



# **Photocatalyst and nanoreactor – two application types of layered double hydroxides**

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**PhD Theses**

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## Introduction and main goals

Nowadays, the environmental conscious production became of utmost importance in both the industrial and laboratory scale chemical syntheses. For keeping the rules of green chemistry, it has come to the fore the development of technologies or materials, which minimize or completely prevent the formation of harmful substances or by-products, or decompose or utilize the potential pollutants in various industrial processes. To achieve these aims, applying multifunctional layered materials, which act as catalysts and ion exchangers seem to be useful. Among these materials, layered double hydroxides (LDHs) may serve this goal, and I dealt with these materials in my experimental work leading to the framework of my dissertation.

LDHs are inorganic anion exchanger clay minerals. They are found in the nature, but generally they are synthesized. The layers of the LDH consists of divalent and trivalent metal ions surrounded by hydroxide ions, and the interlayer space contains exchangeable organic or inorganic anions of various types and sizes. Beside the anion exchanger property, they can be utilized as catalysts, drug carriers, polymer additives, etc. I used these materials as photocatalyst and nanoreactors. As photocatalyst with sufficient band gap value, it may be suitable to facilitate variable redox reactions to decompose various organic contaminants in water by light irradiation. When used as a nanoreactor, one or more reactants are fixed between the layers, and the confined environment allows to suppress side-reactions, thus minimizing the amount of hazardous and environmentally dangerous by-products.

## Experimental part

### *Reagents and synthesis methods*

#### *Synthesis of MnCr-LDH and application as photocatalyst*

Materials used during the synthetic work, NaOH solution and  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  salts. LDH was prepared by co-precipitation method under  $\text{N}_2$  atmosphere. In the last part of the synthesis the filtered sample was exposed to aging. The catalytic activation of MnCr-LDH was measured via the photocatalytic decomposition of methylene blue. The irradiation was performed by mercury lamp. The decomposition of methylene blue was conducted at various pH (7-10) and temperature (8-50°C).

### *Synthesis of acetate- and benzoate intercalated CaAl-LDH and their reactions with benzyl bromide*

The materials used for the synthesis of the intercalated structures and for the interlayer esterification were:  $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$  salts, benzoic acid, sodium acetate, NaOH solution, butanol, ethanol, formamide, methanol and benzyl bromide. The acetate intercalated CaAl-LDH was synthesized by the co-precipitation method using butanol-water solvent mixture. For the preparation of benzoate intercalated CaAl-LDH, the methods of co-precipitation, delamination-restacking and direct anion exchange were also applied. Solvent mixtures used were ethanol-water for co-precipitation and formamide for delamination.

During the interlayer reactions the amount of benzyl bromide (10–130  $\mu\text{l}$ ), the reaction temperature (25–100  $^\circ\text{C}$ ) and the reaction time (1–5 h) were altered.

### *Intercalation and interlayer oxidation of L-cysteinate between the layers of CaAl-LDH*

L-cysteinate was intercalated into CaAl-LDH via the co-precipitation route. A mixed solution contained  $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$  salts, NaOH solution and methanol. During the oxidation reactions the oxidant (peracetic acid,  $\text{H}_2\text{O}_2$ ) were added in various amounts (10  $\mu\text{l}$ –120  $\mu\text{l}$ ) into the methanol suspended intercalated LDH. The resulting mixture was stirred for 10-60 min at room temperature.

### *Preparation of E-, and Z-cinnamate intercalated ZnAl- and MgAl-LDH and the investigation of the light irradiation induced E-Z isomerisation*

The syntheses of E- or Z-cinnamate intercalated LDH were performed by the co-precipitation method in  $\text{N}_2$  atmosphere.

For studying the isomerization reactions, the light irradiation emitted by mercury lamp and monochromatic UV lamps emitting at 254 nm and 365 nm were used. The solid and the suspended forms of the samples were irradiated.

## Novel scientific results

**T1. We were the first to prepare MnCr-LDH by the co-precipitation method. To achieve a close-to-phase-pure LDH, aging was also required.**

The synthesis parameters of the close-to-phase-pure MnCr-LDH were as follows: solution of NaOH (3 M), 100 cm<sup>3</sup> stock solution of Mn(NO<sub>3</sub>)<sub>2</sub>×4 H<sub>2</sub>O (30 mmol) and Cr(NO<sub>3</sub>)<sub>3</sub>×9 H<sub>2</sub>O (15 mmol) salts, N<sub>2</sub> atmosphere, stirring for 24 h at room temperature, filtration, drying and finally aging at 80 °C for 24 h.

