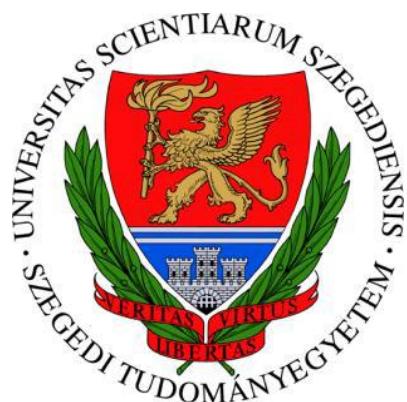


Dehydration-rehydration induced structural changes in pristine and composite layered double hydroxides

PhD Thesis
VALÉRIA BUGRIS



Supervisors: Dr. Ákos Kukovecz
Dr. István Pálunkó

Doctoral School of Chemistry
Department of Applied and Environmental Chemistry
Department of Organic Chemistry
Faculty of Science and Informatics | University of Szeged

2014
Szeged

1. Introduction

Layered double hydroxides (LDHs) are also called anionic clays, and comprise a class of materials built up from positively charged layers (mainly) of bivalent- and trivalent metal hydroxides and negatively charged ions in-between. Many of their representatives are of natural origin; however, for practical uses, they are usually synthesised. Several feasible synthesis methods are available that yield – with some effort – phase-pure materials. LDHs have structures with high regularity; however, the charge-compensating anions between the layers can easily be altered by a large variety of methods. Thus, LDHs are flexible substances, they can be modified and functionalised easily; therefore, they have many uses. They may serve as catalysts or catalyst supports, nanoreactors providing confined space for reactants to get suitably close to each other, transporters of sensitive synthons to the place of the synthesis, containers of medicines, pesticides, fungicides providing their slow release, to mention just a few.

One of the most intriguing properties of an LDH is the so-called "memory effect". On heat treatment the layered structure collapses; however, if it is not too severe – usually below 773 K; however, the accurate temperature depends largely on the specific LDH –, the structure can be recovered in aqueous solution or even in humid air. While the dehydration procedure is well studied, information on rehydration is rather limited. Therefore, *one of the major goals of the work leading to this dissertation is describing the rehydration process of heat-treated LDH comprising of Ca(II) and Fe(III) (CaFe-LDH in the followings) with a variety of instrumental methods, and gathering as much information about it as possible.*

Introducing anion between the layers is called intercalation. A major method of this is the dehydration-rehydration procedure, in which the dehydrated LDH and the anionic form of the material to be intercalated are rehydrated together. During structural reconstruction, the anionic guest enters the interlamellar space. Although the method is fairly general, it does not always work. Thus, *the other two goals are (i) the synthesis of the multiwall carbon nanotube (MWCNT)–CaFe-LDH nanocomposite, preferably with the dehydration-rehydration method; however, if it does not work, then finding a procedure that is operational; and (ii) the synthesis and thorough characterisation of a polyacrylate–CaFe-LDH.* This latter nanocomposite (the polyacrylate is the guest and the LDH is the host) is unusual insofar as works discussing LDHs embedded in the polymer are more frequently encountered in the literature.

2. Experimental

2.1. Materials and synthesis methods

2.1.1. CaFe-LDH

For the synthesis of the CaFe-LDH the co-precipitation method was used. The aqueous solution of 3:1 or 2:1 molar ratio from a mixture of CaCl_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was transformed to double hydroxide with carbonate-free 3 M aqueous NaOH *via* slowly raising the pH of the solution to 13 under N_2 protecting gas. Under these conditions, the materials precipitated with layered structure.

2.1.2. Dehydration-rehydration method

The as-prepared air-dry LDH was heat treated in N_2 atmosphere at 773 K for 5 hours. After this, portions of the obtained dehydrated materials were kept under preset and controlled relative humidity (RH%) atmosphere for two weeks. The RH% values were set with the help of the following saturated aqueous salt solutions:

Relative humidity	Compound used
6%	Lithium bromide ($\text{LiBr} \cdot 2\text{H}_2\text{O}$)
9%	Potassium hydroxide (KOH)
11%	Lithium chloride ($\text{LiCl} \cdot \text{H}_2\text{O}$)
22%	Sodium acetate (CH_3COONa)
29%	Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$)
33%	Magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)
38%	Sodium iodide ($\text{NaI} \cdot 2\text{H}_2\text{O}$)
43%	Potassium carbonate (K_2CO_3)
53%	Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
62%	Ammonium nitrate (NH_4NO_3)
75%	Sodium chloride (NaCl)
84%	Potassium chloride (KCl)
97%	Potassium sulfate (K_2SO_4)

2.2.3. Synthesis methods of carbon nanotube-layered double hydroxide nanocomposites

It has been revealed very quickly that with dehydration-rehydration method could not produce carbon nanotube-layered double hydroxide.

