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Chimie Douce Reactions: A New Route to Obtain Well Crystallized Layer Double Hydroxides

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Layer double hydroxides (LDHs) have been obtained by chimie douce reactions from the $NaNi_{1-y}Co_yO_2$ cobalt substituted sodium nickelate ($0 \leq y \leq 0.5$). These materials exhibit the general formula $Ni_{1-y}Co_y(OH)_2X_{y/n}$, zH_2O, $X^{n-} = CO_3^{2-}$, NO_3^-, Cl^-, OH^-, SO_4^{2-} . . . . The X^{n-} anions and the water molecules are inserted between the hydroxide slabs. The $Ni_{1-y}Co_yO_2$ slabs are built up during the high temperature preparation of the sodium nickelate, while the anions are inserted later on during the chimie douce reaction. It follows that a wider range of materials can be obtained than in the case of classical precipitation reactions. Moreover, the materials are well crystallized. The LDHs have been characterized by X-ray diffraction and by IR spectroscopy. The observed anion selectivity is discussed on the basis of electrostatic interactions and steric effects.

Introduction

The Layer Double Hydroxides (LDHs) are intensively studied for their anion exchange properties and for their use as precursors for the preparation of new catalytic materials (*1*, *2*). Several preparation methods are commonly used, which consist of precipitation reactions in various conditions.

Their formula derives from the classical brucite one ($Mg(OH)_2$) by the partial substitution of a trivalent cation (L) for the divalent one (M). Therefore, in order to compensate the excess of positive charge in the hydroxide slab, anions are inserted into the interslab space. Moreover, as these anions do not occupy the whole available space in the Van der Waals gap of the pristine hydroxide, water molecules are also intercalated in order to increase the lattice stability thanks to the formation of a hydrogen bond network. The structure of these materials can be schematized as shown in Fig. 1. The general formula is $M_{1-y}L_y(OH)_2X_{y/n}$, zH_2O ($X = CO_3^{2-}, NO_3^-, Cl^-, OH^-, SO_4^{2-}$ . . .). As the water molecules do not participate in the charge equilibrium, their water amount is not strictly fixed; nevertheless it is as a rule close to 0.50, as found in the mineral hydrotalcite: $Mg_6Al_2(OH)_{16}CO_3$, $4H_2O$ or $Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.125}$, $(H_2O)_{0.50}$. The name of this material is commonly used to designate in a general way the whole material family. The divalent and trivalent cations can be either diamagnetic ions (Mg^{2+}, Zn^{2+}, Al^{3+} . . . .) or transition element ions (Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{3+} . . .).

The materials obtained by precipitation are often poorly crystallized and can exhibit composition fluctuations. This inhomogeneity results from the difference in precipitation pH of $M(OH)_2$ and $L(OH)_3$ hydroxides. It follows that the y value in the recovered material can be different from solution composition.

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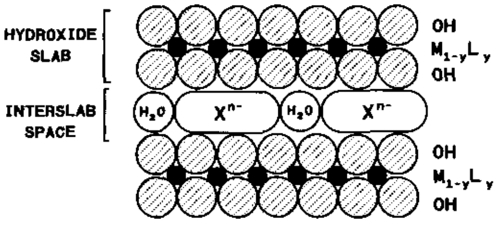


FIG. 1. Schematic representation of the structure of a LDH.

In our lab, interest has been focused for several years on the behavior of cobalt substituted nickel hydroxides as positive electrode material of alkaline batteries (Ni–Cd, Ni–H_2 and Ni–*M*H) (*3, 4*). We have shown that in peculiar conditions a LDH can appear after the discharge of the electrode. In this case these materials are labeled α or α^* according to the habit of people working on nickel hydroxide electrodes. Therefore, we have tried to develop new preparation methods for LDHs using chimie douce techniques which simulate the discharge electrode process, in order to obtain the pure material. As in these experiments a redox reaction occurs, these preparations are limited to materials containing at least one transition element. The results obtained for the (Ni,Co) LDHs are reported in the present paper.

