

FUNCTIONAL MATERIALS – SYNTHESSES, CHARACTERISATION AND CATALYTIC APPLICATIONS

PhD Theses

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1. Introduction

Layered double hydroxides (LDHs) are materials generally containing di- and trivalent metal cations (there are however, known representatives consisting of mono- and/or tetravalent metal ions too) and hydroxide ions in the layers, and – since the layers are positively charged – simple partially or fully hydrated charge-compensating inorganic anions in the interlayer space.

There are two main structural varieties. One is the group of hydrotalcites resembling the structure of brucite [layered $\text{Mg}(\text{OH})_2$]. In this group the layers contain octahedrally coordinated two- and trivalent metal ions, the edge sharing octahedra are connected by hydroxide ions. The other one is the group of hydrocalumites. The divalent ion is the calcium ion here, and it is heptacoordinated, thus, the layer consists of edge-sharing heptacoordinated calcium hydroxide decahedra and hexacoordinated trivalent metal hydroxide octahedra.

The LDHs are versatile substances having many uses; they can serve as catalysts, catalyst supports, flame retardants, containers of biologically active compounds, or organic synthons, sensors, electrodes, to mention just a few. Although there are many known minerals with these structures, for applications they are usually synthesised. These materials have anion exchange ability, thus, various hybrid materials may be prepared with useful functionalities. Since direct ion exchange, especially of bulky inorganic ions, was not an easy exercise, many more other methods were developed. One, which is used in my work leading to these Theses, is the dehydration-rehydration method. It is based on the observation that on heat treatment the layered structure collapses, but it is regenerated on hydration if the temperature of dehydration was not too high (generally, ~ 723 K, however, the accurate temperature is LDH specific). The reconstruction also proceeds if anions, in my work organic anions, are present in the synthesis mixture, and in the reformed structure these anions are intercalated, *i.e.*, ion exchange takes place.

At the beginning of my work several goals have been set out. They are as follows:

1. exploring and finding the optimum experimental conditions for the synthesis of pristine Ca(II)Fe(III)- and Mg(II)Fe(III)-LDHs, representatives of hydrocalumite and hydrotalcite structural types, respectively,
2. characterising these materials with as many tools as it is possible,
3. studying the catalytic activity of the pristine, uncalcined CaFe-LDH,
4. functionalising CaFe-LDH *via* intercalating aromatic, partially or fully saturated N-containing heterocycles – studying the effects of changing the solvents on the intercalation and characterising the obtained organic-inorganic hybrid substances,
5. functionalising chloropropylated silica gel at the N- or the C-terminal,
6. comparing the catalytic activities of the L-prolinate– and DL-pipecolinate–CaFe-LDH samples with those of the L-proline-functionalised silica gel samples and (a purchased) L-prolinol-functionalised resin.

2. Experimental

Materials and synthesis methods

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

Concentrated NaOH (~20 M) stock solutions were prepared from Millipore MilliQ water and *a.r.* grade solid NaOH and their carbonate content was minimised. 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 (10 M, 5 M, 3 M, 2 M, and 1 M). CaCl₂, MgCl₂ (*puriss*), FeCl₃·6H₂O (*puriss special*) were used for the syntheses.

The Ca(Mg)Fe-LDHs were prepared by the co-precipitation method *via* dropwise addition of the two metal salt solutions with various molar ratios (M(II):Fe(III) ranging from 6 to 2) to hot (*ca.* 80 °C), vigorously stirred and N₂-blanketed NaOH solution. The precipitates formed were rapidly filtered until air dry in a CO₂-free atmosphere, 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 and filtered and the obtained crystals were kept at room temperature in a desiccator over P₂O₅.

Intercalated CaFe-LDHs

For intercalation the anions of various N-containing acids, aromatic (indole-2-carboxylate), partially (dihydroindole-2-carboxylate) or fully saturated (L-proline, DL-pipecolate) heterocycles as guests and CaFe-LDH as host with Ca(II):Fe(III) ratio of 3 were used. The carboxylate anions were intercalated into CaFe-LDH with the dehydration-rehydration method, utilising the memory effect of the layered double hydroxides. The heterocyclic compounds and the previously heat-treated LDH (773 K for 5 h) were suspended in ethanol/H₂O/NaOH or acetone/H₂O/NaOH (both with 1:5:1 volume ratios, c_{NaOH} = 3 M) solution and the suspension was stirred for a week. Upon rehydration intercalation occurred. The solid catalyst was filtered and washed with distilled water. The crystals obtained were kept at room temperature in a desiccator over P₂O₅.

