

Transition metal-amino acid–CaAl-layered double hydroxide composites – syntheses, characterization and catalytic applications

PhD Theses

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1. Introduction and aims

Most fine chemical products are synthesized through catalytic pathways providing more sustainable and environmentally benign way of production than the stoichiometric reactions. As a result, many homogenous and heterogeneous catalysts have been developed and synthesized. Most homogenous catalysts are organometallic compounds (from the viewpoint of an organic chemist) or metal complexes (from the viewpoint of an inorganic chemist), in which one or more metal atom(s) or ion(s) is (are) surrounded by organic ligands. These materials usually behave as active and efficient catalysts; however, their recovery and recirculation are problematic or not possible at all. Immobilization of these complexes on/in solid-state host materials is considered to be a novel method to prepare recyclable catalysts. Several immobilization techniques are known resulting in immobilized catalysts having activities and selectivities close to those of the homogeneous ones.

Complexes of metal ions with variable valencies had been successfully grafted covalently on inert host materials (silica gel, Merrifield resin) during a former project of our research group. These organic-inorganic composites proved to be active and selective redox catalysts. *The aim of this work was to immobilize these (or similar) complexes in a layered double hydroxide (CaAl-LDH). The main goal was to immobilize the desired complexes between the layers of the host materials – the process is called intercalation. Beside the structural characterization of these composites, we wanted to learn whether they were active catalysts in redox and coupling reactions.*

The CaAl-LDH, used as host material, is a naturally occurring anion-exchanger mineral with layered structure. The layers contain bi-, and trivalent cations. The $\text{Ca}(\text{OH})_2$, which also has layered structure, forms the basis of the LDH structure, in which Ca(II) ions are isomorphously substituted for Al(III) ions. As a result, the layers are positively charged, which is compensated by interlayered simple or complex, fully or partially hydrated organic or inorganic anions. These anions are exchangeable with more or less difficulties. On exchanging the anions, composites with various structures can be synthesized. Many of them behave as efficient catalysts.

Our goal and hope was to synthesize such amino acid containing composites. Details of this work are revealed in the followings.

2. Experimental part

In the experimental work leading to this dissertation, composites containing CaAl-LDH as host material and amino acid complexes in anionic forms as guests were synthesized by wet chemical methods. CaAl-LDH was prepared by the co-precipitation method. Transition metal ions (Mn(II), Ni(II), Fe(III), Cu(II)) and amino acids (L-cysteine, L-histidine, L-tyrosine) were applied to construct the active centres of the catalysts. The syntheses were performed by direct anion exchange, in two different ways. In one of the methods, the amino acids were complexed with the metal ions and these pre-prepared complexes were incorporated into the host LDH in anionic form. In the other method, the anionic forms of the

amino acids were ion-exchanged first, and then complexation with the metal ions was followed.

The techniques for the characterization of the composites were as follows: powder X-ray diffractometry (XRD – crystal structure and interlayer distance), scanning electron microscopy (SEM – morphologies of the composites), energy dispersive X-ray analysis (EDX – semi-quantitative analysis), SEM–EDX (elemental maps), transmission electron microscopy (TEM – proof of the layered structure), X-ray photoelectron spectroscopy (XPS – oxidation state of the components), UV-visible and inductively coupled plasma optical emission spectroscopies (UV–vis and ICP–OES – quantitative analysis of the components), mid and far IR spectroscopy (FT-IR and far IR – proof of the presence of the organic materials), X-ray absorption spectroscopy (XAS – observation of the coordination number of the complexes and interatomic distance between the metal ions and the coordinating atoms), electron paramagnetic resonance spectroscopy (EPR – geometry of the complexes).

The catalytic activity, selectivity and recycling behaviour of the composites were investigated *via* cyclohexene oxidation using two different oxidants (peracetic acid and dihydroxy iodobenzene formed *in situ* from diacetoxy iodobenzene). Moreover, these parameters were also tested through the Ullmann-type diaryl etherification reaction. The reactions were performed in a batch reactor in the liquid phase, and were followed by gas chromatography. Possible leaching was studied by the ICP–OES method.

3. Novel scientific results

T1. Transition metal (Mn(II), Ni(II), Cu(II), Fe(III))- amino acid (L-histidine, L-cysteine, L-tyrosine) complexes in anionic forms were successfully intercalated or constructed between the layers of CaAl-LDH.