Experimental

The material preparation consists of two main steps:

- *Classical high temperature solid state reactions* in order to get the $Ni_{1-y}Co_yO_2$ slab. For this purpose the $NaNi_{1-y}Co_yO_2$ sodium nickelate is prepared as previously described (*5*).
- *Chimie douce reactions* in order to modify the interslab composition without changing the slab formula.

In a typical experiment, the sodium nickelate ($NaNi_{0.70}Co_{0.30}O_2$, for instance) is hydrolyzed in an oxidizing medium (20 ml of 4 *M* NaClO plus 80 ml of 5 *M* KOH for 1 g of sodium nickelate). KOH is required within the medium as large alkali ions are necessary to stabilize the γ-type oxyhydroxides. For this material the typical formula has been obtained (*5*): $H_{0.20}Na_{0.12}K_{0.21}Ni_{0.70}Co_{0.30}O_2,(H_2O)_{0.47}$. This material is then reduced to give rise to the LDH: $Ni_{0.70}Co_{0.30}(OH)_2(CO_3)_{0.15},(H_2O)_{0.50}$. The choice of H_2O_2 as a mild reducing reagent allows the selective reduction of nickel to the divalent state and of cobalt to the trivalent one. The anions which ensure the charge compensation are inserted during this reduction process.

The preparation flow chart is represented on Fig. 2. A schematic drawing of the packing is also given for each involved material in order to emphasize the modification of interslab composition.

Several comments can be made on this preparation.

- It is more convenient to use sodium nickelate because the larger interslab distance of sodium phases (5.20 Å against 5.00 Å) makes easier the chimie douce reaction. Moreover, in the case of the lithium phase for low cobalt contents, the materials exhibit a departure from the ideal stoichiometry which leads to the presence of nickel ions in the interslab space (*6*).
- The oxidizing hydrolysis step can be supressed; direct reduction of the sodium nickelate with H_2O_2 in presence of the selected sodium salt gives the LDH. Nevertheless, as the interslab distance of the γ-phase is intermediate between those of sodium nickelate and of the LDH, the chemical reactions are easier and give purer products if the oxidizing hydrolysis step is maintained.
- If the reduction reaction is performed in air without special care, the inserted anions are the CO_3^{2-} ones originating from the atmosphere CO_2. As discussed in the following, the carbonate inserted materials ((CO_3)LDHs) are the most stable and LDHs inserted with other anions can only be obtained under special conditions, without CO_2. If the reduction is performed in the

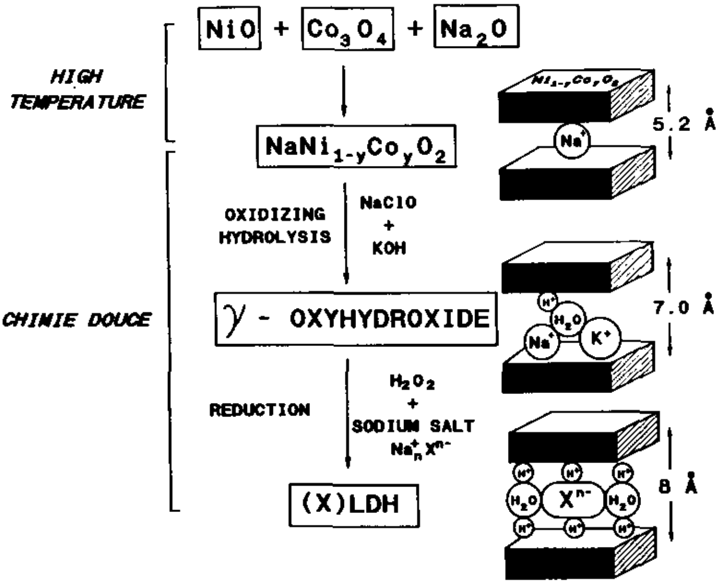


FIG. 2. Preparation flow chart of LDHs by chimie douce reactions (the thickness of the $Ni_{1-y}Co_yO_2$ slab varies with the oxidation state of nickel and cobalt).

absence of anionic species SO_4^{2-}, Cl^-, Br^-, NO_3^- . . . .) and under a CO_2-free atmosphere the charge neutrality is ensured by OH^- anions coming from water.

