

## Final report NKFIH PD 128189

2021

Over the entire duration of the project, almost all areas described in the research proposal have been concerned, except the general synthesis method for oxynitrides. The results, together with the relevant articles, are described in the present report. The main achievements are detailed as follows.

### 1. Syntheses, characterisation and unique applicability of structurally and morphologically modified layered double hydroxides (LDHs)

#### 1.1. Organic-inorganic hybrid LDH-composites – Successful intercalations by means of combined preparation methods

$\beta$ -isocupreidinate ( $\beta$ -iCu) and Co(II)-amino acid complex anions of well-known structure and catalytic activity in various model reactions were incorporated into the interlayer gallery of hydrocalumite (CaAl-LDH) by the partial delamination-restacking method using a modified direct anion exchange process. Silylation of the LDH with trimethyl silane was also carried out to avoid the adsorption of  $\beta$ -iCu on the outer surface and to block the basic sites. The obtained materials were characterized by a range of instrumental methods (X-ray diffractometry, scanning electron microscopy, ATR-IR and grazing incidence IR spectroscopies) and it was proven that the organocatalyst/complex hybrids were located between the layers.

Materials containing immobilized  $\beta$ -iCu were tested as catalysts in the asymmetric Michael addition of a C-nucleophile to  $\beta$ -nitrostyrene. In general, the diastereoselectivities were high, while the enantioselectivities were acceptable in most cases and very good, once 2-propanol was used as solvent. No leaching of  $\beta$ -iCu occurred during the reactions. In contrary, for Co(II)-amino acid intercalated systems, no significant catalytic activity was detected in the redox (cyclohexene oxidation) and coupling test reactions (Ullmann-type reactions) applied.

Our main achievements were reported in the following papers:

1. **Varga, G** ✉; Kozma, V; Kolcsár, VJ; Kukovecz, Á; Kónya, Z; Sipos, P; Pálinkó, I ✉; Szöllősi, Gy

$\beta$ -Isocupreidinate-CaAl-layered double hydroxide composites-heterogenized catalysts for asymmetric Michael addition

*Mol. Catal.* **482** (2020) 110675:1–7.

2. **Varga, G**; Kónya, Z.; Kukovecz, Á; Sipos, P; Pálinkó, I ✉

Co(II)-amino acid–CaAl-layered double hydroxide composites – Construction and characterization

*J. Mol. Struct.* **1179** (2019) 263–268.

### 1.2. Colloid chemistry routes for mesoporous, water-free and cation-inserted LDHs

It was adequately demonstrated that a colloid chemical approach led to fine-tuning not only the morphological feature but also the structural parameters of LDHs. Solvolysis-based co-precipitation methods – inspired by colloid chemical sol-gel methods – proved to be suitable for anchoring Ni(II) as the constituent of the layer lattice of CaFe-, CaAl- and MgAl-LDHs. Furthermore, LDH-like structures could be prepared free of water by applying short-chain alcohols as agents for solvolysis. Instrumental analysis revealed that ordered structures with hexagonally shaped morphologies formed, *i.e.* structures analogous to LDHs and water-free environments. Both Ni(II)-doped LDHs and water-free layered structures were active, highly selective and recyclable catalysts in the Knoevenagel condensation of benzaldehyde and malononitrile or coupling reactions under mild reaction conditions unlike the analogous LDHs, whose application was successful solely upon activation.

Moreover, hierarchical LDH materials of mesoporous features can be obtained with the combined colloid approach, too. Sodium dodecyl sulphate (SDS) was used as a sacrificial template to tune the interfacial properties of the LDH materials during the synthetic process. Results of various characterization studies revealed a clear relationship between the colloidal stability of the SDS-LDH precursors and the structural features of the final materials, which was entirely SDS-free. As a proof of concept, the mesoporous LDH was applied as adsorbent for removal of nitrate and dichromate anions from aqueous samples, and excellent efficiency was observed in both sorption capacity and recyclability.

It was also found that, by using the toolbox of colloid chemistry, LDHs could be applied as nanoreactors, allowing for highly selective, finetuned cysteine-oxidation among the layers. By performing interlamellar oxidation reactions with peracetic acid as oxidant, oxidation of cysteinate to cystinate in aqueous and cysteinate sulfenic acid in acetonic suspensions occurred. The oxidations could be performed under mild conditions, at room temperature, under neutral pH and in air.

Our main achievements were reported in the following papers:

3. **Varga, G**; Szabados, M; Kukovecz, Á; Kónya, Z; Varga, T; Sipos, P; Pálinkó, I ✉

Layered double alkoxides a novel group of layered double hydroxides without water content  
*Mater. Res. Lett.* **8** (2020) 68–74.

