SYNTHESIS, MODIFICATION AND DELAMINATION OF LAYERED DOUBLE HYDROXIDES IN THE PRESENCE OF ORGANIC MOLECULES

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PhD Theses

Supervisors: **Professor István Pálinkó**
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1. Introduction and main goals

The majority of industrial chemical processes are catalytic, therefore development of efficient catalysts is an important task for modern science. Layered double hydroxides (LDHs) are easy to modify, and possess various catalytic applicabilities. Many ways are introduced to synthetize them, and they are still an interest to researchers since decades.

Our aim was to develop an economical route to produce LDHs with high purity and good crystallinity. Besides, we investigated the delamination and restacking of LDHs in a range of solvents in order to carry out a variable anion exchange method. Finally, coenzyme NAD intercalated in Ca_2Al–LDH and the catalytic properties of this composite were tested in a redox reaction.

The inspected materials were: Mg_2Al–LDH, Ca_2Al–LDH, Ca_2Ga–LDH. The motivations of our work were that (i) the anions sitting in the interlamellar gallery are often hard the exchange keeping the structure of the LDH intact and (ii) the synthesis of pure LDHs with highly regular morphology is time- and energy-consuming.

2. Experimental part

We performed the syntheses of LDHs by the common, well-known co-precipitation method, but in the presence of long-chained alcohols to examine their effects on particle morphology. We also optimized a novel sol-gel method, where metal alkoxides were hydrolysed in aqueous solutions without organic solvents. The effects of dissolved sodium nitrate, sodium hydroxide and ageing were also investigated.

Delamination experiments were carried out using five alcohols and five amides. The degree of exfoliation was estimated by measuring the particle size. The restoration of the original structure, i.e. restacking of the delaminated layers were also attempted applying various treatments.

The NAD-containing Ca_2Al–LDH catalyst was prepared after the intercalation of its building block, nicotinate ion. Later, its activity in the

transformation of hydroquinone to *p*-benzoquinone with H_2O_2 was tested at room temperature, in water.

The following instruments were applied for analysis: powder X-ray diffractometry (XRD, structural characteristics), infrared spectroscopy (IR, investigation of intercalated anions), scanning electron microscopy (SEM, morphology), energy-dispersive X-ray analysis (EDS, elemental composition), dynamic light scattering (DLS, average size of solvated particles), UV-visible spectrophotometry (UV-Vis, inspection of redox reaction). The approximate size of intercalated organic anions was determined by molecular modelling.

3. Novel scientific results

T1. We pointed out that not only low molecular weight organic solvents, but alcohols with six to eight carbon atoms present during co-precipitation assist the crystallization of layered double hydroxides.

Samples obtained at room temperature have more regular morphology; however, particle diameter increases to 5-20 μm with no difference in their thickness after ageing at 60 °C. Due to the minor incorporation of alcohols, the majority of LDHs are less hydrated and possess smaller basal spacing.

T2. Layer double hydroxides agitated in 1-butanol undergo structural changes. IR spectra attest the presence of 1-butanol in Ca_2Al-LDH after stirring, but Ca_2Ga-LDH partially decomposes to metal hydroxides, while a probably tetragonal, anhydrous material with yet undescribed composition is acquired from Mg_2Al–LDH.

T3. An optimized, green sol-gel type reaction was developed to produce Ca_2Al- and Mg_2Al-LDH. Their crystals are highly symmetrical and for Ca_2Al–LDH, they also have well-developed, highly regular crystals of exceptional size.

Starting from metal alkoxides we engineered a sol-gel method without using organic solvents. For hydrolysis, water and (mixed) aqueous solution of $NaNO_3$ and NaOH were used. To obtain Ca-containing LDH, $NaNO_3$ was needed [while Ca_2Al–NO_3^--LDH was formed], otherwise Ca_2Al–CO_3^{2-}-LDH

and katoite were present at the end of the synthesis. The formation $Mg_2Al–OH^–$-LDH was hindered by $NaNO_3$, nevertheless, pure product was obtained *via* applying water and NaOH solution. The crystals of both LDHs are symmetrical. Suggested by XRD patterns, their aspect ratio surpass those of the co-precipitated ones. In addition, $Ca_2Al–NO_3^–$-LDH crystallized in micrometre scale particles.

