Fe^{II} species of the LDH(Co^{II}–Fe^{II}) were oxidised and a pure and well crystallised LDH(Co^{II}–Fe^{III}) was observed.

2.2. Synthesis of the LDH[Fe^{II}–Fe^{III}] (green rust)

2.2.1. Coprecipitation of soluble Fe^{II} and Fe^{III} species

The coprecipitation method was used to determine the flexibility of the x values of LDH[Fe^{II}–Fe^{III}–SO_4] (Ruby et al., 2003) and LDH[Fe^{II}–Fe^{III}–CO_3] (Ruby et al., 2006b). These experiments were conducted in a gas-tight reactor with continuous N_2 bubbling in aqueous solution in order to avoid the oxidation of ferrous ions Fe^{II}. A systematic study of the titration of Fe^{II} and Fe^{III} by NaOH in a sulphate solution showed that only LDH[Fe^{II}–Fe^{III}–SO_4] with a unique composition $x = 0.33$ was formed (Ruby et al., 2003). When the coprecipitation was realised at values of $x > 0.33$ or $x < 0.33$, {LDH[Fe^{II}–Fe^{III}–SO_4–$x = 0.33$], Fe_3O_4} and {LDH[Fe^{II}–Fe^{III}–SO_4-$x = 0.33$], $Fe(OH)_2$} mixtures were respectively formed. Nevertheless, the formation of a LDH[Fe^{II}–Fe^{III}–SO_4] with a ratio $x = 0.25$ was achieved by performing an anion exchange of LDH [Fe^{II}–Fe^{III}–Cl^-] precipitated at the same x value (Hansen et al., 2001). Some flexibility of the x values was also observed for LDH[Fe^{II}–Fe^{III}–CO_3] that can be prepared in the range $x \in [\sim 0.25, 0.33]$. For the preparation of the LDH[[Fe^{II}–Fe^{III}–CO_3] at $x = 0.25$, $FeCl_3$ and $FeCl_2$ salts had to be dissolved by the addition of a Na_2CO_3 solution. Indeed, if $Fe_2(SO_4)_3$ and $FeSO_4$ solutions were used, LDH[Fe^{II}–Fe^{III}–SO_4] was