EXPLORATORY RESEARCH PROJECTS
COD PROIECT: 75/2013

Title of the project:
Self-Assemblies of Nanoparticles of Metal Oxides–Layered Double Hydroxides as Novel Formulations for Photocatalytic Applications.

Project Leader:

Profesor dr.ing. Gabriela Carja

Brief report of the scientific research activities developed during 2015

2. Photocatalytic applications of self-assembled nanoarchitectures MexOy/LDHs and/or Me/LDHs in the process of the decomposition of some polluted organic compounds

In 2015, the research activities of the project 75/2013 aimed to develop research work for photocatalytic testing of the decomposition of some polluted organic substances (e.g. phenols and phenols derivates) using self-assembled nanoarchitectures type Me/LDHs of MexOy/LDHs. The research was developed through international collaboration with research groups from University of Antwerp Belgium (group of Professor Pegie Cool), University of Salamanca, Spain (group of Professor Vicente Rives), Chiba University of Japan (group of Professor Yasuo Izumi) but also through national collaboration with Institute of Biochemistry of the Romanian Academy (Dr. Norica Nichita). The obtained results were disseminated as:

I. Published papers in ISI quoted Journals:

1. Applied Catalysis A (Elsevier Press) 504, pp. 238-247, 2015 (I.F. 3.942)

Tailoring assemblies of plasmonic silver/gold and zinc-gallium layered double hydroxides for photocatalytic conversion of carbon dioxide using UV-visible light

Kawamura, S., Puscasu, M.C. (postdoc, member of the project team), Yoshida, Y., Izumi, Y., Carja, G. (project leader).

2. Nano Research (Springer Press) 8 (11), pp. 3512-3523, 2015 (I.F. 7.010)

Self-assemblies of plasmonic gold/layered double hydroxides with highly efficient antiviral effect against the hepatitis B virus

Carja, G. (project leader), Grosu, E.F. (Ph. d. Student, member of the project team), Petrarean, C., Nichita, N.

3. Catalysis Today (Elsevier Press) 252, pp 7-13, 2015 (I.F. 3.893)

Photo-responsive behavior of γ-Fe_2O_3 NPs embedded into ZnAlFe-LDH matrices and their catalytic efficiency in wastewater remediation

Seftel, E.M., Puscasu, M.C. (member of the project team, postdoc), Mertens, M., Cool, P., Carja, G (project leader).

4. Journal of Alloys and Compounds (Elsevier Press) Volume 648, 5 Pages 864–873, 2015 (I.F.2.999).

Mesoporous CeTiSiMCM-48 as novel photocatalyst for degradation of organic compounds

M. Mureseanu (member of the project team), V. Parvulescu, T. Radu, M. Filip, G. Carja (project leader).

5. Catalysis Letters (Springer Press), August 2015, Volume 145, Issue 8, pp 1529-1540 (I.F.2.307)

CuII(Sal-Ala)/CuAlLDH Hybrid as Novel Efficient Catalyst for Artificial Superoxide Dismutase (SOD) and Cyclohexene Oxidation by H_2O_2

M. Mureseanu (member of the project team), M. Puscasu (postdoc, project leader), S. Somacescu, Gabriela Carja (project leader).

6. International Journal of Materials and Product Technology 51 (3), pp. 228-240, 2015.

Removal of some organic pollutants by using solar irradiation

Puscasu, C.M., Carja, G., Zaharia, C.