Functionalised chloropropylated silica gel and polystyrene

For immobilisation N-protected or C-protected L-proline (*tert*-butoxycarbonyl-L-proline – Boc-Pro-OH, L-proline methylester – H-Pro-OMe) was used and the solid phase was chloropropylated silica gel (SG – particle size: 230–400 mesh, BET surface area: 500 m²/g, functionalisation: 8%). These materials as well as the 2-propanol solvent were of *a.r.* grade and were used without further purification.

The protected amino acids were covalently grafted onto the modified silica gel surface with esterification (N-protected proline) or N-alkylation (C-protected proline) reactions. After 24 h reflux in a basic isopropanolic suspension (KOH was used) the materials obtained were filtered washed and dried. Then, the protecting groups were removed. The ester was hydrolysed with sulphuric acid (2 h reflux), while the *tert*-butoxycarbonyl group was removed

via a 2 h reflux under vigorous stirring at moderate temperature (338 K) in a 1:1 mixture of CH_2Cl_2 and CF_3COOH (products of Reanal).

The resin-anchored L-prolinol-2-chlorotriyl ether was a commercial product. The resin in the acid-labile chlorotriyl resin was polystyrene cross-linked with 1% divinyl benzene.

Characterisation methods

Powder X-ray diffraction (XRD) patterns of the air-dried and heat-treated solid samples were registered in the $2\Theta = 3\text{--}60^\circ$ range on Rigaku Miniflex II and DRON-2 instruments, using CuK_α and FeK_α ($\lambda = 1.5418 \text{ \AA}$ and 1.9374 \AA) radiations, respectively. Reflection positions were determined *via* fitting a Gaussian function. Reflection positions were found to be reproducible within 0.05° (2Θ), therefore the uncertainty of the basal spacing was estimated as $\pm 0.01 \text{ nm}$.

The Fe(III) content of the LDH samples were determined with a Thermo's IRIS Intrepid II ICP–OES spectrometer.

^{57}Fe Mössbauer spectra of the samples were recorded with conventional Mössbauer spectrometers (Wissel and Ranger) in transmission geometry at 78 K or 295 K. A $^{57}\text{Co/Rh}$ γ -radiation source of $3 \times 10^9 \text{ Bq}$ activity was used. The spectrometers were calibrated with α -iron at room temperature. Spectrum evaluation was carried out using the MOSSWIN code.

The X-ray absorption spectra (XAS) were measured at beamline I511-3 at the MaxLab facility, Lund, Sweden. The station is based on a superconductive undulator radiation source connected to the 1.5 GeV MAX II storage ring. X-ray radiation in the 50–1500 eV energy range can be obtained from this system.

Thermal analytical measurements (TG/DTG) were performed using a Setaram Labsys derivatograph working under N_2 flow at $2^\circ\text{C}/\text{min}$ heating rate.

The morphology, approximate composition and the elemental map of the samples were examined with scanning electron microscope (SEM – Hitachi S-4700 microscope with varying acceleration voltage) coupled to a Röntec QX2 energy dispersive X-ray fluorescence spectrometer (EDX).

The layer thickness of the Ca_3Fe -LDH sample was estimated from the transmission electron microscopic (TEM) dark-field image taken by a FEI TECNAI G^220 X-TWIN microscope at 200 kV accelerating voltage.

The quantities of the intercalated carboxylate anions were measured by UV-Vis spectres-copy.

The Fourier-transform infrared (FTIR) spectra of the pristine, the organic anion-intercalated LDH and the functionalised silica gel or resin samples were recorded on a BIORAD FTS-65A/896 spectrometer equipped with a DTGS detector. Spectral resolution was 2 cm^{-1} and 256 scans were used for each spectrum. The spectra were baseline corrected and smoothed using the WIN-IR software package.

The sizes of the various intercalated carboxylate ions were determined after performing full geometry optimisation with the PM3 semiempirical quantum chemical method included in the Hyperchem 8.0 molecular modelling package.