In the precipitation technique, the material is formed in one step, so that the stability of the overall LDHs, which depends on the size and the charge of inserted anions, restricts the values of the M^{II}/L^{III} ratio to a narrow domain. In contrast, in the case of the technique reported in this paper, the preparation is carried out in two separate steps. The M^{II}/L^{III} ratio is only restricted by the solid solution range of the $NaM_{1-y}L_yO_2$ precursor phase. During the chimie douce step, anions are inserted in order to compensate the excess of charge due to L^{III} cations. The amount of negative charge brought by the anions is fixed by the slab composition and the structure has to accommodate these anions even if the final material is not the most stable in the studied system.

Results and Discussion

In a first step, experiments have been realized in air for $0 < y \leq 0.50$. The limit value $y = 0.50$ corresponds to the largest amount of cobalt which can be substituted for nickel in the $NaNiO_2$ precursor phase. In this case the LDH's are mainly inserted with CO_3^{2-} anions. As it will be discussed in the following, a special behavior is observed for $y < 0.20$ or $y > 0.40$. In the first step, materials with interstratified structure are obtained, while in the second one, OH^- anions are simultaneously inserted in order to participate in the charge compensation. Consequently, the main experiments have been realized for $y = 0.20$ and $y = 0.30$ so as to avoid the difficulties.

X-Ray Diffraction Characterization

Contrarily to the material obtained by precipitation, the LDHs obtained by the chimie douce technique are well crystallized, as shown by the shape of the X-ray diffraction patterns, reported as an example in Fig. 3, for LDHs inserted with CO_3^{2-} and SO_4^{2-} anions. These phases crystallize in the rhombohedral system (S.G.: $R3m$) with the $P3$ structural type (5). The hexagonal parameters of CO_3^{2-}, NO_3^-, and SO_4^{2-} LDHs are

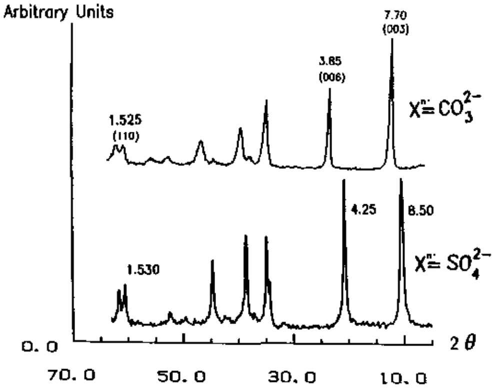


FIG. 3. X-ray diffraction patterns of LDHs inserted with CO_3^{2-}, NO_3^{2-}, and SO_4^{2-} anions (the amount of cobalt (y) is equal to 0.30).

reported in Table I. The interslab distances, which are equal to one third of the c parameters, are also reported.

The variation of the a parameter reflects rather the interactions between the anionic species: the a parameter increases with the charge of the inserted anions.

The variation of the interslab distance results from the competition between steric effects (the larger the anions, the larger the distance) and electrostatic ones (the higher the anion charge, the higher the electrostatic attraction to the (Ni^{2+}, Co^{3+}) layer and the lower the interslab distance). The difference in interslab distance for CO_3^{2-} and NO_3^- results from the high cohesiveness of the structure in the case of the CO_3^{2-} inserted LDHs. As CO_3^{2-} and NO_3^- anions both have planar structures, the difference in size between them can be neglected in first approximation. In contrast, the steric effect accounts for the very important increase of the interslab distance observed when SO_4^{2-} ions are inserted. Since the free SO_4^{2-} anion exhibits a tetrahedral structure, whatever the SO_4^{2-} anion orientation, two layers of oxygen atoms are locally inserted between the OH layers. Nevertheless the increase in the interslab distance when SO_4^{2-} anions are inserted leads to discuss about their orientation. As shown in Fig. 4, two main orientations between the $(Ni_{1-y}Co_y)(OH)_2$ slabs can be assumed. From geometrical considerations, provided that the S–O bond length is equal to 1.50 Å, the thickness of SO_4^{2-} anions is equal to 4.8 Å according to the first hypothesis and 4.5 Å according to the second one. Schematically, the interslab distance can be considered as the sum of the thickness of a $(Ni_{1-y}Co_y)(OH)_2$ slab and of inserted species. Assuming the $Ni(OH)_2$ thickness to equal 4.6 Å (*7*), the interslab distances of (SO_4) LDH are expected to be equal to 9.4 or 9.1 Å depending on the model considered (Fig. 4). These values are considerably larger than the experimental one (8.50 Å) (Table I). In fact, the oxygen layers are not exactly superposed as the triangular lattices are shifted; moreover the SO_4^{2-}–$(Ni_{1-y}^{2+}Co_y^{3+})$ attraction tends to decrease the interslab distance. Consequently the model with 9.1 Å as interslab distance seems more convenient than the other one.