The basic method of sample preparation was co-precipitation of Ca(II) and Fe(III) salts. Several modifications of the co-precipitation method were tested:

Method A: pristine or acid-treated MWCNT plus solution of Ca(II) and Fe(III) salts with or without the Na salt of dodecyl benzene sulfonate (DBS); precipitation with NaOH; stirring at 80 °C for one week.

Method B: pristine or acid-treated MWCNT with or without DBS dispersed in NaOH; then, addition of the Ca(II)- and Fe(III)-containing solution dropwise; stirring at 298 K for one week.

Method C: dispersing acid-treated MWCNT in NaOH by sonication; then, addition of the solution containing the salt mixture in one portion; stirring (sonication, then mechanical) at 25 °C for one week.

All samples were vacuum-filtered on Versapor-129 membrane and were kept in desiccator over P₂O₅.

Acid treatment (cc. H₂SO₄ and fuming HNO₃) of MWCNTs was applied for oxidatively generating sidewall defects containing hydroxyl and/or carboxylic groups.

For the layer-by-layer (LbL) deposition experiments, delamination of LDH intercalated with DBS was performed either using DMF (suspension D) or hexamethylenetetramine (suspension E). The LbL deposition was carried out on quartz slides for microscopy using the following sequence: (1) dipping the slide into suspension D or E, (2) rinsing it with distilled water, (3) dipping it into the suspension of pristine carbon nanotubes; then, (4) rinsing it with distilled water. The sequence was repeated five more times.

2.2.4. Intercalated CaFe-LDHs

The polyacrylate anions were intercalated into CaFe-LDH with the dehydration-rehydration method, utilising the "memory effect" of the layered double hydroxides.

CaFe-LDH was prepared by the co-precipitation method as described earlier. The host materials were calcined at 773 K for 5 hours in N₂ atmosphere before attempting intercalation. The polyacrylate solution was suspended in aqueous ethanol and was stirred for a week. The calcined layered double hydroxide was added to this solution, and the mixture was stirred again for a week at 353 K under N₂ atmosphere. Upon rehydration, intercalation occurred. The solid material was filtered and washed with distilled water. The crystals obtained were kept at room temperature in a desiccator over P₂O₅.

2.2.5. Characterisation methods

The fundamental method for studying LDHs is powder X-ray diffractometry (XRD). The diffractograms were taken in the $2\Theta = 3\text{--}60^\circ$ range on Rigaku Miniflex II instruments, using CuK α ($\lambda = 1.5418 \text{ \AA}$) radiation in Bragg-Brentano geometry. Reflection positions were determined *via* fitting a Gaussian function.

The *in situ* XRD measurements were carried out at MAX-lab, at beamline I711. I711 is a crystallography beamline used for single crystal and powder diffraction. It utilises a 13-period, 1.8 T, multipole-wiggler designed to operate in the 0.85 (14.6 keV) to 1.55 Å (8.0 keV) region. The dehydrated (200 °C, 2 h) LDH samples (CaFe-LDH or MgAl-LDH) were placed in a quartz capillary (inner diameter: 1 mm), loosely plugged with cotton at both sides. Aqueous ethanol (1:9 volume ratio) was bubbled through it, applying N₂ as carrier with a flow rate of 10 cm³/min at 298 K. Diffractograms were collected at the middle of the sample.

In order to learn about the thermal behaviour of the materials, the thermogravimetric curves and their derivatives were registered using a Setaram Labsys derivatograph. TG-DTG curves were recorded in N₂ atmosphere at 4 °C/min heating rate.

The Fe³⁺-content of the pristine LDH was determined by a Thermo's IRIS Intrepid II ICP-OES spectrometer, and was found to be 6.859×10^{-4} mol/g.

The morphologies of the pristine LDH and the intercalated composite were studied by a Hitachi S-4700 scanning electron microscope (18 kV acceleration voltages) at various

magnifications. The elemental maps of the substances were determined using a Röntec QX2 energy dispersive X-ray fluorescence spectrometer (equipped with Be window) coupled to the microscope.

The layered structures of the pristine and intercalated materials were studied by transmission electron microscopy (TEM – FEI TECNAI G²20 X-TWIN, 200kV accelerating voltage). Layer thickness and interlayer distance could be estimated from the dark-field image.

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

The Fourier-transform infrared (FT-IR) spectra of the pristine and the organic anion-intercalated LDH samples were recorded in diffuse reflectance geometry on a BIORAD FTS-65A/896 spectrometer equipped with a DTGS detector. Spectral resolution was 4 cm⁻¹ and 256 scans were collected for a spectrum. The spectra were baseline corrected and smoothed using the WIN-IR software package.