The success of the synthesis was indicated by powder X-ray diffractometry, infrared spectroscopy, SEM images and SEM-EDX elemental map.

**T2. The photocatalytic activity of MnCr-LDH has been proven. During the photodegradation of methylene blue, the photocatalytic performance was outstanding, it was nearly the same as that of Degussa P25 titanium dioxide.**

After the variation of several parameters (pH, methylene blue concentration, time, temperature) the optimal conditions of the reaction were as follows: 1 mg of MnCr-LDH, 200 cm<sup>3</sup> of methylene blue solution (30 mg/dm<sup>3</sup>, pH = 9), stirring for 60 min in dark before the irradiation, stirring for 300 min with light irradiation at room temperature.

The LDH was applied in another four cycles without the reduction of the photocatalytic activity.

**T3. It has been pointed out that the efficient photocatalytic degradation requires the presence of the layered structure, upon its decomposition the photocatalytic activity systematically decreases, and finally, it is totally lost.**

Increasing the calcination temperature for MnCr-LDH results in the gradual loss of the layered structure (250°C, 500°C) to total degradation (750°C). Concomitantly, the catalytic activity also decreased until disappearing over the collapsed structure.

**T4. Through the optimization of the reaction conditions we were the first to apply CaAl-LDH as a nanoreactor in the benzyl bromide assisted interlayer esterification reactions with acetate and benzoate ions, while bromide entered into the interlayer space replacing the intercalated organic anions.**

The optimal reaction conditions for the interlayer esterification reactions with intercalated acetate or benzoate anions: 0.1 g of acetate or benzoate intercalated CaAl-LDH, 130 µl of benzyl bromide, stirring at 100°C for 5 h.

**T5. We were the first to apply CaAl-LDH for the interlayer oxidation of L-cysteinate to L-cysteine sulfinic acid and L-cysteine sulfonate. The reaction required the presence of LDH.**

The reaction conditions were as follows: 0.1 g L-cysteinate intercalated CaAl-LDH (Cys-LDH), 60  $\mu$ l and 100  $\mu$ l peracetic acid (Cys-LDH:oxidant = 1:2, 1:4), stirring for 60 min at room temperature. Based on the X-ray diffractograms, infrared and Raman spectra, it was determined that the oxidation has started with on the use of 60  $\mu$ l of oxidant. On addition of 100  $\mu$ l peracetic acid a mixture of L-cysteine sulfinic acid and L-cysteine sulfonate were formed, while the layered structure of LDH started to deteriorate.

**T6. We successfully synthesized *E*- and, as new materials, *Z*-cinnamate intercalated MgAl- and ZnAl-LDHs, and on the basis of experimental measurements of various kinds and molecular modelling results, structural arrangements of the intercalants were proposed in the interlayer space.**

It is suggested that *Z*-cinnamate assumes bilayer arrangement among in the interlayer regions of both LDHs. Similar conclusion can be drawn for *E*-cinnamate intercalated in both LDH, with a lower expansion of the interlayer distance due to the structural difference between the two isomers.

**T7. It was found that the photoinduced interlayer isomerization could be performed with success using the *E*-cinnamate intercalated MgAl-LDH. For the rapid and selective achievement of the reaction (no photodimerization occurred), the intercalation of *E*-cinnamate was required, i.e., the layered double hydroxide functioned as a nanoreactor.**

The formation of *Z*-cinnamate was confirmed by infrared, UV-VIS and  $^{13}\text{C}$  CP solid phase MAS NMR spectroscopic measurements.

## Practical use of the results

The results presented here are of fundamental by nature. Nevertheless, the MnCr-LDH photocatalyst is thought to be suitable for industrial use, mainly in environmentally friendly technologies, thorough development work is necessary (increasing the stability and enhancing reusability, developing economical regeneration method, etc.).