T4. We exfoliated Ca_2Al-, Mg_2Al- and Mg_2Al–DBS-LDH (DBS: dodecylbenzenesulfonate) in alcohols and amides. It was found that Mg_2Al-LDH was easier to delaminate using ultrasonic irradiation than Ca_2Al-LDH both in alcohols and amides. The polarity of amides favours the delamination and the formation of stable colloids. Layer separation is more profound for Mg_2Al-LDH on increasing the chain length of the alcohol, but this is not the case for Ca_2Al–LDH.

On the basis of DLS results, the reason may be attributed to the different layer thickness of the samples. The intercalation of the surfactant DBS anion leads to a differing lamellar charge density, thus in alcohols, the LDH is exfoliated to maximum extent without ultrasonic treatment. In amides, larger colloid stability was observed in less polar medium compared to the inorganic Mg_2Al-LDH.

T5. The layers of Mg_2Al-LDH delaminated in 1-octanol or formamide were attempted to restack in solutions of nine sodium salts. It was found that restacking was only successful in the presences of $Cl^–$ ions (delamination occurred in 1-octanol or formamide), $SO_4^{2–}$ ions (delamination occurred in formamide), $PO_4^{3–}$ or $[Co(NO_2)_6]^{3–}$ ions (delamination occurred in 1-octanol). Other anions led to partial or unsuccessful structure restoration.

The salts used for restacking were: NaCl, CH_3COONa, Na-gluconate, Na_2SO_4, Na_2CO_3, $Na_2Cr_2O_7$, Na_3-citrate, Na_3PO_4, $Na_3[Co(NO_2)_6]$. The LDH structure delaminated in formamide could not be rebuilt in the presence of $Na_3[Co(NO_2)_6]$ and by-product was formed after hydration in the presence of $Na_2Cr_2O_7$ and Na_3PO_4. Restacking was not successful in the presence of

gluconate, and by-products were obtained in the presence of CH_3COONa, Na_2SO_4, $Na_2Cr_2O_7$ and Na_3-citrate.

T6. Anionic co-enzyme-modified Ca_2Al–NAD-LDH was synthetized by direct anion exchange and the dehydration-rehydration method, which performed as catalyst of high conversion in the oxidation reaction of hydroquinone to *p*-benzoquinone.

Without catalyst and $Ca_2Al–Cl^-$-LDH as catalyst, minimal conversion was detected and using NaNAD only granted a small percentage of transformation. Meanwhile, more than 90% conversion was achieved by immobilized NAD, due to adsorption of hydroquinone on the LDH, where NAD bound on the surface and gallery-liquid interface catalysed the reaction.

4. Applicability of the results

Although our research was of fundamental-type, the developed sol-gel technique may be useful in the synthesis of other pure LDHs if the alkoxides are available. We hope that the methods useful to obtain LDH single crystals, which are otherwise difficult to acquire.

5. List of scientific papers

5.1 Publications in refereed journals directly related to the topic of the dissertation

(1) **Szabolcs Muráth**, Csilla Dudás, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: From nicotinate-containing layered double hydroxides (LDHs) to NAD coenzyme–LDH nanocomposites – Syntheses and structural characterization by various spectroscopic methods
J. Mol. Struct. 1140 (2017) 39–45.
Impact factor$_{2017}$: 2.011 Independent citations: 0

(2) **Szabolcs Muráth**, Zoltán Somosi, Ildikó Tóth, Etelka Tombácz, Pál Sipos, István Pálinkó: Delaminating and restacking MgAl-layered double hydroxide monitored and characterized by a range of instrumental methods
J. Mol. Struct. 1140 (2017) 77–82.
Impact factor$_{2017}$: 2.011 Independent citations: 1

(3) **Szabolcs Muráth**, Zoltán Somosi, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: Novel route to synthesize CaAl- and MgAl-layered double hydroxides with highly regular morphologies
J. Sol-Gel Sci. Techn. (2018) doi: 10.1007/s10971-018-4903-8
Impact factor$_{2017}$: 1.745 Independent citations: 0