TABLE I

VARIATIONS OF THE HEXAGONAL PARAMETERS OF Ni–Co LDHs (y = 0.30) VS THE NATURE OF THE X^{n-} ANION

X^{n-} anions	M–M intraslab distance $a \pm 0.005$ Å	$c \pm 0.03$ Å	Interslab distance $d \pm 0.01$ Å
CO_3^{2-}	3.046	23.07	7.69
NO_3^-	3.016	23.55	7.85
SO_4^{2-}	3.058	25.50	8.50
SO_4^{2-} (160°C)	3.060	23.70	7.90

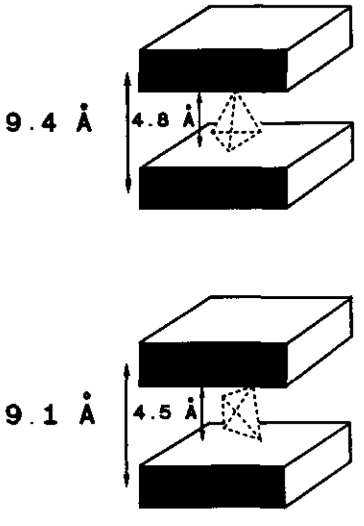


FIG. 4. Possible orientations of a SO_4^{2-} anion in the interslab space.

Thermal treatment of the (SO_4)LDH's. The $Ni_{0.7}Co_{0.3}(OH)_2(SO_4)_{0.15}, zH_2O$ phase studied previously has been heated at 160°C for 4 h in air. The X-ray diffraction pattern of the recovered material shows strong similarities to the original one but with a strong decrease in the interslab distance. It can be indexed in the hexagonal system with the following parameters: a = 3.060 Å, c = 23.70 Å. The interslab distance (7.90 Å), close to that found for (CO_3) LDHs and (NO_3) LDHs (Table I), suggests that only one oxygen layer arising from the SO_4^{2-} anions is located between the $(Ni_{1-y}Co_y)O_2$ slabs. Consequently the SO_4^{2-} ions must be directly linked to the metal cation, the apical oxygen atom of the sulfate anion replacing one OH group of the hydroxide (*8*, *9*).

Infrared Study

All these materials have been characterized by infrared spectroscopy in the 200 to 4000 cm^{-1} frequency range. The experiments were performed on a Perkin–Elmer 983 spectrometer, the materials being dispersed, either in Nujol or in hexachlorobutadiene.

The infrared spectra of these materials are reported in Fig. 5 in comparison with that of the β(II) $Ni(OH)_2$ hydroxide. A detailed infrared study of the (CO_3) LDH has been previously reported (*10*), so that interest is mainly focused in this paper on the anion bands. Nevertheless, it should be noticed that the appearance of large bands at 3350 and 1650 cm^{-1} ($\nu(H_2O)$ stretching and $\gamma(H_2O)$ bending modes of water molecules) emphasizes the presence of water in all LDHs in contrast with β(II) $Ni(OH)_2$.

The strong similarity between the IR spectra of the (NO_3) and (CO_3) LDHs shows that both inserted anions have the same symmetry (D_{3h}) in the interslab space. As in the case of the (CO_3) LDHs, the shifting of the frequency vibration shows that the NO_3^- anions are symmetrically hydrogen bonded with the interlamellar H_2O molecules and the hydroxyls of the hydroxide slabs.

