PhD Theses

Preparation of Layered Double Hydroxides by Ultrasonically-Enhanced Mechanochemical Technique

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Introduction and aims

In the last decades, the class of materials called Layered Double Hydroxides (LDHs) received increased attention. These substances have layered structure, most often consisting of di- and trivalent metal ions surrounded by hydroxide ions in octahedral arrangement. The layers have positive charge and to achieve charge neutrality, fully or partially hydrated anions reside between the layers. The constituents of the layers and the interlayered anions can be varied in a wide range. On heating, LDHs are transformed to mixed oxides, which can be rehydrated to reconstitute the original LDH structure, if the heat treatment was not too severe. LDHs can be found in nature, but for application they are mostly synthesized. During the years several methods were developed for the preparation and modification of LDHs. Since LDHs are versatile materials having relatively large specific surfaces and anion exchange capacity, they are often applied as catalysts, catalyst supports, adsorbents, ion exchangers or active agent transporters or stabilizers in healthcare and even as polymer additives.

In this work, the mechano-hydrothermal technique was developed further by applying ultrasonic irradiation to synthesise CaAl-, CaFe-, CaAlFe- and ZnAl-LDHs. The synthesis parameters were investigated and the introduction of several different anions (oxo, halogenides and azide) into the interlamellar space was also attempted. In the first step of the method, the starting materials were mechanical activated in a mixer mill, and then the milled powder were treated with water or aqueous solutions of the anions to be introduced under ultrasonic irradiation. This method could combine the advantageous characters of the solution-based and solid-state reactions.

Our goals were to prepare phase-pure or close to phase-pure LDHs with large and regular crystals and to study the effects of the reaction parameters on the efficiency of the syntheses and the structures of the LDHs formed. We also wanted to learn about the intercalation capability of this ultrasonically-enhanced method. For structural characterization, the major method was powder X-ray diffractometry (XRD), but other techniques like infrared and X-ray absorption spectroscopies, thermogravimetric analysis, scanning electron microscopy and energy dispersive X-ray analysis were also applied.

Experimental

Applied materials and synthesis methods

The ZnAl-, CaAl-, CaFe-, and the CaAlFe-LDHs were prepared from the suitable metal-hydroxides; however, the $Zn(OH)_2$ and the $Fe(OH)_3$ had to be synthesized.

Synthesis of ZnAl-, CaAl, CaAlFe- and CaFe-LDHs

The first step of LDH preparation was the milling of the starting reagents (under anhydrous conditions) in a mixer mill. The milled powders were transferred into glass ultracentrifuge tubes and water or aqueous anion-containing solution was added. Then, the tubes were placed in ultrasonic bath and were treated with ultrasonic irradiation. Finally, the products were washed and dried at various temperatures (between 40°C and 60 °C) in an oven.

The reaction conditions were varied systematically to achieve phase-pure or close to phase-pure samples with high crystallinities. Various factors were varied like the effect of milling time, the duration, the intensity and the impulse character of the ultrasonic irradiation, the anion concentration of the aqueous solution and the temperature of the ultrasonic bath. Depending on the specific goals of the investigations, the samples were not purified in every case; however, if they were, the calcium-containing samples were washed with distilled water to remove the generated soluble secondary products, and the ZnAl-LDHs were treated by NH_3 solution, which could dissolve selectively the remained, unreacted $Zn(OH)_2$/ZnO particles without destroying the LDH crystals. Phase-pure ZnAl-LDHs could be prepared with this method, and they were calcined in a muffle furnace at 900 °C for 1 hour in order to examine their applicability as zinc spinel precursors.

Intercalation of oxo, halogenides and azide anions into LDHs

The ZnAl-LDHs were synthesised with hydroxide and carbonate interlayered anions, but chloride-containing CaAlFe-LDHs were also prepared. Furthermore, F^-, Cl^-, Br^- and I^- anions could be intercalated into CaAl-LDH. These and perchlorate and azide anions could also be introduced in-between the layers of CaFe-LDH.

Methods of structural characterization

The powder X-ray diffraction patterns of the prepared LDHs were recorded on a Rigaku Miniflex II instrument. For the assignation of the reflections of the samples obtained, the PCPDFWIN (2.01 version) program and the JCPDS-ICDD (Joint Committee on Powder Diffraction Standards – International Centre for Diffraction Data – 1998) database were applied. The basal spacings of the LDHs were calculated from the most intense reflections using the Bragg's equation. The FWHM (full with at half maximum) values and the average crystallite sizes were determined by the Xpowder (2004.04.47 PRO version) software package.

The Fourier-transform infrared spectra of LDHs were registered on a BIORAD FTS-65 A/896 FT-IR spectrophotometer equipped with a DTGS (deuterated triglycine sulphate) detector. A spectrum was made from 256 scans, with 4 cm^{-1} resolution in the 4000–650 cm^{-1} wavenumber range.