5.2 Conference participations directly related to the topic of the dissertation

(1) Csilla Dudás, **Szabolcs Muráth**, Bence Kutus, Mónika Ádok, Pál Sipos, István Pálinkó: Layered double hydroxide aided synthesis of biomimetic electron transfer catalysts
18th International Symposium on Intercalation Compounds, Strasbourg, Franciaország, 2015
(2) **Szabolcs Muráth**, Zoltán Somosi, Ildikó Tóth, Etelka Tombácz, Pál Sipos, István Pálinkó: Réteges kettős hidroxidok delaminációs és aggregációs tulajdonságai
XXXVIII. Kémiai Előadói Napok, Szeged, Magyarország, 2015
(3) **Szabolcs Muráth**, Zoltán Somosi, Ildikó Tóth, Etelka Tombácz, Pál Sipos, István Pálinkó: A comprehensive study on delamination and restacking of magnesium-aluminum layered double hydroxide
59th Scientific Conference for Students of Physics and Natural Sciences, Vilnius, Litvánia, 2016
(4) **Szabolcs Muráth**, Csilla Dudás, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: From nicotinate-containing layered double hydroxides (LDHs) to NAD coenzyme–LDH nanocomposites – syntheses and structural characterization by various spectroscopic methods
33rd European Congress on Molecular Spectroscopy, Szeged, Magyarország, 2016
(5) **Szabolcs Muráth**, Zoltán Somosi, Ildikó Tóth, Etelka Tombácz, Pál Sipos, István Pálinkó: Delaminating and restacking MgAl-Layered double hydroxide monitored and characterized by a range of instrumental methods
33rd European Congress on Molecular Spectroscopy, Szeged, Magyarország, 2016

(6) **Szabolcs Muráth**, Pál Sipos, István Pálinkó: Synthesis of layered double hydroxides in the presence of long-chained alcohols
XXVI. International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Szlovákia, 2017
(7) **Szabolcs Muráth**, Pál Sipos, István Pálinkó: A szintéziskörülmények hatása réteges kettős hidroxidok morfológiájára
2017. évi Vegyészkonferencia, Hajdúszoboszló, Magyarország, 2017

5.3 Publications in refereed journals not directly related to the topic of the dissertation

(1) Dávid Srankó, **Szabolcs Muráth**, Mónika Sipiczki, Mária Szabó, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: A possible nanoreactor: CaFe-L(ayered)D(ouble)H(ydroxide) with intercalated cinnamate derivatives
Mater. Sci. Forum 730-732 (2013) 65–70.
Impact factor$_{2013}$: 0 Independent citations: 1
(2) Dávid Ferenc Srankó, Sophie Canton, Anders Enghdahl, **Szabolcs Muráth**, Ákos Kukovecz, Zoltán Kónya, Mónika Sipiczki, Pál Sipos, István Pálinkó: 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. 1044 (2013) 279–285.
Impact factor$_{2013}$: 1.599 Independent citations: 0
(3) Gábor Varga, Ákos Kukovecz, Zoltán Kónya, László Korecz, **Szabolcs Muráth**, Zita Csendes, Gábor Peintler, Stefan Carlson, Pál Sipos, István Pálinkó: Mn(II)-amino acid complexes intercalated in CaAl-layered double hydroxide – Well-characterized, highly efficient, recyclable oxidation catalysts
J. Catal. 335 (2016) 125–134.
Impact factor$_{2016}$: 6.844 Independent citations: 13

(4) Márton Szabados, Krisztián Pásztor, Zita Csendes, **Szabolcs Muráth**, Zoltán Kónya, Ákos Kukovecz, Pál Sipos, István Pálinkó: Synthesis of high-quality, well-characterized CaAlFe-layered triple hydroxide with the combination of dry-milling and ultrasonic irradiation in aqueous solution at elevated temperature

Ultrason. Sonochem. 32 (2016) 173–180.

Impact factor$_{2016}$: 4.218 Independent citations: 5

(5) Gábor Varga, Szilveszter Ziegenheim, **Szabolcs Muráth**, Zita Csendes, Ákos Kukovecz, Zoltán Kónya, Stefan Carlson, László Korecz, Erika Varga, Péter Pusztai, Pál Sipos, István Pálinkó: Cu(II)-amino acid–CaAl-layered double hydroxide complexes, recyclable, efficient catalysts in various oxidative transformations

J. Mol. Catal. A-Chem. 423 (2016) 49–60.

Impact factor$_{2016}$: 4.211 Independent citations: 5

(6) Zita Timár, Gábor Varga, **Szabolcs Muráth**, Zoltán Kónya, Ákos Kukovecz, Viktor Havasi, Albert Oszkó, István Pálinkó, Pál Sipos: Synthesis, characterization and photocatalytic activity of crystalline Mn(II)Cr(III)-layered double hydroxide

Catal. Today 284 (2017) 195–201.