Comparison of the IR spectra of both (SO_4) LDHs shows clearly the influence of the 160°C thermal treatment on the linking

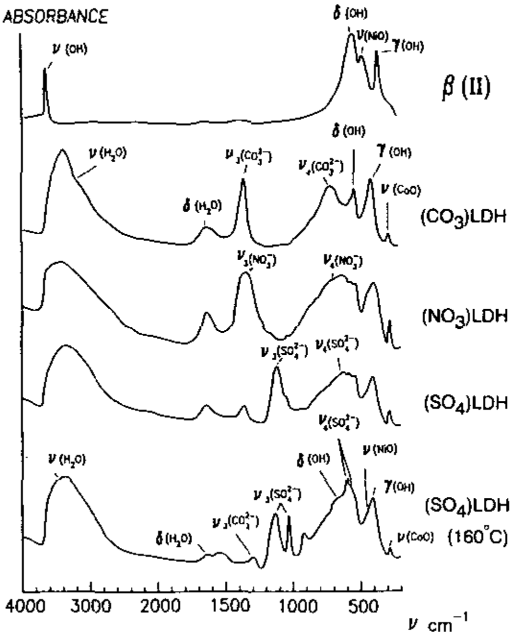
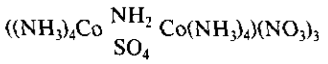


FIG. 5. Infrared spectra of some LDHs in comparison with that of β(II)-$Ni(OH)_2$.

TABLE II

SO_4^{2-} ANION VIBRATIONS VS ITS SYMMETRY

Material	Symmetry	ν_1	ν_2	ν_3	ν_4(cm^{-1})	Ref.
Free SO_4^{2-} anion	T_d			1104	613	(11)
$[Co(NH_3)_5SO_4]Br$	C_{3v}	970	438	1032–1044	645	(11)
				1117–1143	604	(11)
 $((NH_3)_4Co\underset{SO_4}{\overset{NH_2}{}}Co(NH_3)_4)(NO_3)_3$	C_{2v}	995	462	1050–1060	641	
				1170	610	
				1105	571	
(SO_4) LDH	T_d			1100	610	
$(SO_4$ − 160°C) LDH	C_{3v}	950	440	1040	600	
				1140	650	

between the SO_4^{2-} anion and the lattice. Two different configurations have to be considered:

- If the SO_4^{2-} anions are free in the lattice (T_d symmetry) two vibrations are IR active (ν_3 and ν_4).
- If the anions are linked to the lattice by one oxygen, the symmetry becomes C_{3v} and both ν_3 and ν_4 bands are split into two subbands respectively.

The various vibration frequencies of sulfate anions according to the anion symmetry are compared in Table II (*10, 11*) in comparison with the ν_3 frequency of both (SO_4) and $(SO_4$ − 160°C) LDHs. The comparison of the overall data shows clearly that the SO_4^{2-} anions are in T_d symmetry in (SO_4) LDHs and in C_{3v} symmetry in the thermally treated material. This change in symmetry agrees with the direct bonding of the anion with a metal cation as suggested by the X-ray study.

As previously discussed in the case of the (CO_3) LDHs, the hydrogen bonding between the CO_3^{2-} anion and the H atoms belonging to OH or H_2O leads to an important modification of the vibration frequency. In the case of the (SO_4) LDHs, the ν_3 (SO_4^{2-}) band is only slightly displaced in comparison with the theoretical value of a free sulfate ion (Table II). This result suggests that the SO_4^{2-} orientation is not compatible with the formation of a strong network of hydrogen bands as in the case of the (CO_3) LDHs.

Anion Selectivity

We have previously shown that the (CO_3) LDHs are the most stable materials as they are always obtained if no special care is taken during the reduction step. This point has been reported by several authors (*12, 13*) and particularly by Mendiboure *et al.* who have proposed the following stability scale for the anion insertion in the $Fe_{0.75}Ni_{0.25}(OH)_2(CO_3)_{0.125},(H_2O)_{0.5}$ reevesite related material:

$$CO_3^{2-} \gg SO_4^{2-} > Cl^- > NO_3^- > CH_3COO^-.$$

In all these materials, the anions are inserted between two hydroxyl layers, and the electrostatic interactions between the negatively charged anion and the L^{3+} cation within the slab are weak as a result of the long distances beween these ions (larger than 4 Å). These very weak ionic bonds lead to an anion lability emphasized by the facility with which these anions are removed by oxidation of the LDHs, as occurs during the charging of the α-nickel hydroxide electrode of a nickel–cadmium battery. Hence, it follows that, if several ions are present in the solution, anion exchange reactions occur spontaneously in order to obtain the most stable material even if the energy difference is small.