To obtain information about the thermal behaviour of the LDHs, we used a Setaram Labsys derivatograph operating in air. The device recorded mass loss–temperature, derivative mass loss–temperature and heat flow–temperature functions.

The morphologies of the LDHs were studied with a Hitachi S-4700 scanning electron microscope. The components of the samples were analysed quantitatively and qualitatively by energy dispersive X-ray measurements (EDX).

The XAS measurements of the layered double hydroxides were performed in the MaxIV-lab synchrotron of Lund University at beamline I811. The studies were carried out on the K-edge of iron, and the data were collected in the fluorescent mode. The results were processed by the Demeter software.

Novel scientific results

T1. The mechano-hydrothermal technique was enhanced significantly by applying ultrasonic irradiation. This method allowed the preparation of well-developed crystals with increased particle size.

The ultrasonic irradiation aided the formation of LDHs in various ways. The thus prepared CaAl-LDH were formed with larger crystallite size. For ZnAl-LDH, the ultrasonic treatment increased the conversion of the starting material to the LDH relative to the mechanically-stirred or the non-stirred syntheses.

T2. We were the first to prepare close-to-phase-pure CaFe- and CaAlFe-LDHs by ultrasonic irradiation aided mechano-hydrothermal technique.

The parameters of the close-to-phase-pure CaFe-LDH preparation were as follows: 2:1 Ca^{II}:Fe^{III} molar ratio, 90 min dry milling (100 ball/sample mass ratio, 11.6 Hz grinding frequency), 12 h ultrasonic irradiation (at 60 W performance and continuous sonication), 0.1 M Na_2CO_3 or 0.4 M NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$, NaN_3 aqueous solution, 70 °C.

The parameters of the close-to-phase-pure CaAlFe-LDH preparation were as follows: 3:1:1 Ca^{II}:Al^{III}:Fe^{III} molar ratio, 60 min dry milling (100 ball/sample mass ratio, 11.6 Hz grinding frequency), 4 h ultrasonic irradiation (at 60 W performance and continuous sonication), 0.1 M Na_2CO_3 or 0.2 M NaCl aqueous solution, 75 °C.

T3. For obtaining phase-pure ZnAl-LDH, a purification method was developed capable of removing the unnecessary zinc-containing chemicals without the destruction of the LDH phase.

The 25 weight% aqueous ammonia solution was found to be the optimal for the purification. This way, it was possible to eliminate the unreacted zinc-containing starting materials in the form of zinc tetramine complex. During the washing process, 20 ml ammonia solution was added to 0.1 g of as-prepared ZnAl-LDH sample, and after sonication for 5 min, the LDH was collected and washed by distilled water.

T4. During the preparations of CaFe–Cl^-- and CaAlFe–Cl^--LDHs, we could prove that the ultrasonically-enhanced mechano-hydrothermal method did not demand CO_2-free atmosphere to avoid the intercalation of carbonate anions. It was also found that the CaFe-LDHs could also be synthesized with F^-, Br^-, I^-, NO_3^-, ClO_4^- and N_3^- interlayer anions without inert, CO_2-free atmosphere.

In the diffractograms, the success of intercalation was indicated by the shift of reflections of the LDH samples in the x-axis, and the lack of the reflections of the carbonate-containing LDHs. Infrared spectroscopy measurements attested as well that there were no significant amounts of intercalated carbonate ions in the samples. The concentrations of anions in the applied aqueous solution was the conclusive parameter to prevent the intercalation of carbonate anions.

T5. Azide anions have been built in-between the layers of CaFe-LDH for the first time by the ultrasonically-enhanced mechano-hydrotermal technique. The interaction between the azide anions and the layers were proved to be strong; the layers were able to stabilize the azid anions until 300 °C preventing their decomposition to N_2 molecules.

XRD measurements indicated the successful intercalation of the azide ions, and allowed us to place the azide ions into the well-known anion affinity sequence of intercalation. The IR spectra attested the presence of azide anion in the original as well as in the heat-treated (300 °C) samples.

Practical use of the results

We have shown that the ultrasonically-enhanced mechano-hydrothermal technique is a relatively simple (consisting of a few synthesis steps only) and efficient method to prepare LDHs. Due to ultrasonic treatment the applied temperature can be decreased compared to the traditional methods, which is important from the viewpoint energy management and environmental protection. This method combines the advantageous features of the liquid-phase and solid-state synthesis methods, therefore, it can be suitable to prepare, or to ease the synthesis of pristine LDHs and intercalated ones, which could not be generated with difficulties if at all applying only liquid-phase or solid-state techniques. For demonstration, the intercalation process of azide anions is a good example, which can generate hazardous, explosive metal azide salts in the liquid phase, while in solid state reactions, the mechanical forces cause the decomposition of azide anions before they can enter the interlayer space.