Successful intercalation was achieved in two ways: incorporating the anionic form of the pre-synthesized complexes from solution or washing the amino acid-intercalated and suspended LDH with an aqueous solution of the metal ion. Using a range of organic solvents, adjusting the optimal concentration range and applying efficient washing method, predominantly the interlayer anions were exchanged.

T2. Systematically combining the various spectroscopic and analytical methods, we were able to determine the amount of the intercalated complexes, the coordination number of the metal ions, the structure of the intercalated complexes and the interatomic distances between the metal ion and the coordinating atoms of the ligand. Knowing these pieces of information and the layer thickness of the LDH, models for the intercalated structures could be suggested.

The steps of the protocol used were the following. The amount of the incorporated amino acid and the metal ion were measured by UV–vis spectroscopy and the ICP–OES method, respectively. The metal ion/amino acid ratio was calculated from these data. The coordination number and the oxidation state of the metal ions, and the metal-ligand bond distances were determined with XAS and in some cases with XPS and EPR measurements. The far IR spectra

revealed, which O/N donor atom was coordinated to the metal ion. The EPR spectra provided with information on the coordination sphere for the Cu(II) and the Mn(II) ions.

T3. All composites proved to be active, selective and recyclable catalysts in cyclohexene oxidation.

These composites were more active and selective than the covalently grafted complexes.

T4. Using peracetic acid, epoxide selectivity was detected in all cases; however, *cis* diol formation was experienced on applying the *in situ* formed dihydroxy iodobenzene as the oxidant.

The different composites displayed similar conversions and selectivities using peracetic acid, therefore, a single mechanism was assumed in explaining their behaviour. It was assumed that the oxidant was deprotonated first, and then it was coordinated to the metal ion substituting a water molecule. It was followed by an oxygen transfer to the double bond of a non-coordinated cyclohexene. If the cyclohexene was also coordinated to the metal ion the epoxide ring could have opened and similar selectivity could have been observed as in the stoichiometric reaction having low epoxide selectivity. Our experimental results revealed outstanding epoxide selectivity in all instances.

For the *in situ* formed dihydroxy iodobenzene, the *cis* diol product could not be formed through the opening of the epoxide ring (it would have given the *trans* diol), *i.e.*, the mechanism of the oxidation was different from that of the peracetic acid. It was assumed that the addition of two OH groups occurred in a concerted manner to the double bond of the cyclohexene.

T5. Cu(II)-, and Fe(III)-containing composites displayed good activities and recycling abilities in the Ullman-type diaryl etherification as catalysts.

It was shown that with added base increased the conversion of the reaction substantially. The Fe(III)-containing composites with organic bases showed better results than with inorganic ones. On the contrary, for the Cu(II)-containing composites, the highest conversion was experienced with K_2CO_3 .

4. Practical use of the results

The results presented here are of fundamental nature. Nevertheless, layered double hydroxides and their intercalated derivatives offer many applications having good selectivity and activity in the cyclohexene oxidation and other similar redox reactions. It is presumed that these composites can be applied in a range of industrial reactions targeting the production of fine chemicals in an environmentally benign way.

5. Publications

5.1. Papers related to the Theses published in refereed journals

(1) **Varga G**, Kukovecz Á, Kónya Z, Korecz L, Muráth Sz, Csenedes Z, Peintler G, Carlson S, Sipos P, Pálinkó I:

Mn(II)-amino acid complexes intercalated in CaAl-layered double hydroxide – well-characterized, highly efficient, recyclable oxidation catalysts,
J. Catal. **335**, 125–134 (2016).

Impact factor: 6.844

Independent citation: 8

(2) **Varga G**, Ziegenheim Sz, Muráth Sz, Csenedes Z, Kukovecz Á, Kónya Z, Carlson S, Korecz L, Varga E, Pusztai P, Sipos P, Pálinkó I:

Cu(II)-amino acid–CaAl-layered double hydroxide complexes, recyclable, efficient catalysts in various oxidative transformations,
J. Mol. Catal. A **423**, 49–60 (2016).

