Mechanochemical Preparation and Structural Characterization of Layered Double Hydroxides and their Amino Acid-Intercalated Derivatives

PhD Theses

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1. INTRODUCTION

Layered double hydroxides (LDHs) are clay-like materials, which usually contain di- and trivalent metal ions in the layers. The presence of the trivalent metal cations in the brucite-like layers creates an excess positive charge. This is compensated by the fully or partially hydrated charge compensating anions residing between the layers. The charge compensating anions between the layers can be various, from simple inorganic anions like NO_3^-, to large organic anions like amino acids. A characteristic of the LDHs is that these anions can be exchanged, thus giving a unique opportunity for the modification of these materials.

Although in the majority of the cases divalent and trivalent cations are found in the layers, there have been reports of incorporating tetravalent cations in the LDHs. The literature concerning Sn(IV)-containing LDHs is controversial; some researchers claim that they managed to synthesize such materials while other groups disapprove these claims. One of the goals of the work leading to this dissertation was to synthesize Sn(IV)-containing LDHs beyond doubt.

Profiting from the anion-exchange capabilities and large surface areas, the major application fields of the LDHs are catalysis, playing the role of the catalyst or the catalyst support, and the synthesis of biologically active compounds, playing the role of the container for the organic synthons. They are also used as flame retardants, sensors, and electrodes to mention just a few. These materials can be found in nature as minerals, but there are usually synthesized. The most frequently used synthesis techniques are solution-based methods, such as co-precipitation or urea hydrolysis. The same can be stated for the intercalation; here, the solution based methods also predominate, like direct anion exchange or the dehydration-rehydration method.

In the work leading to this dissertation, a less widely used method was applied for both the intercalation and the preparation of the LDHs, mechanochemistry that is. For the synthesis, a two-step milling operation was used, where the first step was dry milling of the precursors (usually the hydroxides or the salts of the di- and trivalent metals), followed by wet milling (after the addition of minute amount of water or NaOH solution to the system). An additional aim of the work was to prepare the Ca(II)Al(III)- and Ca(II)Fe(III)-LDHs *via* mechanochemistry, and to optimize the reaction parameters in order to obtain close to phase-pure LDHs. A further goal was to functionalize the

LDHs *via* intercalating the anions of various amino acids between the layers, also using mechanochemical methods. All prepared materials were studied with as many characterization methods as possible, in order to get a close to complete picture about their structures.

2. EXPERIMENTAL

Materials and synthesis methods

Ca(II)Sn(IV)-LDHs

Concentrated NaOH (~20 M) stock solutions were prepared from Millipore MilliQ water and *a.r.* grade solid NaOH, and their carbonate content was minimized. The exact concentration was determined through accurate density measurement. The solution was stored in an airtight, caustic resistant Pyrex bottle. This solution was kept carbonate-free, and was used for the making of the NaOH solution actually used in the synthesis (0.1 M, 1 M, 3 M)

During the syntheses of Sn(IV)-containing LDHs, both solution-based and mechanochemical methods have been applied. In the co-precipitation method, LDHs were prepared *via* dropwise addition of the two metal salt solutions ($CaCl_2$ and $SnCl_4$) in various molar ratios to a vigorously stirred NaOH solution. The mixture of the two solutions was agitated for 24 hours. The precipitate was filtered until air dry with the aid of caustic resistant vacuum filter unit (Nalgene, USA) equipped with an appropriate membrane (Versapor 0.45 μm, Pall Corporation). The solid reaction products were kept at room temperature in desiccators over dry SiO_2. Some of the samples have been aged for 6 hours at a temperature of 70°C.

