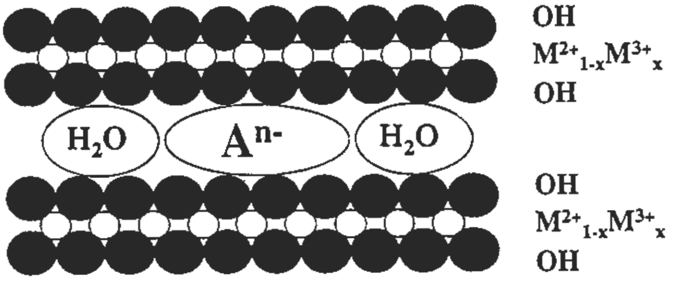
Layered Double Hydroxides: Structure, Synthesis and Applications

David J. Finnie Literature Seminar November 30, 1993

Layered double hydroxides (LDH's) occur in nature as platelike minerals such as hydrotalcite, $[Mg_6Al_2(OH)_{16}]CO_3 \cdot 4H_2O$. The first synthetic hydrotalcite was prepared in 1942 by Feitknecht [1], but its structure was not determined until 1968 [2]. In 1970, the applications of LDH's for catalysis were realized [3], and since then their catalytic activity has been heavily investigated. This talk will first examine the structure and synthesis of LDH's, then discuss their anion-exchange capabilities, and finally explore their applications as catalyst precursors as well as their use in other practical applications.

The layered structure of LDH's is composed of cationic metal-hydroxide layers, $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}$, and intercalated anions A^{n-} which are usually hydrated. The metal-hydroxide layers have the CdI_2-type structure, i.e., double layers of close-packed hydroxide oxygens with the octahedral holes in each layer completely filled with metal cations. The LDH structure is formed by substituting a fraction of the Mg^{2+} cations with trivalent cations such as Al^{3+}, placing a positive charge on the metal-hydroxide sheets. The charge is neutralized by the intercalation of anions into the intersheet space, where the water of crystallization also resides [4, 5, 6]:



Therefore, the general formula for LDH's is $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$. Using this formula, hydrotalcite is written as $[Mg_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125} \cdot 0.50H_2O$. Alkali earth metals and divalent and trivalent transition metals can form LDH's, with few restrictions other than cation size; the metal must have an ionic radius similar to Mg^{2+} to fit properly into the hydroxide sheets [7]. The value for x ranges from 0.2 to 0.33 [8]. Above $x = 0.33$, the compounds formed are poorly crystalline. For values of $x < 0.20$, $M(OH)_2$ forms along with the LDH [9].

The most common synthetic technique for the preparation of LDH's is coprecipitation of the metal hydroxides $M(OH)_2$ and $M(OH)_3$ from aqueous solution. This coprecipitation is most easily achieved through variation in pH, as the pH range over which both metal hydroxides precipitate is usually in the range pH 8-10 [7]. There are three coprecipitation methods: increasing pH, constant pH at low supersaturation, and constant pH at high supersaturation [1, 10-14]. The second method, constant pH at low supersaturation, generally leads to microcrystalline products. The other two coprecipitation techniques yield nanocrystalline or amorphous products. A new synthetic route to LDH's has recently been examined by Delmas and coworkers [9]. This "Soft Chemistry" approach involves classical high-temperature solid-state synthesis of $NaNi_{1-x}Co_xO_2$ sodium nickelate-type slabs from the metal oxides followed by oxidation to an oxyhydroxide and then reduction to the LDH. Because the metal-oxide sheets formed in the high-temperature step are retained throughout the redox steps, the product crystals obtained are generally larger than those obtained by the coprecipitation techniques [15, 16].