Impact factor: 4.211

Independent citation: 2

(3) **Varga G**, Timár Z, Muráth Sz, Kónya Z, Kukovecz Á, Carlson S, Sipos P, Pálinkó I: Syntheses, characterization and catalytic activities of CaAl-layered double hydroxide intercalated Fe(III)-amino acid complexes,

Catal. Today **x**, xx (2017) (DOI: 10.1016/j.cattod.2016.12.005).

Impact factor: 4.636₂₀₁₆

Independent citation: –

(4) **Varga G**, Timár Z, Muráth Sz, Kónya Z, Kukovecz Á, Carlson S, Sipos P, Pálinkó I: Ni-amino acid–CaAl-layered double hydroxide composites – construction, characterization and catalytic properties in oxidative transformations,

Top. Catal. **x**, xx (2017) (DOI: 10.1007/s11244-017-0824-y).

Impact factor: 2.486₂₀₁₆

Independent citation: –

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

(5) Ziegenheim Sz, **Varga G**, Sipos P, Pálinkó I:

Ni-aminosav komplexek interkalálása Ca₂Al-LDH rétegei közé (Intercalating Ni amino acid complexes among the layers of Ca₂Al-LDH),

XXXVIII. Kémiai Előadói Napok, Program és előadásösszefoglalók, ISBN:978-963-9970-64-9, Szeged, 2015. pp. 59–63.

(6) **Varga G**, Csenedes Z, Bajnóczi ÉG, Carlson S, Sipos P, Pálinkó I:

Structural features of metal-amino acid complexes intercalated in layered double hydroxide
Max IV Lab Activity Report. Lund: Lund University, 2016. Paper I_811_809.

5.3. Other papers published in refereed journals

(7) Csenedes Z, Dudás Cs, **Varga G**, Bajnóczi ÉG, Canton SE, Sipos P, Pálinkó I:

Superoxide dismutase inspired Fe(III)-amino acid complexes covalently grafted onto chloropropylated silica gel – syntheses, structural characterisation and catalytic activity,
J. Mol. Struct. **1044**, 39–45 (2013).

Impact factor: 1.599

Independent citation: 2

(8) **Varga G**, Csendes Z, Peintler G, Berkesi O, Sipos P, Pálinkó I:
Using low-frequency IR spectra for the unambiguous identification of metal ion–ligand coordination sites in purpose-built complexes,
Spectrochim. Acta, Part A **122**, 257–259 (2014).

Impact factor: 2.353

Independent citation: 1

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

Impact factor: 3.615

Independent citation: 1

(10) **Varga G**, Csendes Z, Bajnóczi ÉG, Carlson S, Sipos P, Pálinkó I:
Fe-amino acid complexes, immobilised on silica gel as active and highly selective catalysts in cyclohexene epoxidation
Res. Chem. Intermed. **41**, 9155–9169 (2015).

Impact factor: 1.833

Independent citation: –

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

Impact factor: 1.780

Independent citation: 1

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

Impact factor: 1.265

Independent citation: 1

(13) Csendes Z, **Varga G**, Nagy NV, Bajnóczi ÉG, Sipiczki M, Carlson S, Canton SE, Metzinger A, Galbács G, Sipos P, Pálinkó I:
Synthesis, structural characterisation, and catalytic activity of Mn(II)–protected amino acid complexes covalently immobilised on chloropropylated silica gel,
Catal. Today **241**, 264–269 (2015).

Impact factor: 4.312

Independent citation: 1

(14) Ferencz Zs, Szabados M, **Varga G**, Csendes Z, Kukovecz Á, Kónya Z, Carlson S, Sipos P, Pálinkó I:
Mechanochemical synthesis and intercalation of Ca(II)Fe(III)-layered double hydroxides,
J. Solid State Chem. **233**, 236–243 (2016).

Impact factor: 2.299

Independent citation: 6

(15) Truong Ngoc Hung, Ádám A, **Varga G**, Dudás Cs, Kele Z, Sipos P, Pálinkó I:
Thionation of a cyanoxime derivative to form the sulphur-containing derivative, a novel ligand for complexation with transitional metal ions,
Struct. Chem. **28**, 475–478 (2017).

Impact factor: 1.582₂₀₁₆

Independent citation: –

(16) Timár Z, **Varga G**, Muráth Sz, Kónya Z, Kukovecz Á, Havasi V, Oszkó A, Pálinkó I, Sipos P:

Synthesis, characterization and photocatalytic activity of crystalline Mn(II)Cr(III)-layered double hydroxide,

Catal. Today **284**, 195–201 (2017).