The pristine uncalcined LDHs were tested in the epoxidation of 2-cyclohexen-1-one using aqueous hydrogen-peroxide as oxidant under mild reaction conditions (vigorous stirring

at 298 K for 2 h) applying various solvents (methanol, ethanol, 2-methyl-2-propanol, acetone, formamide, 1,4-dioxane, cyclohexane, n-hexane). Temperature dependence (288–343 K range) and recycling properties were also examined.

The reaction was followed by gas chromatography (GC – Hewlett-Packard 5890 Series II: 50 m long HP-1 column, flame ionisation detector).

The catalytic activities of the L-prolinate– and DL-pipecolate–CaFe-LDH, the functionalised chloropropylated silica gel and functionalised resin samples were tested in the intermolecular cross-aldol dimerisation-condensation of acetone with various aldehydes (benzaldehyde – on all the solid materials, 2-nitro- and 4-nitrobenzaldehyde and 2-thiophene carbaldehyde – on the functionalised silica gel and resin samples). The reactions were run for 24 h at room temperature under vigorous stirring. Various solvents were used like double-distilled water, DMSO or the acetone reactant itself. The composition of the initial mixture was generally as follows: 4–5 cm³ of solvent, 1–1 cm³ of the reactants (if the aldehydes were liquid) or 0.15 g when they were solid and 0.3 g of catalyst. Recycling study with the L-prolinate–CaFeLDH sample was also performed.

The chemical compositions of the mixtures were determined with an YL6100GC-6000 series gas chromatograph (30 m long Cyclosil B column, mass selective and flame ionisation detectors).

3. Novel scientific results

T 1. The optimum synthesis conditions were identified both for CaFe- and MgFe-LDHs.

- 1.1 It has been found that if the LDHs are intended to be used for intercalation chemistry the syntheses should be performed under N₂ blanket. The NaOH concentration should not exceed 3 M.

T 2. Although in hydrocalumites the M(II):M(III) ratio is 2 – in all other compositions M(OH)₂ is also formed –, for CaFe-LDH this ideal compositions suffers from instability. The 3:1 composition is proved to be ideal for further works of longer duration, since it is stable in air and contains Ca(OH)₂ of only ~10 w%.

- 2.1 It has been found that on increasing Ca(II) to Fe(III) ratios from 2 to 6, the quantity of Ca(OH)₂ almost linearly increases from 0 w% to ~60 w%. At the same time stabilities of the materials increased – the ideal hydrocalumite structure (Ca(II):Fe(III) = 2) is the least stable (XRD and ⁵⁷Fe Mössbauer spectroscopy).
- 2.2 ⁵⁷Fe Mössbauer measurements revealed that Fe(III) was in a high-spin, somewhat disordered octahedral environment in both CaFe- and MgFe-LDHs at every composition.

T 3. The intercalation chemistry of Ca₃Fe-LDH could be tremendously influenced by the choice of solvent mixture used. The ethanol:H₂O:NaOH and the acetone:H₂O:NaOH solvent mixtures allowed the intercalation of N-containing aromatic, partially as well as fully saturated N-containing heterocycles in horizontal or perpendicular orientation to the layers, respectively, with preserving the layered structure in both cases.

- 3.1 The layer thickness, inevitable for assuming reasonable spatial arrangements was estimated from TEM dark-field image and was measured to be 0.19 nm, in good agreement with the 0.178 nm determined by others from high-precision XRD data.
- 3.2 The dimensions of the intercalated anions were estimated from those of the parallelepipeds used for the inclusion of the anions to be intercalated optimised by the PM3 semiempirical quantum chemical method. These dimensions gave clues for the reasonable prediction of the spatial arrangements of the anions in the interlamellar space.

T 4. The uncalcined CaFe-LDHs were found to be useful and efficient catalysts in an epoxidation reaction – they were significantly more active than the calcined derivatives.

- 4.1 The epoxidation of 2-cyclohexen-1-one over uncalcined CaFe-LDHs were performed in various solvents (formamide, n-hexane, cyclohexene, methanol, ethanol, 2-methyl-2-propanol, acetone and 1,4-dioxane) and temperatures. Formamide and 313 K were the most advantageous solvent and temperature, respectively, however, the reactions could be conducted with high activities in n-hexane, cyclohexane as well as methanol.
- 4.2 The uncalcined MgAl-hydrotalcite, MgFe-hydrotalcite and CaAl-hydrocalumite were less active than CaFe-hydrocalumite but they are still more efficient than the calcined derivatives (mixed oxides) or another oxide (like titania).