4. **Varga, G**; Somosi, Z; Kónya, Z; Kukovecz, Á; Pálinkó, I; Szilagy, I ✉

A colloid chemistry route for the preparation of hierarchically ordered mesoporous layered double hydroxides using surfactants as sacrificial templates  
*J. Colloid Interface Sci.* **581** (2021) 928–938.

5. **Varga, G**; Karádi, K; Kukovecz, Á; Kónya, Z; Sipos, P; Pálinkó, I ✉

Placing Ni(II) Ions in Various Positions In/On Layered Double Hydroxides: Synthesis, Characterization and Testing in C–C Coupling Reactions  
*Catal. Lett.* **149** (2019) 2899–2905.

6. Timár, Z; Truong, Ngoc Hung; Pravda, C; Kónya, Z; Kukovecz, Á.; Sipos, P✉; Varga, G✉; Palinko, I  
Oxidation of cysteinat anions immobilized in the interlamellar space of CaAl-Layered Double Hydroxide  
*Materials* **14** (2021) 1202:1–10.

## **2. Perovskite-type structures, bismuthites and Bi-based catalysts – Well-known structures, unexploited catalytic capability**

### *2.1. Water-tolerant, recyclable Lewis-acid catalyst with Brønsted acid/base feature – potential candidate for a cooperative catalyst*

Both Bi- and Ce-based CeBi mixed oxides were prepared by a modified sol-gel process from their precursor salts. The main features of the mixed as well as the parent oxides were studied in detail. After characterizing the morphology, the acid-base properties, the oxidation states of the cationic components and the porosity of these structures, the catalytic activities were probed in the Koevenagel condensation of benzaldehyde and diethyl malonate as well as toluene oxidation to benzaldehyde reactions. Based on the catalytic activities of the oxides in the individual reactions, a catalyst mixture from the Bi- and Ce-based mixed oxides was used successfully in the toluene to benzaldehyde oxidation and benzaldehyde to benzylidene malonate Knoevenagel condensation domino reaction under environmentally benign conditions. The mixture of an exhaustively characterised Ce-based and Bi-based BiCe oxide catalytic system proved to be suitable for promoting a toluene oxidation, benzaldehyde–benzaldehyde condensation with diethyl malonate one-pot domino reaction system with 100% selectivity towards the condensation product under mild conditions and in water as solvent. In addition, clear trend between the acidity of the surface of the catalyst and the catalytic activity was revealed. Our main achievements were reported in the following papers:

7. Varga, G✉; Kukovecz, Á; Kónya, Z; Sipos, P; Pálkó, I✉  
Green and selective toluene oxidation–Knoevenagel-condensation domino reaction over Ce- and Bi-based CeBi mixed oxide mixtures  
*J. Catal.* **381** (2020) 308–315.

### *2.2. Sillen-type structures – well-defined cooperative catalysts for concerted reactions*

Efficient self-supported Cu(I)Bi(III) and Cu(II)Bi(III) bimetallic catalysts with layered structures were designed and developed. To synthesize them, a modified coprecipitation method was used. The host structure consisted of a Sillen-type bismutite/bismuth oxyhalide framework, with copper(II) or copper(I) ions loaded as guests. The heterogeneous catalyst

enabled Ullmann-type C–N coupling or C–N and/or C–S arylations under mild reaction conditions and with high chemoselectivities, thus furnishing valuable amines and phenothiazines *via* heterocyclization with wide substrate tolerance. As corroborated by detailed catalytic studies, the cooperative, bifunctional catalyst, bearing Lewis acid sites along with copper catalytic sites. Importantly, the catalysts were successfully recycled and reused multiple times, persevering its original structural order as well as its initial activity.

Their silver-analogous also proved to be efficient catalyst to promote protodecarboxylations and decarboxylative deuterations of carboxylic acids. In this case, after an initial batch method development, a chemically intensified continuous flow process was established in a simple packed-bed system which, enabled gram-scale protodecarboxylations without detectable structural degradation of the catalyst.

Our main achievements were reported in the following papers:

8. **Varga, G**✉; Kocsis, M; Kukovecz, Á; Kónya, Z; Djerdj, I; Sipos, P; Pálinkó, I✉  
Cu<sup>I</sup>BiOI is an efficient novel catalyst in Ullmann-type CN–couplings with wide scope—A rare non-photocatalytic application  
*Mol. Catal.* **493** (2020) 111072:1–8.