The dielectric properties of materials were characterised by dielectric relaxation spectroscopy (DRS) measurements performed on a Novocontrol Alpha-A FRA instrument in the 5×10^{-3} – 10^7 frequency range. Data were collected with the WinDETA software, while for data processing OriginPro 8.1 was applied.

3. Novel scientific results

T1. ^{57}Fe Mössbauer spectroscopy was used for studying the structure of the transformed phase left behind after heat treatments of CaFe-LDH at various temperatures. Structural information obtained with this method – together with X-ray diffractometry on these residues and complemented with literature information – allowed us to deduce novel structural information about these phases. It has been revealed that the LDH to brownmillerite transformation occurred upon heat treatment and even the fine details of further transformations of this phase could be identified.

T2. For the first time, the steps of the rehydration procedure of heat-treated CaFe-LDH – which has lost its layered structure due to heat treatment – were identified and monitored by numerous instrumental methods (static and time-dependent X-ray diffractometry, thermogravimetry, dielectric relaxation, FT-IR and ^{57}Fe Mössbauer spectroscopies). Three rehydration steps were identified. These steps were found to be sequential, although overlaps could be observed: first, the dehydroxylated layers started to rehydroxylate; however, in an overlapping process, the reappearance of interlayer water also began; finally, physisorbed water molecules could also be identified before the full reconstruction of the interlamellar space was finished.

T3. Dielectric relaxation spectroscopy was found to be essential in identifying the positions of water molecules in the rehydration procedure. Its full potential could be exploited by applying the following approach. The partially rehydrated sample was first flash-cooled to low temperature, then allowed to warm up to ambient temperature while registering the spectra at regular time intervals. This way, water molecules that slipped out of our measurement window at room temperature could be observed as well, *i.e.* the samples were measurable after rehydration in a larger relative humidity range. The ability of measuring temperature dependence allowed the determination of the activation energies of the steps of the rehydration procedure.

T4. It has been found by synchrotron-based time-dependent X-ray diffractometry that the rehydration mechanisms of CaFe-LDH and MgAl-LDH – dehydrated under mild conditions (473 K, 2 hours) – differ significantly. Recovering the original layered structure was found to be a one-step abrupt process for CaFe-LDH, while it occurred in a continuous fashion for the MgAl-LDH.

T5 Preparation of hierarchical MWCNT–CaFe-LDH nanostructures was attempted. It was found that MWCNT provides good surface for LDH deposition when an auxiliary tenside and/or oxidatively treated MWCNTs are used. The layer-by-layer technique was suitable for building a sandwich-like structure by stratifying delaminated LDH and MWCNT in the presence of a tenside.

T6. Polyacrylate–CaFe-LDH nanocomposite could be prepared by dehydration-rehydration method as confirmed by a range of instrumental methods (XRD, the combination of SEM and SEM–EDX and IR spectroscopy). On the basis of dielectric relaxation spectroscopic measurements on the flash-cooled and gradually warmed-up samples, a novel structural model could be suggested as follows: large portions of the polymer ions were among the layers (the polymer largely lost its mobility observed without the LDH), but some mobility was retained, indicating that parts of the polymer is on the outer surface, wrapping the LDH from the outside as well.

4. Practical use of the results

Layered double hydroxides and their intercalated derivatives offer many uses. The results described and discussed in the dissertation contribute to a deeper understanding of the fine structural details of LDHs, and help in devising functional nanocomposites, which may have diverse uses.

5. Publications

5.1. Papers related to the Theses published in refereed journals

1. **V. Bugris**, H. Haspel, Á. Kukovecz, Z. Kónya, M. Sipiczki, P. Sipos, I. Pálinkó:
Rehydration of dehydrated CaFe-L(ayered)D(ouble)H(ydroxide) followed by thermogravimetry, X-ray diffractometry and dielectric relaxation spectroscopy,
J. Mol. Struct. **1044**, 26–31 (2013).
Impact factor (IF): 1.599
2. **V. Bugris**, H. Haspel, Á. Kukovecz, Z. Kónya, M. Sipiczki, P. Sipos, I. Pálinkó:
Water types and their relaxation behavior in partially rehydrated CaFe-mixed binary oxide obtained from CaFe-layered double hydroxide in the 155–298 K temperature range,
Langmuir **29**, 13315–13321 (2013).
IF: 4.384
3. V. Tóth, M. Sipiczki, **V. Bugris**, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó:
Carbon nanotube–layered double hydroxide nanocomposites,
Chem. Pap. **68**, 650–655 (2014).
IF: 1.193
4. **V. Bugris**, M. Ádok-Sipiczki, T. Anitics, E. Kuzmann, Z. Homonnay, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó:
Thermal decomposition and reconstruction of CaFe-layered double hydroxide studied by X-ray diffractometry and ^{57}Fe Mössbauer spectroscopy,
J. Mol. Struct. (in press, DOI: 10.1016/j.molstruc.2014.10.039).
IF: 1.599
5. M. Sipiczki, **V. Bugris**, Sz. Mészáros, D.F. Srankó, Zs. Ferencz, M. Szabados, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó,:
Réteges kettős hidroxidok – különleges, könnyen funkcionálható összetett anyagok (Layered double hydroxides – special, easily functionalised materials),
Magy. Kém. Foly. **120**, 106–115 (2014).