T 5. Active and selective immobilised organocatalysts could be prepared through ionically intercalating L-prolinate or DL-pipecolate in the interlamellar space of Ca₃Fe-LDH.

- 5.1 L-prolinate–CaFe-LDH displayed appreciable enantioselectivity in the cross-aldol dimerisation of acetone and benzaldehyde. The catalyst could be recycled, but the enantioselectivity was gradually lost due to the base-catalysed enolisation of the carboxylic group leading to progressive racemisation. At the same time selectivity towards condensation was found to increase gradually.
- 5.2 The DL-pipecolate–CaFe-LDH had low activity in the cross-aldol dimerisation–condensation reaction, however, its selectivity for condensation was very high. Since no chiral information was introduced into the system, racemate was formed.

T 6. It has been found experimentally that for the catalytic activities of covalently immobilised N-containing heterocycles freely available secondary nitrogens are inevitable.

- 6.1 Covalently functionalised silica gel could be prepared by immobilising N- or C-protected L-proline on chloropropylated silica gel. After deprotection L-proline anchored only at the C-terminal was active in cross-aldol dimerisation of acetone and benzaldehyde with moderate and 2-nitrobenzaldehyde with high conversion rates, and with high selectivities. Moderate enantioselectivity was achieved in the reaction with benzaldehyde.
- 6.2 The commercially available L-prolinol anchored on polystyrene resulted in dimers with moderate enantioselectivities in a similar reaction, but with a larger variety of aldehydes.

4. Practical use of the results

The results presented here is of fundamental nature. Nevertheless, layered double hydroxides and their intercalated derivatives offer many uses. In this work the catalytic properties of the uncalcined and intercalated varieties are demonstrated. Other functionalised solids like those displayed in this work can also have many applications. Once again their catalytic properties are highlighted in the dissertation.

5. Publications

5.1. Papers related to the Theses published in refereed journals

1. **Sipiczki, M.**, Srankó, D.F., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Synthesis and characterisation of alkaline earth–iron(III) double hydroxides,
Chem. Pap. **65**, 840–846 (2011).
IF: 1.096₂₀₁₁ IH: –
2. **Sipiczki, M.**, Srankó, D.F., Szöllösi, Gy., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Preparation, characterisation and some reactions of organocatalysts immobilised
between the layers of a CaFe-layered double hydroxide,
Top. Catal. **55**, 858–864 (2012).
IF: 2.624₂₀₁₁ IH: –
3. **Sipiczki, M.**, Kuzmann, E., Homonnay, Z., Megyeri, J., Sipos, P., Pálinkó, I.:
The structure and stability of CaFe layered double hydroxides with various Ca:Fe
ratios studied by Mössbauer spectroscopy, X-ray diffractometry and microscopic
analysis,
J. Mol. Struct. (in press, DOI: 10.1016/j.molstruc.2012.10.060).
IF: 1.634₂₀₁₁ IH: 1
4. **Sipiczki, M.**, Kuzmann, E., Homonnay, Z., Megyeri, J., Pálinkó, I., Sipos, P.:
Mössbauer and XRD investigations of layered double hydroxides (LDHs) with
varying Mg/Fe ratios,
Hyperfine Interactions **217**, 145–149 (2013).
IF: – IH: –
5. **Sipiczki, M.**, Ádám, A.A., Anitics, T., Csendes, Z., Peintler, G., Sipos, P., Pálinkó, I.:
The catalytic epoxidation of 2-cyclohexen-1-one over uncalcined layered double hydr-
oxides using various solvents,
Catal. Today (in preparation).
IF: 3.407₂₀₁₁ IH: –

5.2. Book chapter related to the Theses

1. **Sipiczki, M.**, Sipos, P., Pálinkó, I.:
Synthesis, characterisation and applications of genuine layered double hydroxide thin
films,
Hydroxides: Synthesis, Types and Applications (Carillo, A.C., Griego, D.A., eds.), No-
va Science Publishers, Inc., ISBN 978-1-62081-042-2, Ch. 8, pp. 221–239, 2012.