-Disseminations of the obtained results at international conferences:

Nanotech 2015 - Nanotechnology Conference and Expo 14-17 iunie, 2015 Washington DC, SUA, Symposium of Advanced Materials and Application

Evolutions of self-assembled Bi_2O_3/LDHs nanostructures to mixtures of mixed oxides and their photocatalytic effiecency under UV and solar light K. Katsumata, M. Puscasu, E. Seftel, E.F. Grosu, K. Ikeda, P. Cool, G. Carja

8th International Conference on Environmental Engineering and Management, 9-12 September, 2015, Iasi, Romania

Nanocomposites of Plasmonic Gold/Layered Double Hydroxides with Enhanced Photocatalytic Performances for Phenol Degradations

E-F. Grosu, K-I. Katsumata, K Ikeda, M. Vizitiu, D. Sibiescu, G. Carja

NANOAPP – Nanomaterials And Applications, 23-26 iunie, 2015, Maribor, Slovenia

Nanostructured mixtures of mixed oxides derived from layered double hydroxides reconstructed in Ga2(SO4)3 and In(C2H3O2)3 aqueous solutions for efficient UV and solar-driven photocatalysis

E. F. Grosu, L. E. Dartu, E. M. Seftel, G. Carja

Thus, the obtained results have ben focussed on the experimentsal tests regarding the photocatalytic effieciency of Me/LDHs of MexOy/LDHs nanoarchitectures for degrading some polluted compounds (mainly phenol and its derivates). The following photocatalysts were designed, characterized and tested as successful photo-responsive compositions: nanoparticles of γ-Fe_2O_3 embedded into ZnAlFe-LDHs matrices, self-assemblies of nanoparticles of silver gold and ZnALDHs, MgAlLDH, ZnFeAlLDH and ZnGaLDHs matrices. Moreover the toxicity and environmentally-friendship of the catalysts are important characteristics thus the cytotoxicity and bio-compatibility of the AuNPs/LDHs type catalysts were also studied. In this regards the results point out that silver/gold/LDHs formulations are defined by a low toxicity (cytotoxicity). We also found that Au/LDHs catalysts showed also antiviral activity.

2.2. Experimental tests regarding the photocatalytic decomposition of some toxic organic compounds:

The photocatalytic activity for all catalysts was evaluated in the photodegradation reaction of phenol, 4-nitrophenol and 2,4-dinitrophenol in aqueous solution under ultraviolet and/or solar irradiation. The light- sources used for irradiating the catalysts are presented in Figure 1A and 1B.

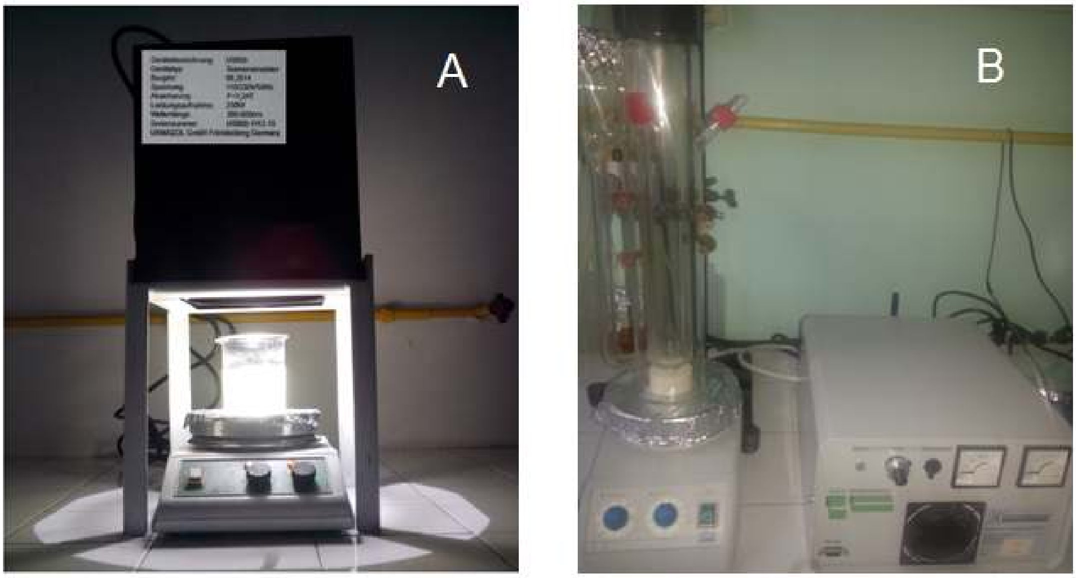

Fig1. A) The solar simulator US800(250W) B) The photo-reactor equipped with Jasco UV lamp (300 W).