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

1. **V. Bugris**, H. Haspel, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó:
Egy dielektrikus relaxációs spektroszkópiai mérőrendszer összeállítása és alkalmazása egy réteges kettős hidroxid rehidratációs folyamatainak tanulmányozására (Assembling a dielectric relaxation spectroscopy measuring system and its application for studying the rehydration processes of layered double hydroxide),
Kémiai Előadói Napok (Chemistry Lectures), Program és előadásösszefoglalók, ISBN 978-96-331-5062-7, 2011, pp. 201–205.

2. **V. Bugris**, R. Puskás , M. Sipiczki , Á Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó :
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.
3. V. Tóth, M. Sipiczki, **V. Bugris**, Á. Kukovecz, Z. Kónya, Nagy, L., P. Sipos, I. Pálinkó:
Carbon nanotube–layered double hydroxide nanocomposites,
Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (M. Melník, P. Segľa, M. Tatarko), ISBN 978-80-227-3918-4, Press of Slovak University of Technology, Bratislava, 2013, pp. 6–13.
4. D.F. Srankó, Á.G. Tasi, **V. Bugris**, D. Haase, S.E. Canton, P. Sipos, I. Pálinkó:
In situ XRD study of the rehydration–reconstruction–intercalation kinetics and mechanism of layered double hydroxides containing various di- and trivalent metals,
MAX-LAB Activity Report 2012 (U. Johansson, A. Nyberg, R. Nyholm, eds.), 2013, I711_1.
5. M. Sipiczki, **V. Bugris**, Sz. Mészáros, J. Török, D.F. Srankó, Á. Kukovecz, Z. Kónya, J. Halász, P. Sipos, I. Pálinkó,:
Layered double hydroxides – excellent functional materials that can be easily functionalised further,
Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (M. Melník, P. Segľa, M. Tatarko), ISBN 978-80-227-3918-4, Press of Slovak University of Technology, Bratislava, 2013, pp. 324–342.

5.3. Other papers published in refereed journals

1. Z. Csendes, **V. Bugris**, L. Lackó, I. Labádi, J.T. Kiss, I. Pálinkó:
Superoxide dismutase mimicking Cu(II)–mixed amino acid complexes covalently grafted onto silica gel – an FT-IR study,
Anal. Bioanal. Chem. **397**, 549–555 (2010).
IF: 3.841
2. Z. Csendes, I. Lajter, **V. Bugris**, J.T. Kiss, I. Pálinkó:
Structural characterisation of silica gel anchored, biomimetic, mixed ligand Co(II)–amino acid complexes,
Vibr. Spectr. **53**, 132–135 (2010).
IF: 2.083

3. H. Haspel, N. Laufer, **V. Bugris**, R. Ambrus, P. Szabó-Révész, Á. Kukovecz:
Water-induced charge transport processes in titanate nanowires: An electrodynamic
and calorimetric investigation,
J. Phys. Chem. C **116**, 18999–19009 (2012).
IF: 4.814
 4. H. Henrik, **V. Bugris**, Á. Kukovecz:
Water sorption induced dielectric changes in titanate nanowires,
J. Phys. Chem. C **117**, 16686–16697 (2013).
IF: 4.835
 5. H. Haspel, **V. Bugris**, Á. Kukovecz:
Water-induced changes in the charge-transport dynamics of titanate nanowires,
Langmuir **30**, 1977–1984 (2014).
IF: 4.384

5.4. Other full paper published in conference proceeding

1. Z. Csendes, **V. Bugris**, P. Sebők, Zs. Major, J.T. Kiss, I. Pálinkó:
Covalently immobilized, silica gel or resin-supported C-protected cysteine or cystine
Fe and Ni complexes – synthesis and structural characterization with FT-IR spectroscopy,
Insights into Coordination, Bioinorganic and Applied Inorganic Chemistry, (M.
Melník, P. Segl'a, M. Tatarko,), ISBN 978-80-227-3085-3, Press of Slovak University
of Technology, Bratislava, 2009, pp. 54–61.

Journal papers

related to the Theses: 5

others: 5

Cumulative impact factors

related to the Theses: 8,775

others: 19.957