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

1. **Sipiczki, M.**, Srankó, D., Sipos, P., Pálinkó, I.:
Alkáliföldfémeket és vasat tartalmazó réteges kettős hidroxidok előállításának optimalizálása (Layered double hydroxides containing alkaline earth metals and iron – optimisation of their synthesis),
Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, ISBN 978-96-3315-020-7, pp. 176–180 (2010).
2. **Sipiczki, M.**, Mayer, A., Szöllősi, Gy., Kiss, J.T., Sipos, P., Pálinkó, I.:
Organic-inorganic hybrid functional materials – synthesis, characterization and catalytic applications,
New Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segľa, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava, 2011, pp. 496–503.
3. **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Indole-2-carboxylate- and dihydroindole-2-carboxylate-CaFe layered double hydroxide nanocomposites – synthesis, characterisation and the effect of synthesis variables,
Proc. ECCM15 (15th European Conference on Composite Materials) Venice (Italy), 2012, pp. 1–7.
4. **Sipiczki, M.**, Bugris, V., Mészáros, Sz., Török, J., Srankó, D.F., Kukovecz, Á., Kónya, Z., Halász, J., Sipos, P., Pálinkó, I.:
Layered double hydroxides – excellent functional materials that can be easily functionalised further,
Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segľa, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava (accepted manuscript).

5.4. Conference presentations related to the Theses

1. Mayer, A., **Sipiczki, M.**, Szöllősi, Gy., Kiss, J.T., Pálinkó, I.:
Synthesis, structural characterization and some applications of immobilized organocatalysts,
30th European Congress on Molecular Spectroscopy (EUCMOS XXX), Florence (Italy), 2010, PS1-96, Book of Abstracts, p. 302. (poster presentation)

2. **Sipiczki, M.**, Sipos, P., Pálinkó, I.:
Intercalating N-containing saturated heterocycles into layered double hydroxides – the effect of solvent,
Women Chemists and Innovation in the Visegrad Countries – 2010, Keszthely (Hungary), 2010, p. 23. (oral presentation)
3. Kuzmann, E., **Sipiczki, M.**, Srankó, D., Pálinkó, I., Homonnay, Z., Vértes, A., Sipos, P.:
Mössbauer investigation of layered double hydroxides comprising of Fe(III) and various alkaline earth metal ions,
7th Seeheim Workshop on the Applications of the Mössbauer Spectroscopy, Frankfurt (Germany), Book of Abstracts, 2011, P-46. (poster presentation)
4. **Sipiczki, M.**, Srankó, D., Szöllősi, Gy., Sipos, P., Pálinkó, I.:
N-containing saturated heterocycles intercalated in layered double hydroxide – easily processable immobilised organocatalysts,
Hybrid Materials 2011 – Second International Conference on Multifunctional Hybrid and Nanomaterials, Strasbourg (France), 2011, C.2.6.3. (poster presentation)
5. **Sipiczki, M.**, Srankó, D., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó I.:
Preparation, characterisation and some reactions of organocatalysts immobilised between the layers of a layered double hydroxide,
Europacat 10, Glasgow (United Kingdom), 2011, PT6. (poster presentation)
6. **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó I.:
N-tartalmú heterociklusos organokatalizátorok immobilizálása réteges kettős hidroxidokban (Immobilisation of N-containing heterocyclic organocatalysts in layered double hydroxides),
MKE 1. Nemzeti Konferencia, 2011, Sopron (Hungary), Program és előadásösszefoglalók, J-O-26, p. 35. (oral presentation)
7. **Sipiczki, M.**, Puskás, R., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Intercalation of N-containing heterocycles into CaFe–L(ayered)D(ouble)H(ydroxide) – the effect of solvent,
16th International Symposium on Intercalation Compounds (ISIC16), Seč-Ústupy (Czech Republic), 2011, Book of Abstracts, p. 234. (poster presentation)
8. **Sipiczki, M.**, Kuzmann, E., Homonnay, Z., Megyeri, J., Sipos, P., Pálinkó, I.:
The stabilities of CaFe layered double hydroxides with various Ca:Fe ratios studied by Mössbauer spectroscopy, X-ray diffractometry and thermal analysis,
XXXI European Conference on Molecular Spectroscopy (EUCMOS XXXI), Cluj (Romania), 2012, O-91, Book of Abstracts p.155. (oral presentation)