9. Meszaros, R; Márton, A; Szabados, M; **Varga, G**✉; Konya, Z; Kukovecz, A; Fulop, F✉; Palinko, I; Otvos, SB✉  
Exploiting a Silver–Bismuth Hybrid Material as Heterogeneous Noble Metal Catalyst for Decarboxylations and Decarboxylative Deuterations of Carboxylic Acids under Batch and Continuous Flow Conditions  
*Green Chem.* **23** (2021) 4685–4696.

10. Kocsis, M; Ötvös, SB; Samu, GF; Fogarassy, Zs; Pécz, B; Kukovecz, Á; Kónya, Z; Sipos, P; Pálinkó, I; **Varga, G**✉  
Copper-Loaded Layered Bismuth Subcarbonate—Efficient Multifunctional Heterogeneous Catalyst for Concerted C–S/C–N Heterocyclization  
*ACS Appl. Mater. Interfaces* **13** (2021) 42650–42661.

### 2.3. Layered double sulphides – In progress

As previously reported, by applying the mechanochemically-assisted co-precipitation method, the tin-sulphide-based materials were synthesized successfully without applying harsh reaction conditions for the first time, to the best of our knowledge. Additionally, the presented method proved to be highly successful not only in the precipitation of well-known structures but also for the syntheses of novel type of layered sulphides. In the structure of the latter, Na(I), Li(I), Cu(II), Co(II) as well as Zn(II) cations can be incorporated. Consequently, it was found beyond doubt that a group of metal sulphide ion exchangers (so-called KMS) indeed belong to the family of layered sulphides with the layer composition of  $M(I)_{2x}M(II)_xSn_{3-x}S_6 \times n H_2O$  (M: Li, K, Na; M(II): Cu(II), Co(II), Zn(II), Mn(II), Mg(II);  $x = 0.5–0.95$ ;  $y = 2–5$ ). These structures

are analogous to layered double hydroxides. However, the tests of their catalytic capability are now under way. It has already become evident, that sulphide analogous of mixed oxides detailed above (section 2.1.) have higher activity compared to the oxides, nevertheless, with lower ability for recycling.

### 3. A side project

In parallel with testing Ni(II)-containing LDHs, catalytic ability of Pt-based polymer–noble metal catalysts were also studied under the same reaction conditions for comparison. However, the catalysts exhibited notable activity for different reactions, while remarkable results have been obtained with using Pt-polymer composites. A hierarchically porous polymer (HPP) consisting of micropores (~1 nm) within a 3D continuous mesoporous wall (~15 nm) was used to support well-defined Pt nanoparticles (2 nm in diameter) as a heterogeneous catalyst for the Suzuki–Miyaura cross-coupling reaction in the liquid phase. The ligand-capped nanoparticles were loaded into the polymer and treated with plasma to expose the active surface. The dual porosity was essential: the block polymer-templated mesopores provided the reactants facile access to the nanoparticle center, which was firmly immobilized on the microporous surface. Compared to inorganic mesoporous silica supports, which are intrinsically susceptible to basic hydrolysis, the Pt-HPP featured higher activity for all halide leaving groups, even in green solvents. Moreover, excellent recyclability was also achieved and only 5% decrease in activity was observed after 10 cycles. Pt-HPP was one of the most active heterogeneous catalysts for aryl chloride substrates compared to Pt or Pd counterparts.

Our main achievements were reported in the following papers: (\*S.K. and G.V. contributed equally to this work.)

11. Kim, S; **Varga, G\***; Seo, M✉ ; Sápi, A✉ ; Rácz, V; Gómez-Pérez, JF; Sebők, D; Lee, J; Kukovecz, Á; Kónya, Z  
Nesting Well-Defined Pt Nanoparticles within a Hierarchically Porous Polymer as a Heterogeneous Suzuki–Miyaura Catalyst  
*ACS Appl. Nano Mater.* **4** (2021) 4070–4076.

### 4. Conclusion

The primary aim of the project was to prepare multifunctional catalysts capable for performing well in various widely differing transformations. With catalysts like LDH/Sillen-type structures, we were able to run one-pot syntheses producing complex molecules with outgoing chemoselectivity and/or enantioselectivity. As described above, bismuth-based cooperative catalysts proved to be suitable for promoting complex tandem/concerted reactions in a recyclable manner.

## **5. Summary**

Contrary to the envisioned 3-5 research papers in refereed journals during the project, **11** research papers were published in peer-reviewed journals, cumulative impact factor of which is **66.571**. Most of the results were also presented at international conferences in-person or on-line.