Impact factor$_{2017}$: 4.667 Independent citations: 5

(7) Gábor Varga, Zita Timár, **Szabolcs Muráth**, Zoltán Kónya, Ákos Kukovecz, Stefan Carlson, Pál Sipos, István Pálinkó: Ni-amino acid–CaAl-layered double hydroxide composites – Construction, characterization and catalytic properties in oxidative transformations

Top. Catal. 60 (2017) 1429–1438.

Impact factor$_{2017}$: 2.439 Independent citations: 1

(8) Gábor Varga, **Szabolcs Muráth**, Lilla Ujvári, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: Mn(II)-containing LDH composites – synthesis, characterization and an application in Ullmann diaryl etherification

React. Kinet. Mech. Cat. 121 (2017) 175–184.

Impact factor$_{2017}$: 1.515 Independent citations: 0

(9) Gábor Varga, **Szabolcs Muráth**, Áron Bajcsi, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: Borate-containing layered double hydroxide composites – Synthesis, characterization and application as catalysts in the Beckmann rearrangement reaction of cyclohexanone oxime
React. Kinet. Mech. Cat. 121 (2017) 241–254.

Impact factor$_{2017}$: 1.515 Independent citations: 1

(10) Gábor Varga, Zita Timár, **Szabolcs Muráth**, Zoltán Kónya, Ákos Kukovecz, Stefan Carlson, Pál Sipos, István Pálinkó: Syntheses, characterization and catalytic activities of CaAl-layered double hydroxide intercalated Fe(III)-amino acid complexes
Catal. Today 306 (2018) 42–50.

Impact factor$_{2016}$: 4.667 Independent citations: 1

(11) **Szabolcs Muráth**, Szilárd Sáringer, Zoltán Somosi, István Szilágyi: Effect of ionic compounds of different valences on the stability of titanium oxide colloids
Colloids Interfaces 2 (2018) 32

Impakt faktor: n.a. Idegen hivatkozás: 1

5.4 Conference participations not directly related to the topic of the dissertation

(1) Dávid Srankó Ferenc, **Szabolcs Muráth**, Mónika Sipiczki, Szabó Mária, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: A possible nanoreactor: CaFe–L(ayered)D(ouble)H(ydroxide) with intercalated cinnamate derivatives
VI International Materials Symposium, Guimarães, Portugal, 2011

(2) Dávid Srankó Ferenc, **Szabolcs Muráth**, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: CaFe-L(ayered)D(ouble)H(ydroxide)–acrylate nanohybrids – synthesis and structural characterisation
16th International Symposium on Intercalation Compounds, Seč-Ústupky, Czech Republic, 2011

(3) Dávid Srankó Ferenc, **Szabolcs Muráth**, Canton Sophie, Ákos Kukovecz, Kónya; Zoltán, Sipos; Pál, Pálinkó; István: Radiation induced topotactic [2+2] dimerization of acrylate derivatives among the layers of a CaFe layered double hydroxide followed by IR spectroscopy
31st European Congress on Molecular Spectroscopy, Cluj-Napoca, Romania, 2012
(4) **Szabolcs Muráth**, Dávid Srankó Ferenc, Mónika Sipiczki, Pál Sipos, István Pálinkó: Fahéjsavanalógok [2+2] topotaktikus ciklizációja CaFe réteges kettős hidroxid rétegei között
XXXV. Kémiai Előadói Napok, Szeged, Hungary, 2012
(5) **Szabolcs Muráth**, Gábor Schuszter, Ágota Tóth: Kezdő lépések a réteges kettős hidroxidok képződési mechanizmusának felderítésére
XXXVI. Kémiai Előadói Napok, Szeged, Hungary, 2013
(6) **Szabolcs Muráth**, Pál Sipos, István Pálinkó: Studying the formation mechanism of layered double hydroxides
18th International Symposium on Intercalation Compounds, Strasbourg, France, 2015
(7) Zsolt Ferencz, Márton Szabados, Csilla Hancsák-Dudás, Gábor Varga, **Szabolcs Muráth**, Mónika Ádok-Sipiczki, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: Electron microscopic techniques in the characterisation of pristine and composite layered double hydroxides
12th Multinational Congress on Microscopy, Eger, Hungary, 2015

Publications in scientific journals

In the scope of the dissertation: 3	total: 14
Cumulated impact factor	
In the scope of the dissertation: 5.767	total: 31.675
Independent citations	
In the scope of the dissertation: 1	total: 32