9. **Sipiczki, M.**, E. Kuzmann, E., Homonnay, Z., Megyeri, J., Pálinkó, I., Sipos, P.:
Mössbauer, X-ray and thermogravimetry investigations of layered double hydroxides (LDHs) with varying Mg/Fe ratios,
International Symposium on the Industrial Applications of the Mössbauer effect (ISIAME), Dalian (China), 2012, T1_P1-6, Book of Abstracts p. 62. (poster presentation)
10. **Sipiczki, M.**, **Ádám, A.A.**, Anitics, T., Csendes, Z., Peintler, G., Sipos, P., Pálinkó, I.:
The catalytic epoxidation of 2-cyclohexen-1-one over uncalcined layered double hydroxides using various solvents,
10th Congress on Catalysis Applied to Fine Chemicals, Turku (Finland), 2013, (accepted as poster presentation).
11. **Sipiczki, M.**, **Ádám, A.A.**, Anitics, T., Peintler, G., Sipos, P., Pálinkó, I.:
Uncalcined layered double hydroxides as excellent epoxidation catalysts,
11th European Congress on Catalysis (EUROPACAT XII), Lyon (France), 2013 (accepted as poster presentation).
12. **Sipiczki, M.**, Kukovecz, **Á.**, Kónya, Z., Sipos, P., Pálinkó, I.:
N-containing heterocyclic carboxylate–CaFe layered double hydroxide nanocomposites – synthesis, characterisation and some catalytic reactions,
17th International Zeolite Conference, 2013, Moscow (Russia), (accepted as poster presentation).
13. **Sipiczki, M.**, Bugris, V., Mészáros, Sz., Török, J., Srankó, D.F., Kukovecz, **Á.**, Kónya, Z., Halász, J., Sipos, P., Pálinkó, I.:
Layered double hydroxides – excellent functional materials that can be easily functionalised further,
XXIV. International Conference on Coordination and Bioinorganic Chemistry (XXIV ICCBIC), Smolenice (Slovak Republic), 2013 (accepted as oral presentation).

5.5. Other papers published in refereed journals

1. Szilágyi, I., Berkesi, O., **Sipiczki, M.**, Korecz, L., Rockenbauer, A., Pálinkó, I.:
Preparation, characterization and catalytic activities of immobilized enzyme mimics,
Catal. Lett. **127**, 239–247 (2009).
IF: 2.021₂₀₀₉ IH: 1
2. Srankó, D., **Sipiczki, M.**, Bajnóczi, É.G., Darányi, M., Kukovecz, **Á.**, Kónya, Z., Canton, S.E., Norén, K., Sipos, P., Pálinkó, I.:
A SEM, EDX and XAS characterization of Ba(II)Fe(III) layered double hydroxides,
J. Mol. Struct. **993**, 62–66 (2011).
IF₂₀₁₁: 1.634 IH: 2

3. Srankó, D., Muráth, Sz., **Sipiczki, M.**, Szabó, M., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
A possible nanoreactor: CaFe-L(ayered)D(ouble)H(ydroxide) with intercalated cinnamate derivatives,
Mater. Sci. Forum **730-732**, 65–70 (2013).
IF: – IH: –
4. Srankó, D.F., Canton, S., Enghdal, A., Kukovecz, Á., Kónya, Z., Muráth, Sz., **Sipiczki, M.**, Sipos, P., Pálinkó, I.:
Radiation induced topotactic [2+2] dimerisation of acrylate derivatives among the layers of a CaFe layered double hydroxide followed by IR spectroscopy,
J. Mol. Struct. (in press, DOI: 10.1016/j.molstruc.2012.09.063).
IF: 1.634₂₀₁₁ IH: –
5. Bugris, V., Haspel, H., Kukovecz, Á., Kónya, Z., **Sipiczki, M.**, Sipos, P., Pálinkó, I.:
Rehydration of dehydrated CaFe-layered double hydroxide followed by thermogravimetry, X-ray diffractometry and dielectric relaxation spectroscopy,
J. Mol. Struct. (in press, DOI: 10.1016/j.molstruc.2012.10.040).
IF: 1.634₂₀₁₁ IH: 1

5.6. Other full papers published in conference proceedings

1. Srankó, D., **Sipiczki, M.**, Szabó, M., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Cinnamát–réteges kettős hidroxid nanokompozitok készítése és szerkezeti jellemzése (Preparation and structural characterisation of cinnamate–L(ayered) D(ouble) H(ydroxide) nanocomposites),
Műszaki Kémiai Napok 2010, Konferencia Kiadvány (Conference of Chemical Engineering 2010, Conference Proceedings), ISBN 978-963-9696-8, Veszprém (Hungary), pp. 202–206 (2010).
2. Srankó, D., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Double hydroxides containing alkaline earth and iron(III) ions – synthesis, and characterisation,
New Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segl'a, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava, 2011, pp. 536–544.
3. Bugris, V., Sipiczki, M., Puskás, R., Kukovecz, Á., Kónya, Z., Sipos, P., **Pálinkó, I.**:
Polyacrylate-CaFe layered double hydroxide nanocomposites – structural characterisation by dielectric relaxation spectroscopy,
Proc. ECCM15 (15th European Conference on Composite Materials.) Venice (Italy), 2012, pp. 1–7.