Publications, conference presentations

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Papers related to the Theses and published in refereed journals

[1] **Márton Szabados**, Rebeka Mészáros, Szabolcs Erdei, Zoltán Kónya, Ákos Kukovecz, Pál Sipos, István Pálinkó: Ultrasonically-enhanced mechanochemical synthesis of CaAl-layered double hydroxides intercalated by a variety of inorganic anions
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Impact factor: 4.556 $_{2015}$ Independent citations: 2

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Impact factor: 4.556 $_{2015}$ Independent citations: 0

[3] **Márton Szabados**, Csaba Bús, Mónika Ádok-Sipiczki, Zoltán Kónya, Ákos Kukovecz, Pál Sipos, István Pálinkó: Ultrasound-enhanced milling in the synthesis of phase-pure, highly crystalline ZnAl-layered double hydroxide of low Zn(II) content
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Impact factor: 2.280 $_{2015}$ Independent citations: 0

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[2] Mészáros Rebeka, **Szabados Márton**, Sipos Pál, Pálinkó István: Ultrahangos kevertetéssel segített újszerű szintézis CaAl réteges kettős hidroxidok előállítására, *XXXVII. Kémiai Előadói Napok,* Szeged, Hungary, 2014, pp. 46–50, ISBN 978-963-9970-53-3

[3] Bús Csaba, **Szabados Márton**, Sipos Pál, Pálinkó István: Cink-aluminát spinel újszerű előállítása, *XXXVIII. Kémiai Előadói Napok,* Szeged, Magyarország, 2015, pp. 64–68, ISBN 978-963-9970-64-9

[4] **Márton Szabados**, Zsolt Ferencz, Gábor Varga, Stefan Carlson, Pál Sipos, István Pálinkó: Comparative structural study of layered double hydroxides prepared and intercalated by commonly as well as scarcely applied methods, *Max IV Lab Activity Report. Lund: Lund University, 2016, Paper I811_808*

Conference presentations related to the Theses

[1] **Márton Szabados**, Rebeka Mészáros, Zsolt Ferencz, Pál Sipos, István Pálinkó: Ultrasound assisted technique to prepare phenolate contained layered double hydroxides, *III. Interdiszciplináris Doktorandusz Konferencia*, Poster session, Pécs, Hungary, 2014. apr. 15-17.

[2] **Márton Szabados**, Ákos Kukovecz, Zoltán Kónya, Pál Sipos, István Pálinkó: A sonochemical method to synthetize and modify layered double hydroxides, *4th International Colloids Conference*, Poster session, Madrid, Spain, 2014. jun. 15-18.

[3] **Márton Szabados**, Csaba Bús, Ádok Mónika, Pál Sipos, István Pálinkó: Combination of novel methods to prepare pristine and hierarchically-ordered ZnAl-layered double hydroxides, *12th YoungChem, International Congress of Young Chemists*, Poster session, Szczecin, Poland, 2014. oct. 8-12.

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[6] **Márton Szabados**, Diána Makk, Pál Sipos, István Pálinkó: The effect of ultrasonic treatment in a novel synthesis route of layered double hydroxides, *2015 International Congress on Ultrasonics*, Poster session, Metz, France, 2015. May 11-14.

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Journal of Solid State Chemistry, **233**, pp. 236–243 (2016).
Impact factor: 2.265 $_{2015}$ Independent citations: 1

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[1] **Márton Szabados**, András Sápi, Ákos Kukovecz, Zoltán Kónya: Self-cleaning surfaces based on titanate nanowires, *YISAC 2011 18th young investigators' seminar on analytical chemistry*, Oral presentation, Novi Sad, Serbia, 2011. June 28 - July 1.

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[3] **Márton Szabados**, Rebeka Mészáros, Zsolt Ferencz, Pál Sipos, István Pálinkó: Ultrasound assisted technique to prepare phenolate contained layered double hydroxides, *III. Interdiszciplináris Doktorandusz Konferencia*, Poster session, Pécs, Hungary, 2014. apr. 15-17.

[4] **Márton Szabados**, Rebeka Mészáros, Zsolt Ferencz, Csilla Hancsákné Dudás, Pál Sipos, István Pálinkó: Ultrasound/assisted adsorption/intercalation of phenol/phenolate on/in CaFe-layered double hydroxide, *32nd European Congress on Molecular Spectroscopy*, Poster session, Düsseldorf, Germany, 2014. aug. 24-29.

[5] **Szabados Márton**, Nagy László, Kukovecz Ákos, Kónya Zoltán, Sipos Pál, Pálinkó István: ZnCaAl réteges kettős hidroxid előállítása és alkalmazása dimetil-karbonát szintézisében, *MKE 2. Nemzeti Konferencia*, Poster session, Hajdúszoboszló, Hungary, 2015. aug. 31 - sept. 2.

Full journal papers, total: **6**	related to the topic of the Theses: **3**
Cumulative impact factor, total: **16.028**	related to the topic of the Theses: **11.392**
Independent citations, total: **9**	related to the topic of the Theses: **2**