The mechanochemical syntheses were applied in two ways, either using a mixer mill or a simple agate mortar. In the mixer mill, the rotation frequency was 11.6 s^{-1}, and it was kept constant throughout the syntheses, just like the total weight of the precursors (3 g). Two methods were scrutinized: the one-step and the two-step millings. In the former one, only dry milling was employed, and the precursors were ground for 3 hours. In the latter one, in addition to dry milling (1 h), wet milling (2 h with 0.7 ml added water) was also applied. After the synthesis, the products were kept at room temperature in a desiccator over dry SiO_2. When using the agate mortar with a pestle, the results of the above-mentioned methods were meant to be reproduced, thus the

methods applied were analogous to those mentioned above in both the one-step (dry) and two-step (dry and wet) millings. In this case, the starting materials (3 g altogether) were ground until a uniform, fine powder was obtained, and then, the mixture was divided into two parts. One of them was placed in a desiccator, and was studied without further treatment. To the other part 0.35 ml of water was added; then grinding was continued until a uniform and homogenous mixture was obtained. The product thus received was dried, and kept in a desiccator.

Ca(II)Al(III)- and Ca(II)Fe(III)-LDHs

The syntheses of the Ca(II)Al(III)- and Ca(II)Fe(III)-LDHs were attempted using mechanochemical methods only. They were somewhat analogous to the mechanochemical methods presented above. They were carried out either by manual grinding using a simple agate mortar or by milling using a mixer mill. When using the agate mortar, the precursors were placed into the mortar and ground for 5 min. This was followed by the addition of a certain amount of NaOH solution or water, after which the mixture was ground for 1 additional hour. In the mixer mill, the precursors were placed in the grinding jars, and milled for 1 h (dry milling), after which a certain amount of water was added to the system, and, then, a 2 h grinding (wet milling) was applied. A set of parameters, the amount of added water and/or NaOH solution the ball/sample weight ratio, the grinding frequency, the dry milling time, and the wet milling time were systematically varied in order to obtain the LDH in as phase-pure form as it was possible.

Intercalation of the LDHs

The intercalation of the anionic forms of the various amino acids into the layers of various LDHs was attempted *via* mechanochemical methods. A slightly modified two-step grinding procedure was applied. The first step was dry milling, where the precursors were ground for 1 h; then, a certain amount of NaOH solution and the amino acid were added, which was followed by 2 h of wet grinding. After this, the products were washed, dried and stored in a desiccator at room temperature. The addition of the precursors, the amino acids and the NaOH into the grinding jars, as well as the sealing of the jars were performed under N_2 atmosphere in a glove-box. This way, the disturbing CO_2 could be excluded. The ball/sample weight (B/S) ratio was kept at 100 throughout

the reactions. This was derived from the optimization of the synthesis of the pristine LDHs.

The optimization of the intercalation process was attempted *via* the systematic change of several reaction parameters, such as the NaOH:Fe molar ratio, the Fe:amino acid molar ratio, and the forms of the amino acid.

Characterization methods

Powder X-ray diffraction (XRD) patterns of the solid samples were registered in the 2θ = 3–60° range on a Rigaku Miniflex II and DRON-2 instruments, using CuKα (λ = 1.5418 Å) radiations in Bragg-Brentano geometry. Reflection positions were determined via fitting a Gaussian function. They were found to be reproducible within 0.05° (2θ); therefore, the uncertainty of the basal spacing was estimated as ±0.01 nm.

The Fourier-transform infrared (FTIR) spectra of the pristine, and the organic anion intercalated LDHs were recorded on a BIORAD FTS-65A/896 spectrometer equipped with a DTGS detector in diffuse reflectance. Spectral resolution was 4 cm^{-1} and 256 scans were used for a spectrum. The spectra were baseline-corrected and smoothed using the WIN-IR software package. The samples were finely ground and combined with KBr (without pressing into pellets).

Raman spectra were recorded on a BIO-RAD Digilab Division dedicated FT-Raman spectrometer equipped with liquid nitrogen cooled germanium detector and CaF_2 beam-splitter. The excitation line was provided by a Spectra Physics T10-106C Nd:YVO4 laser at 1064 nm. The spectra were recorded in the 3600–100 cm^{-1} range with 4 cm^{-1} resolution. 1024 scans were collected for each spectrum. The excitation power was 280 mW at the sample position. The spectrometer was controlled by the BIO-RAD Win IR 3.3 software. The samples were placed in a standard NMR tube. Spectra were recorded at room temperature. Data were processed by the GRAMS/AI 7.00 software.