4. Muráth, Sz., Srankó, D.F., **Sipiczki, M.**, Sipos, P., Pálinkó, I.:
Fahéjsavanalógok [2+2] topotaktikus ciklizációja CaFe réteges kettős hidroxid rétegei között (The [2+2] topotactic cyclisation of cinnamic acid analogues between the layers of CaFe-layered double hydroxide),
Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, ISBN 978-963-315-099-3, pp. 155–159 (2012).
5. Tóth, V., **Sipiczki, M.**, Pallagi, A., Sipos, P., Pálinkó, I.:
A szárítás módjának hatása a Ca₂Al-réteges kettős hidroxid (Ca₂Al-LDH) szerkezetére és kísérlet glukonátionokkal interkalált Ca₂Al-LDH előállítására (Effect of the drying method on the structure of Ca₂Al-layered double hydroxide and the possible intercalation of the gluconate ion),
Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, ISBN 978-963-315-099-3, pp. 221–225 (2012).
6. Muráth, Sz., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
La(III)-doping of hydrotalcites with various Mg(II)/Al(III) ratios,
Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segl'a, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava (accepted manuscript).
7. Tóth, V., **Sipiczki, M.**, Pallagi, A., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Synthesis of CaAl-Layered Double hydroxide (CaAl-LDH) of the hydrocalumite type and its interaction with gluconate ions,
Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segl'a, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava (accepted manuscript).
8. Tóth, V., Bugris, V., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Nagy, L., Sipos, P., Pálinkó, I.:
Carbon nanotube-layered double hydroxide nanocomposites,
Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segl'a, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava (accepted manuscript).
9. Ferencz, Zs., Szabados, M., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Mechanochemical synthesis of M(II)Sn(IV) layered double hydroxides,
Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Melník, M., Segl'a, P., Tatarko, M.), ISBN 978-80-227-3509-4, Press of Slovak University of Technology, Bratislava (accepted manuscript).

5.7. Other conference presentations

1. Srankó F.D., **Sipiczki, M.**, Bajnóczi, G.É., Pálinkó, I., Sipos, P.:
Alkáliföldfém- és vastartalmú réteges kettős hidroxidok előállításának lehetőségei (Synthesis possibilities of layered double hydroxides with alkaline earth metal and iron(III) ions),
Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, 2009, Szeged (Hungary), p. 11. (oral presentation)
2. Srankó, D.F., Bajnóczi, É.G., **Sipiczki, M.**, Canton, S.E., Norén, K., Haase, D., Sipos, P., Pálinkó, I.:
Synthesis and structural characterization of novel Ba(II)Fe(III) layered double hydroxides,
23rd MaxLab Annual User Meeting, 2010, Lund (Sweden). (poster presentation)
3. Srankó, D., **Sipiczki, M.**, Szabó, M., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Cinnamát-réteges kettős hidroxid nanokompozitok készítése és szerkezeti jellemzése (Preparation and structural characterisation of cinnamate-L(ayered) D(ouble) H(ydroxide) nanocomposites),
Műszaki Kémiai Napok 2010, Veszprém (Hungary), Nanotechnológia #4, (2010). (oral presentation)
4. Srankó, D., **Sipiczki, M.**, Bajnóczi, É.G., Darányi, M., Kukovecz, Á., Kónya, Z., Canton, S.E., Norén, K., Sipos, P., Pálinkó, I.:
A SEM, EDX and XAS characterization of Ba(II)Fe(III) layered double hydroxides,
30th European Congress on Molecular Spectroscopy (EUCMOS XXX), Florence (Italy), 2010, OR-1-B-C-1, Book of Abstracts, p. 154. (oral presentation)
5. Srankó, D.F., **Sipiczki, M.**, Canton S.E., Norén, K., Sipos, P., Pálinkó, I.:
Preparation and characterisation of cinnamate-L(ayered)D(ouble)H(ydroxide) nanocomposites,
Annual Meeting and Nanosafety Symposium, AF-Borgen, Lund (Sweden), 2010. (poster presentation)
6. Srankó, D., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Double hydroxides containing alkaline earth and iron(III) ions – synthesis, and characterisation,
XXIII International Conference on Coordination and Bioinorganic Chemistry (XXIII ICCBIC) – Book of Abstracts, Smolenice, Slovak Republic, 2011, p. 140. (oral presentation)