## Publications

### *Papers directly related to the Theses published in refereed journals*

[1] **Z. Timár**, G. Varga, Sz. Muráth, Z. Kónya, Á. Kukovecz, V. Havasi, A. Oszkó, I. Pálinkó, P. Sipos: Synthesis, characterization and photocatalytic activity of crystalline Mn(II)Cr(III)-layered double hydroxide

*Catal. Today* **284** (2017) 195–201.

Impact factor<sub>2017</sub>: 4.667

Independent citations: 12

[2] **Z. Timár**, D. Sztankovics, G. Varga, P. Sipos, I. Pálinkó: Esterification reactions with acetate- or benzoate-containing CaAl-layered double hydroxide samples

*J. Mol. Struct.* **1186** (2019) 303–306.

Impact factor<sub>2018</sub>: 2.120

Independent citations: 2

[3] **Z. Timár**, G. Varga, M. Szabados, K. Csankó, T. Alapi, C. Forano, V. Prevot, P. Sipos, I. Pálinkó: Structural insight into the photoinduced *E*→*Z* isomerisation of cinnamate embedded in ZnAl and MgAl layered double hydroxides

*J. Mol. Struct.* in press, DOI: 10.1016/j.molstruc.2020.128561.

Impact factor<sub>2018</sub>: 2.120

Independent citations: 0

### *Papers directly related to the Theses published as full papers in conference proceedings*

[1] **Z. Timár**, M. Kocsis, G. Varga, P. Sipos, I. Pálinkó: Intercalation of CaAl-layered double hydroxide with benzoate or acetate ion

*Modern Trends in Coordination, Bioinorganic, and Applied Inorganic Chemistry, XXVI* International Conference on Coordination and Bioinorganic Chemistry, ISBN: 978-80-89597-65-9, Smolenice, Slovakia, 2017, 131–137.

[2] **Z. Timár**, Y. Gulyás, A. Gácsi, G. Varga, P. Sipos, I. Pálinkó: Intercalation and oxidation of cysteinate between the layers of Ca<sub>2</sub>Al layered double hydroxides

*Progressive Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry, XXVII* International Conference on Coordination and Bioinorganic Chemistry, ISBN: 978-80-8208-014-1, Smolenice, Slovakia, 2019, 98–103.

*Other papers published in refereed journals*

[1] Z. Csendes, G. Varga, H. Schmehl, **Z. Timár**, S. Carlson, S.E. Canton, É.G. Bajnóczi, D. Sebők, I. Dékány, G. Elek, P. Sipos, I. Pálinkó: Superoxide dismutase inspired immobilised Ni(II)-protected amino acid catalysts – synthesis, characterisation, and catalytic activity  
*J. Mol. Catal. A* **395** (2014) 93–99.

Impact factor<sub>2014</sub>: 3.615

Independent citations: 1

[2] G. Varga, **Z. Timár**, H. Schmehl, Z. Csendes, É.G. Bajnóczi, S. Carlson, P. Sipos, I. Pálinkó: Bioinspired covalently grafted Cu(II)-C-protected amino acid complexes – selective catalysts in the epoxidation of cyclohexene  
*React. Kinet. Mech. Catal.* **115** (2015) 33–43.

Impact factor<sub>2015</sub>: 1.265

Independent citations: 1

[3] G. Varga, **Z. Timár**, Z. Csendes, É.G. Bajnóczi, S. Carlson, S.E. Canton, L. Bagi, P. Sipos, I. Pálinkó: Building, characterising and catalytic activity testing of Co-C-protected amino acid complexes covalently grafted onto chloropropylated silica gel  
*J. Mol. Struct.* **1090** (2015) 138–143.

Impact factor<sub>2015</sub>: 1.780

Independent citations: 1

[4] G. Varga, **Z. Timár**, Sz. Muráth, Z. Kónya, Á. Kukovecz, S. Carlson, P. Sipos, I. 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<sub>2016</sub>: 2.486

Independent citations: 5

[5] G. Varga, **Z. Timár**, Sz. Muráth, Z. Kónya, Á. Kukovecz, S. Carlson, P. Sipos, I. 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<sub>2018</sub>: 4.888

Independent citations: 5

*Other full paper published in conference proceeding*

[1] **Z. Timár**, Z. Csendes, P. Sipos, I. Pálinkó: Cu(II)–C-védett aminosav komplexek előállítása, szerkezetvizsgálata és felhasználása a ciklohexén oxidációjában (Synthesis and structural characterisation of immobilised Cu(II)-C-protected amino acid complexes and their use in the oxidation of cyclohexene)

*XXXVI. Kémiai Előadói Napok: Program és előadás-összefoglalók*, ISBN: 978-963-3150-99-3, Szeged, Hungary, 2013, 218–222.