Thermal analytical measurements (TG/DTG) were performed using a Setaram Labsys derivatograph working under N_2 flow at 2°C/min heating rate. Both the weight loss vs. temperature (thermogravimetry – TG) and the differential weight loss *vs.* temperature (differential thermogravimetry – DTG) curves were recorded. Approximately 20 mg sample (measured accurately into a ceramic crucible sample holder) was applied in each experiment. Measurements were started right after removing the samples from the desiccators.

The morphology of the samples was examined with scanning electron microscope (SEM – Hitachi S-4700 microscope with varying acceleration voltage). The samples were fixed on a double-sided adhesive carbon tape. They were coated with gold in order to obtain images with more contrast using a sputter coater (Quorum Technologies SC7620). The thickness of the gold layer was a few nanometers. The approximate composition and the elemental map of the substances were investigated by a Röntec QX2 energy dispersive X-ray spectrometer (EDX) coupled to the microscope.

The X-ray absorption spectra (XAS) were measured at the Fe K-edge beamline I811 at the MaxLab facility in Lund, Sweden. The station is based on a superconductive undulator injection device connected to the 1.5 GeV MAX II storage ring. This superconducting multipole wiggler beamline equipped with a water-cooled channel cut Si(111) double crystal monochromator can deliver at 10keV, approximately 2×10^{15} photons/s/0.1% bandwidth with horizontal and vertical FWHM of 7and 0.3 mrad, respectively. A beam-size of 0.5mm × 1.0 mm (width × height) was used.

3. NOVEL SCIENTIFIC RESULTS

T1. Ca(II)Sn(IV)-LDH was successfully synthesised using a two-step mechanochemical method.

1.1. It was verified that by using co-precipitation method, the Ca(II)Sn(IV)-LDH could not be synthesized. The two-step milling operation proved to be suitable method for the preparation of Ca(II)Sn(IV)-LDH. The necessary hydroxide groups for the formation of the layers were provided by the added water.

T2. We were the first to intercalate the cystine and valine anions into Ca(II)Sn(IV)-LDH by using a two-step milling procedure.

2.1. The success of the intercalations was confirmed by XRD, IR, Raman, SEM and SEM-EDX measurements.

T3. Through the optimization of the synthesis conditions, we were able to mechanochemically prepare Ca(II)Al(III)-LDH, in a close to phase-pure form.

3.1. XRD measurements confirmed that using manual grinding, LDH could be synthesized; however, the major phases were the unreacted precursors meaning that the energy provided by manual grinding was not sufficient.

3.2. With the two-step milling operation in a mixer mill, a close to phase-pure LDH could be synthesized, after the optimization of the reaction conditions. It has been revealed that although the addition of water (wet milling) is of utmost importance, the major parameter was the ball/sample mass ratio, *i.e.*, the mechanochemical energy exerted (this has to be minimum 100).

T4. For the first time, we identified the optimum synthesis parameters for the mechanochemical synthesis of pristine Ca(II)Fe(III)-LDH in a mixer mill.

4.1. The optimum set of parameters for the mechanochemical synthesis of phase-pure Ca(II)Fe(III)-LDH is as follows: Ca:Fe molar ratio of 2, ball to substrate mass ratio of 100, grinding frequency of 11.6 Hz, 1 h dry milling, 2 h wet milling, H_2O:Fe molar ratio of 22.15.

T5. We succeeded in identifying the optimal reaction conditions for the mechanochemical intercalation of the anions of cystine and tyrosine into Ca(II)Fe(III)-LDH, and uncovered fine details of the intercalation properties of the host and the guest anions.

5.1. The optimization of the intercalation was performed with the slightly modified two-step grinding procedure. It was revealed that the tyrosinate ion was readily intercalated, while the formation of inorganic anion-intercalated LDH (pristine LDH) always competed with that of the cystinate-intercalated LDH.

5.2. On the basis of calculating the interlayer distances for the organically intercalated LDHs and the knowledge of the dimensions the amino acid anions, it was revealed that the cystinate anions could be accommodated in a double-layer manner, in which the anions lay parallel with the layers; the tyrosinate ions can behave similarly, although a single layer, perpendicularly oriented arrangement can also be an option.