7. Srankó, D., Muráth, Sz., **Sipiczki, M.**, Szabó, M., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
A possible nanoreactor: CaFe–L(ayered)D(ouble)H(ydroxide) with intercalated cinnamate derivatives,
VI International Materials Symposium MATERIAIS 2011, Guimarães (Portugal), 2011, Book of Abstracts. p. 169. (oral presentation)

8. Muráth, Sz., Srankó, D.F., **Sipiczki, M.**, Sipos, P., Pálinkó, I.:
Fahéjsavanalógok [2+2] topotaktikus ciklizációja CaFe réteges kettős hidroxid rétegei között (The [2+2] topotactic cyclisation of cinnamic acid analogues between the layers of CaFe-layered double hydroxide),
Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, 2012, p. 155. (oral presentation)

9. Tóth, V., **Sipiczki, M.**, Pallagi, A., Sipos, P., Pálinkó, I.:
A szárítás módjának hatása a Ca₂Al-réteges kettős hidroxid (Ca₂Al-LDH) szerkezetére és kísérlet glükonátionokkal interkalált Ca₂Al-LDH előállítására (Effect of the drying method on the structure of Ca₂Al-layered double hydroxide and the possible intercalation of the gluconate ion),
Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, 2012, p. 221. (oral presentation)

10. Bugris, V., Haspel, H., Kukovecz, Á., Kónya, Z., **Sipiczki, M.**, Sipos, P., Pálinkó, I.:
Rehydration of dehydrated CaFe-layered double hydroxide followed by thermogravimetry, X-ray diffractometry and dielectric relaxation spectroscopy,
XXXI European Conference on Molecular Spectroscopy (EUCMOS XXXI), Cluj (Romania), 2012, O-03, Book of Abstracts p.67. (oral presentation)

11. Bugris, V., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Polyacrylate–CaFe layered double hydroxide nanocomposites – structural characterisation by dielectric relaxation spectroscopy,
15th European Conference on Composite Materials (ECCM 15), Venice (Italy), 2012, Tue_P319. (poster presentation)

12. Csendes, Z., **Sipiczki, M.**, Varga, G., Bagi, L., Nagy, N.V., Peintler, G., Sipos, P., Pálinkó, I.:
Application of Mn(II)–protected amino acid complexes covalently immobilised on chloropropylated silica gel in redox transformations,
10th Congress on Catalysis Applied to Fine Chemicals, Turku (Finland), 2013, (poster presentation)

13. Muráth, Sz., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
La(III)-doping of hydrotalcites with various Mg(II)/Al(III) ratios,
XXIV. International Conference on Coordination and Bioinorganic Chemistry, Smolenice (Slovak Republic), 2013, submitted.

14. Tóth, V., **Sipiczki, M.**, Pallagi, A., Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Synthesis of CaAl-Layered Double hydroxide (CaAl-LDH) of the hydrocalumite type
and its interaction with gluconate ions,
XXIV. International Conference on Coordination and Bioinorganic Chemistry, Smolenice (Slovak Republic), 2013, submitted.

15. Tóth, V., Bugris, V., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Nagy, L., Sipos, P., Pálinkó, I.:
Carbon nanotube-layered double hydroxide nanocomposites,
XXIV. International Conference on Coordination and Bioinorganic Chemistry, Smolenice (Slovak Republic), 2013 (accepted as oral presentation).

16. Ferencz, Zs., Szabados, M., **Sipiczki, M.**, Kukovecz, Á., Kónya, Z., Sipos, P., Pálinkó, I.:
Mechanochemical synthesis of M(II)Sn(IV) layered double hydroxides,
XXIV. International Conference on Coordination and Bioinorganic Chemistry, Smolenice (Slovak Republic), 2013 (accepted as oral presentation).

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