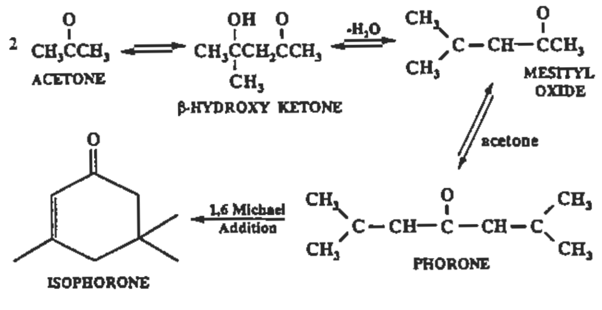
The intercalated anion plays a key role in the chemistry of the LDH. The effect of the anion on interlayer spacing is based on two competing effects, steric and electrostatic [5]. Larger anions spread the mixed-metal hydroxide sheets farther apart, while more highly charged anions pull them together. Unless prepared under strictly CO_2-free conditions, carbonate will be the preferentially intercalated anion. Other anions can be exchanged for carbonate by reaction with their dilute acids [6, 7, 14, 17]. Rapid expulsion of CO_2 drives the exchange:

$$LDH{\cdot}CO_3^{2-} + 2HCl \rightarrow LDH{\cdot}2Cl^- + CO_2\uparrow + H_2O$$

Carbonate and nitrate are both D_{3h} planar molecules, and are fully and symmetrically hydrogen-bonded to water in the interlayer space [4]. Tetrahedral anions such as sulfate and perchlorate adopt one of two arrangements, either with three oxygens facing one hydroxide sheet while the fourth points towards the other (3/1) or with two oxygens facing each sheet (2/2) [5]. Because perchlorate is singly charged, twice many of the anions must intercalate to neutralize the charge on the slabs relative to sulfate. Therefore, perchlorate adopts the 3/1 arrangement, which allows more efficient packing of the tetrahedral anion in the interlayer space, while sulfate adopts the 2/2 arrangement. Other anions such as alkyl sulfates form monolayers, or bilayers with alcohols, in the interlayer space [12, 18]. The more facile exchange of nitrate versus carbonate from the LDH structure has been used to aid in the synthesis of LDH's containing very bulky anions [19]. When a very large anion such as $H_2W_{12}O_{40}^{6-}$ is intercalated the layers spread very far apart (15 Å [20]) and the material is called "pillared." The pillaring of LDH's with polyoxometalate (POM) anions has been of recent interest because of the possible use of pillared materials as catalysts. Several routes for the preparation of these pillared compounds have been developed, including direct synthesis from the nitrate-LDH or through intermediate formation of LDH's with intercalated organic anions [19, 20, 21].

The thermal decomposition of LDH's proceeds through three steps [22, 23, 24]. The first step is the complete loss of the interlayer water. The second step is the loss of one further equivalent of water from the metal-hydroxide layers to form an amorphous mixed-metal oxide. In the case of carbonate, the anion decomposes to CO_2 and O^{2-}. If the anion does not decompose, it remains trapped in this amorphous material. Up to this point the decomposition is reversible; placing the amorphous material in an aqueous solution of the anion regenerates the LDH. Further heating, however, irreversibly leads to the crystallization of metal oxides and spinels.

The amorphous mixed-metal oxides formed by the thermal decomposition of LDH's act as basic catalysts [25]. Two specific reactions of interest are the polymerization of alkene oxides [26] and the aldol condensation of aldehydes and ketones [27]. For the polymerization of propylene oxide, hydrotalcite calcined at 723 K (forming the amorphous mixed-metal oxide) yields the most highly active catalyst, while uncalcined hydrotalcite shows no catalytic activity. In the presence of LDH's calcined at 723 K acetone condenses to form a β-hydroxy ketone; loss of water and further condensation with another equivalent of acetone leads to the formation of isophorone:



More recently, LDH's have found application as ion-exchangers and flame-retardants [7, 28]. Their anion-exchange capabilities, coupled with their high thermal stability, allow LDH's to trap anions such as CrO_4^{2-} and $Fe(CN)_6^{3-}$ in waste water streams. Heating the LDH with the ecologically undesirable anion converts the LDH to a water-insoluble metal-oxide matrix with the anion trapped for disposal. LDH's act as flame-retardants through their thermal decomposition properties; by releasing water and non-flammable gases, LDH's quench flame and dilute combustible materials.

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