4. PRACTICAL USE OF THE RESULTS

The results presented here are of fundamental nature. Nevertheless, layered double hydroxides and their intercalated derivatives offer many practical uses starting from catalytic applications to pharmaceutical and environmental uses. Given the fact that the LDHs presented in the dissertation were prepared using mechanochemistry, this novel method can provide access to LDHs that cannot be prepared by wet chemical methods, and can present new applications in the industry, since powders are easier to handle than solutions on large scale.

5. PUBLICATIONS

5.1. Papers related to the Theses published in refereed journals

[1.] Ferencz, Zs., Szabados, M., Ádok-Sipiczki, M., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.: Mechanochemically assisted synthesis of pristine Ca(II)Sn(IV)-layered double hydroxides and their amino acid intercalated nanocomposites,
J. Mater. Sci. **49**, 8478–8486 (2014).
I(mpact)F(actor): 2,371 I(degen)H(ivatkozás): 5

[2] Ferencz, Zs., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.: Optimisation of the synthesis parameters of mechanochemically prepared CaAl-layered double hydroxide,
Appl. Clay Sci. **112-113**, 94–99 (2015).
IF: $2{,}467_{2014}$ IH: 4

[3] Ferencz, Zs., Szabados M., Varga G., Csendes, Z., Kukovecz, Á, Kónya, Z., Carlson, S., Sipos, P., Pálinkó, I: Mechanochemical synthesis and intercalation of Ca(II)Fe(III)-layered double hydroxides,
J. Solid State Chem. **233**, 236–243 (2016).
IF: $2{,}133_{2014}$ IH: –

5.2. Papers related to the Theses published as full papers in conference proceedings

[4] Ferencz, Zs., Szabados, M., Sipiczki, M., Kukovecz, Á., Kónya, Z., Sipos, P., and Pálinkó, I.: Mechanochemical synthesis of M(II)Sn(IV) layered double hydroxides**,** In: Melník M, Segľa P, Tatarko M: Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, Bratislava: Slovak Technical University Press, 2013, pp. 47–57 (ISBN:978-80-227-3918-4).

[5] Ferencz, Zs., Szabados, M., Sipos, P. and Pálinkó, I. Ca-Fe Réteges kettős hidroxidok mechanokémiai előállítása, a szintézis optimizálása**,** In: Endrődi B, Laufer N. "XXXVI. Kémia Előadói Napok", Szeged JATE press, 2013, pp. 83–87 (ISBN:978-963-315-145-7).

[6] Szabados, M., **Ferencz, Zs.**, Sipiczki, M., Sipos, P. and Pálinkó, I. Tiszta és hierarchikus szerkezetű CaFe-réteges kettős hidroxidok szintézise dörzsmozsárban, In: Endrődi B,

Laufer N. “XXXVI. Kémia Előadói Napok”, Szeged JATE press, 2013, pp. 88–92 (ISBN:978-963-315-145-7).

5.3 Conference presentations related to the Theses

[1] Ferencz, Zs., Szabados, M., Sipiczki, M., Kukovecz, Á., Kónya, Z., Sipos, P., and Pálinkó, I.: Mechanochemical synthesis of M(II)Sn(IV) layered double hydroxides**,** XXIV. International Conference on Coordination and Bioinorganic Chemistry, Recent Developments in Coordination, Bioinorganic, and Applied Inorganic Chemistry, 2013, Smolenice (Slovakia). (verbal presentation)

[2] Ferencz, Zs., Szabados, M., Sipos, P. and Pálinkó, I. Ca-Fe Réteges kettős hidroxidok mechanokémiai előállítása, a szintézis optimizálása, XXXVI. Kémia Előadói Napok. 2013, Szeged (Hungary). (verbal presentation)

[3] Szabados, M., **Ferencz, Zs**., Sipiczki, M., Sipos, P. and Pálinkó, I. Tiszta és hierarchikus szerkezetű CaFe réteges kettős hidroxidok szintézise dörzsmozsárban, XXXVI. Kémia Előadói Napok, 2013, Szeged (Hungary). (verbal presentation)