Impact factor: 4.636₂₀₁₆

Independent citation: –

(17) **Varga G**, Muráth Sz, Ujvári L, Kukovecz Á, Kónya Z, Sipos P, Pálinkó I:

Mn(II)-containing LDH composites – synthesis, characterization and an application,

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

Impact factor: 1.264₂₀₁₆

Independent citation: –

(18) **Varga G**, Muráth Sz, Bajcsi Á, Kukovecz Á, Kónya Z, Sipos P, Pálinkó I:

Borate-containing layered double hydroxide composites – synthesis, characterisation and an application,

React. Kinet. Mech. Cat. **121**, 241–254 (2017).

Impact factor: 1.264₂₀₁₆

Independent citation: –

(19) Szabados M, **Varga G**, Kónya Z, Kukovecz Á, Carlson S, Sipos P, Pálinkó I:

Ultrasonically enhanced preparation, characterization of CaFe-layered double hydroxides with various interlayer halide, azide and oxo anions (CO₃²⁻, NO₃⁻, ClO₄⁻),

Ultrason. Sonochem. x, xx (2018) (DOI: 10.1016/j.ultsonch.2017.08.041).

Impact faktor: 4.218₂₀₁₆

Idegen hivatkozás: –

(20) Ziegenheim Sz, **Varga G**, Szabados M, Sipos P, Pálinkó I:

Cu(II)Cr(III)-LDH – Synthesis, characterization, intercalation properties and a catalytic application,

Chem. Pap. x, xx (2017).

Impact factor: 1.258₂₀₁₆

Independent citation: –

5.4. Other full paper published in conference proceedings

(21) Csendes Z, Elek G, Zahorán K, Gyuris K, **Varga G**, Kiss JT, Pálinkó I:

Co-protected amino acid complexes covalently grafted onto solid supports – syntheses, structural characterization and testing of catalytic activity,

Proc. 10th Pannonian Internat. Symp. Catal., ISBN:978-83-929430-4-4, Cracow (Poland), 2010, pp.37–44.

(22) **Varga G**, Csendes Z, Sipos P, Pálinkó I:

Egyfajta koordinálódó csoportot tartalmazó átmenetifém-komplexek távoli IR spektrumai - kísérlet korrelációs táblázat összeállítására (The far IR spectra of metal ion complexes containing ligands capable of coordination via one type of functional group),

XXXV. Kémiai Előadói Napok, Program és előadásösszefoglalók, ISBN: 978-963-315-099-3, Szeged, 2012, pp. 135–137.

(23) **Varga G**, Csendes Z, Peintler G, Berkesi O, Sipos P, Pálinkó I:

Using far IR spectra for the unambiguous identification of metal ion-ligand coordination sites in purpose-built complexes,

Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry: XXIV. International Conference on Coordination and Bioinorganic Chemistry, ISBN: 978-80-227-3918-4), Smolenice (Slovak Republic), 2013, pp. 429–433.

(24) Szabados M, Ferencz Zs, **Varga G**, Csendes Z, Carlson S, Sipos P, Pálinkó I:
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.

(25) Karádi KA, **Varga G**, Sipos P, Pálinkó I:

AgBi-kompozitok előállítás, szerkezetük és felhasználási lehetőségeik tanulmányozása (The syntheses, structural characterization and possible utilization of AgBi composites),

XXXIX Kémiai Előadói Napok, Program és előadásösszefoglalók, ISBN:978-963-9970-73-1, Szeged, 2016, pp. 215–219.

(26) Timár Z, Kocsis M, **Varga G**, Sipos P, Pálinkó I:

Intercalation of CaAl-layered double hydroxide with benzoate or acetate ion,

Recent Developments in Coordination, Bioinorganic and Applied Inorganic Chemistry, (Segl'a, P., Tatarko, M.), ISBN 978-80-89597-65-9, Press of Slovak University of Technology, Bratislava, 2017, pp. 131–137.

full journal papers, total: 20

cumulative impact factor, total: 51.455

independent citations, total: 24

related to the topic of the Theses: 4

related to the topic of the Theses: 18.177

related to the topic of the Theses: 10