Two main parameters seem to play an important role with regard to the stability of the interslab space: steric effects and charge distribution.

As about the 0.5 H_2O molecules lies the interslab space, the inserted anions must have a thickness as close as possible to that of the water molecules. From this point of view, CO_3^{2-} and NO_3^- ions seem to be the most favorable. OH^- and X^- (Br^-, Cl^-) ions are significantly larger than H_2O, while SO_4^{2-} ions are considerably larger. If the inserted anions exhibit a size different from that of H_2O a puckering of the $(M,L)(OH)_2$ slabs must occur and this deformation costs energy. Nevertheless, the case of big organic anions must be considered separately; indeed, as the negative charge is localized, the ionic bonding can occur with one or two slabs depending on the anion orientation.

The charge distribution on the anion also plays an important role. According to the second Pauling's rule the charge compensation must occur locally. As the L^{3+} cations are statistically distributed in the (M,L) layer, the anions that ensure the charge compensation between two $(M,L)(OH)_2$ slabs must have delocalized negative charges in order to facilitate the compensation. Therefore anions like NO_3^- and CO_3^{2-} seem to meet this requirement. For the most classical LDHs (with $0.2 \leq y \leq 0.30$) the CO_3^{2-} amount varies from 0.1 to 0.15, which is consistent with the presence of 0.5 H_2O molecules in the interslab space. In the case of the (NO_3) LDHs, the single negative charge of NO_3^- requires an anion concentration varying in the 0.2–0.3 range, which considerably restricts the amount of water molecules. All these results account for the preferential stability of (CO_3) LDHs.

Anion Distribution

The previous point clearly shows that the nature of the anions, their distribution in the interslab space, and the amount of L^{3+} cations in the $(M_{1-y}L_y)(OH)_2$ slabs are directly interrelated.

The relation between the anion distribution and the amount of L^{3+} cations has been investigated only for materials prepared in air, i.e., inserted with carbonate anions. As previously mentioned, interstratified structures are obtained for $y < 0.20$. When the amount of carbonate anions ($y/2$) is low, these anions are not able to occupy the whole interslab space, so that a segregation phenomenon occurs. This behavior will be discussed in detail in a forthcoming paper (*14*).

In the $0.20 < y < 0.50$ range, which is reached in the nickel–cobalt system, a competition takes place between the steric effects, the charge carried by the anions, and the anion selectivity. It is interesting to discuss this point in detail.

Let us consider one interslab space situated between two OH planes belonging to two adjacent $(Ni_{1-y}Co_y)(OH)_2$ slabs. If OH^-, CO_3^{2-}, and H_2O are the only species available for insertion, from the steric point of view, the interslab space can be considered as a plane of oxygen atoms in a triangular lattice (Fig. 1). As 0.5 H_2O molecules are generally found in the interslab space 0.5 sites for oxygen atoms remain for CO_3^{2-} or OH^- anions. If only CO_3^{2-} anions are present, their maximum amount is equal to 0.167 which means that the maximum additional charge carried by the cobalt ions is equal to 0.33 ($y_{\text{max.}} = 0.33$). For $y = 0.50$, the charge compensation can be completely ensured by 0.50 OH^-. For intermediate cobalt amounts, both OH^- and CO_3^{2-} species are inserted.

Experimentally, the amount of carbonate anions is found to be equal to $y/2$ for $0 < y < 0.35$. For higher values of y, it decreases slowly but it is not equal to 0 for $y = 0.50$, as the higher stability of the LDHs inserted with CO_3^{2-} anions vs those with OH^- ones leads to a smaller amount of water.

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