*Conference presentations related to the theses*

[1] **Z. Timár**, G. Varga, Sz. Muráth, Z. Kónya, Á. Kukovecz, P. Sipos, I. Pálinkó: Co(II)Cr(III)- and Mn(II)Cr(III)-layered double hydroxides – syntheses, characterization and photocatalytic activities

*17th Nordic Symposium on Catalysis*, Poster, Lund, Sweden, 2016.

[2] **Z. Timár**, M. Kocsis, G. Varga, P. Sipos, I. Pálinkó: Intercalation of CaAl-layered double hydroxide with benzoate or acetate ion

*XXVI. International Conference on Coordination and Bioinorganic Chemistry*, Oral presentation, Smolenice, Slovakia, 2017.

[3] **Z. Timár**, Y. Gulyás, A. Gácsi, P. Sipos, I. Pálinkó: Oxidation of L-cysteinate ions intercalated between the layers of CaAl-layered double hydroxide

*II. Young Researchers International Conference on Chemistry and Chemical Engineering*, Oral presentation, Budapest, Hungary, 2018.

[4] **Z. Timár**, D. Sztankovics, G. Varga, P. Sipos, I. Pálinkó: Acetate and benzoate intercalated CaAl layered double hydroxides – characterization and application as nanoreactor

*XXXIV. European Congress on Molecular Spectroscopy*, Poster, Coimbra, Portugal, 2018.

[5] **Z. Timár**, Y. Gulyás, A. Gácsi, G. Varga, P. Sipos, I. Pálinkó: Intercalation and oxidation of cysteinate between the layers of Ca<sub>2</sub>Al layered double hydroxides

*XXVII International Conference on Coordination and Bioinorganic Chemistry*, Oral presentation, Smolenice, Slovakia, 2019.

[6] **Z. Timár**, C. Forano, V. Prevot, C. Richard, P. Sipos, I. Pálinkó: Zn<sub>2</sub>Al- and Mg<sub>2</sub>Al-layered double hydroxides as nanoreactors in the photoinduced interlayer isomerization of E-cinnamate  
*International Conference on Clay Science and Technology*, Oral presentation, Paris, France, 2019.

*Other conference presentations*

[1] **Z. Timár**, Z. Csentes, P. Sipos, I. Pálinkó: Cu(II)–C-védett aminosav komplexek előállítás, szerkezetvizsgálata és felhasználása a ciklohexén oxidációjában.

XXXVI. *Kémiai Előadói Napok*, Oral presentation, Szeged, Hungary, 2013.

[2] Z. Csentes, H. Schmehl, **Z. Timár**, S. Carlson, S.E. Canton, É.G. Bajnóczi, G. Varga, D. Sebők, I. Dékány, P. Sipos, I. Pálinkó: Immobilised Ni(II)–protected amino acid catalysts – synthesis, characterisation and catalytic activity

*4th Georgian Bay International Conference on Bioinorganic Chemistry*, Poster, Ontario, Canada, 2013.

[3] **Z. Timár**, G. Varga, Z. Csentes, P. Sipos, I. Pálinkó: Syntheses, Characterization and an application of redox-active composite catalysts

*18th International Symposium on Intercalation Compounds*, Poster, Strasbourg, France, 2015.

[4] **Z. Timár Z.**, Y. Gulyás, V. Havasi, I. Pálinkó, P. Sipos: Ca<sub>2</sub>Al réteges kettős hidroxid nanoreaktorként történő felhasználása levulinsavval történő oxidációs reakcióban

*XLI. Kémiai Előadói Napok*, Oral presentation, Szeged, Hungary, 2018.

Full journal papers: 8

related to the topic of the Theses: 3

Cumulative impact factor: 22.941

related to the topic of the Theses: 8.907

Independent citations: 27

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