[4] Ferencz, Zs., Szabados, M., Sipos, P. and Pálinkó, I. Mechanokémia a réteges kettős hidroxidok szintézisében, XIX Nemzetközi Vegyészkonferencia, 2013, Baia-Mare (Romania). (verbal presentation)

[5] Ferencz, Zs., Szabados, M., Kukovecz, Á., Kónya, Z. Sipos, P. and Pálinkó, I. Mechanochemical intercalation of amino acids into layered double hydroxides, 4th International Colloid Conference – Surface Design and Engineering, 2014, Madrid (Spain). (poster presentation)

[6] Ferencz, Zs., Kukovecz, Á., Kónya, Z. Sipos, P. and Pálinkó, I. Mechanochemistry in the synthesis of Ca-Al layered double hydroxides. 22 ICM&T – International conference on Materials and Technology, 2014, Portorož (Slovenia). (verbal presentation)

[7] Ferencz, Zs. Ádok, M. Sipos, P. and Pálinkó, I. Mechanokémia a réteges kettős hidroxidok szintézisében és interkalációjában, XX Nemzetközi Vegyészkonferencia, 2014, Cluj (Romania). (verbal presentation)

[8] Ferencz, Zs., Szabados, M., Ádok-Sipiczki, M., Kukovecz, Á., Kónya, Z., Sipos, P. and Pálinkó, I. A mechanochemical approach for the synthesis of CaFe-layered double hydroxides, 4th Nanomaterials and Nanotechnology Meeting NanoOstrava 2015, 2015 Ostrava (Czech Republic). (verbal presentation)

[9] Ferencz, Zs., Kukovecz, Á., Kónya, Z., Sipos, P., and Pálinkó, I., Mechanochemistry in the intercalation of CaFe-layered double hydroxides, 18th International Symposium on Intercalation Compounds, 2015, Strasbourg (France). (poster and verbal presentation)

5.4. Other papers published in refereed journals

[1] Ferencz, Zs., Ádok-Sipiczki, M.,Hannus, I., Sipos, P., Pálinkó, I.: Structural features of intercalated CaFe-layered double hydroxides studied by X-ray diffractometry, infrared spectroscopy and computations,
J. Mol Struct. **1090**, 14–18 (2015).
IF: $1{,}602_{2014}$ IH: –

[2] Sipiczki-Ádok, M., Bugris, V., Mészáros, Sz., Srankó D. F., **Ferencz Zs.**, Szabados, M., Kukovecz Á., Kónya Z., Sipos P., and Pálinkó I.: Réteges kettős hidroxidok – különleges, könnyen funkcionalizálható összetett anyagok,
Magyar Kémiai Folyóirat – Kémiai Közlemények **120**, 106–115. (2014).

5.5. Other full papers published in conference proceedings

[1] Tóth, V., **Ferencz, Zs.**, Sipos, P., and Pálinkó, I.: Ca_2Al-réteges kettős hidroxidok interkalálása mechanokémia módszerekkel, In: Endrődi B, Laufer N. "XXXVI. Kémia Előadói Napok", Szeged JATE press, 2013, pp. 93–97 (ISBN:978-963-315-145-7).

[2] Ferencz, Zs., Szabados, M., Kukovecz, Á., Kónya, Z. Sipos, P. and Pálinkó, I. A mechanochemical approach to the synthesis of Mg-Al layered double hydroxides, In: Szélpál Sz.: 1st Innovation in Science 2014- Doctoral Student Conference, eBook of abstracts, 2014, pp. 44–45 (ISBN 978-963-9970-52-6).

[3] Szabados, M., **Ferencz, Zs.**, Kukovecz, Á., Kónya, Z. Sipos, P. and Pálinkó, I. A mechano-sonochemical method to synthetise CaFe-layered double hydroxides, In:

Szélpál Sz.: 1st Innovation in Science 2014 – Doctoral Student Conference, eBook of abstracts, 2014, pp. 62–63 (ISBN 978-963-9970-52-6).

[4] Czene, M, **Ferencz, Zs,** Sipos, P, and Palinko, I. Baeyer-Villiger oxidációs reakció Ca(II)Sn(IV)-réteges kettős hidroxidon (Bayer-Villiger oxidation reaction over Ca(II)Sn(IV)-layered double hydroxide) In: Bohner, B, Mesterházy, E. "XXXVIII. Kémiai Előadói Napok: Program és előadás-összefoglalók", Szeged JATE press, 2015, pp. 54–58 (ISBN:978-963-9970-64-9).

5.6. Other conference presentations

[1] Erdei, Gy., **Ferencz, Zs.,** Rácz, Cs., Csavdári, A.: Táplálékkiegészítőkben használt ciklodextrin zárványkomplexek előállítása és vizsgálata, XIII. Erdélyi Tudományos Diákköri Konferencia, kémia szekció, 2010, Cluj (Romania). (verbal presentation)

[2] Erdei, Gy.,**_Ferencz, Zs**, Rácz, Cs., Csavdári, A. Szabó, G.: Táplálékkiegészítőkben használt β-ciklodextrin zárványkomplexek előállítása és vizsgálata**,** XVI. Nemzetközi Vegyészkonferencia, 2010., Cluj (Romania). (poster presentation)

[3] Erdei, Gy., **Ferencz, Zs.**, Rácz, Cs., Csavdári, A., Szabó, G.: Táplálékkiegészítőkben használt β-ciklodextrin zárványkomplexek előállítása és vizsgálata, 2010. évi őszi Tudományos Diákköri Konferencia, Komplexkémia–Peptidkémia session 2010, Szeged. (verbal presentation)

[4] Erdei, Gy., **Ferencz, Zs**., Rácz, Cs., Csavdári, A., Szabó, G.: Táplálékkiegészítőkben használt β-ciklodextrin zárványkomplexek előállítása és vizsgálata, Erdélyi Múzeum Egyesület, Őszi Természettudományi Konferencia, Chemistry session 2010, Cluj (Roumania). (verbal presentation)

[5] Tóth, V., **Ferencz, Zs.**, Sipos, P., and Pálinkó, I.: Ca_2Al réteges kettős hidroxidok interkalálása mechanokémia módszerekkel, "XXXVI. Kémia Előadói Napok", 2013, Szeged. (verbal presentation)

[6] Ferencz, Zs., Szabados, M., Kukovecz, Á., Kónya, Z. Sipos, P. and Pálinkó, I.: A mechanochemical approach to the synthesis of Mg-Al layered double hydroxides, 1st Innovation in Science 2014 – Doctoral Student Conference, 2014, Szeged. (verbal presentation)

[7] Szabados, M., **Ferencz, Zs.**, Kukovecz, Á., Kónya, Z. Sipos, P. and Pálinkó, I.: A mechano-sonochemical method to synthetise CaFe-layered double hydroxides, 1st Innovation in Science 2014 – Doctoral Student Conference, 2014, Szeged. (verbal presentation)

[8] Czene, M, **Ferencz, Zs,** Sipos, P, and Palinko, I.: Baeyer-Villiger oxidációs reakció Ca(II)Sn(IV)-réteges kettős hidroxidon (Bayer-Villiger oxidation reaction over Ca(II)Sn(IV)-layered double hydroxide), XXXVIII. Kémiai Előadói Napok, 2015. Szeged. (verbal presentation)

[9] Bruszel, B., **Ferencz, Zs.**, Szabados, M., Kukovecz, Á., Kónya, Z. Sipos, P. and Pálinkó, I.: Preparation of Pd^{2+}- and Mn^{2+}-doped CaFe-layered double hyroxides, 18th International Symposium on Intercalation Compounds, 2015, Strasbourg (France). (poster presentation)

Full journal papers, total: **5**	related to the topic of the Theses: **3**
Cumulative impact factor, total: **8.573**	related to the topic of the Theses: **6.971**
Independent citations, total: 9	related to the topic of the Theses: **9**