Using different type of light source irradiation and light filets the experimental procedures for describing the photocatalytic tests might be described as follows: a batch-type reactor, 0.5 g/L catalyst dose was added together with an aqueous solution of pollutant (25 mg/L). The mixture was vigorously stirred in dark for 30 min in order to establish the adsorption–desorption equilibrium between the pollutant and the catalyst surface. Then the reaction mixture (800 mL) was stirred under UV light for several hours using a Pen-Ray-Power Supply lamp (UVP Products, TQ 718, 700 W) at room temperature. From time to time, 4 mL of reaction mixture was sampled, separated by centrifugation and the solution was analyzed using a UV–vis spectrophotometer following the absorbance at 270 nm (phenol), at 317 nm

(4-nitrophenol) and at 356 nm (2,4-dinitrophenol), respectively. After the analysis, the solution was added back into the photocatalytic reactor to maintain the total volume and solid/liquid ratio at a constant value. Some of the obtained important results are presented in Fig. 2-4.

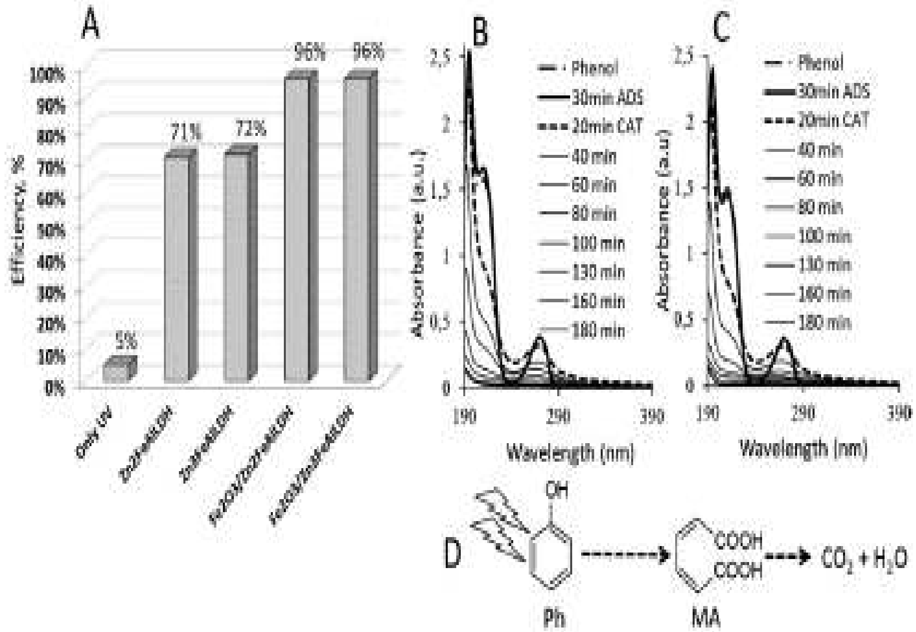

Fig. 2 Photocatalytic results for the degradation of phenol: (A) photo-bleaching and photo-degradation efficiency of phenol in the presence of Fe_2O_3/Zn_xAlFe-LDH and compared with the parent Zn_xAlFe-LDH samples (phenol: 25 mg/L; catalyst dose 0.5 g/L; time: 180 min); (B, C) UV-vis absorption spectra of the phenol solution during the photocatalytic tests in the presence of Fe_2O_3/Zn_2AlFe-LDH and Fe_2O_3/Zn_3AlFe-LDH, respectively, and (D) schematic representation of the photodegradation pathway.

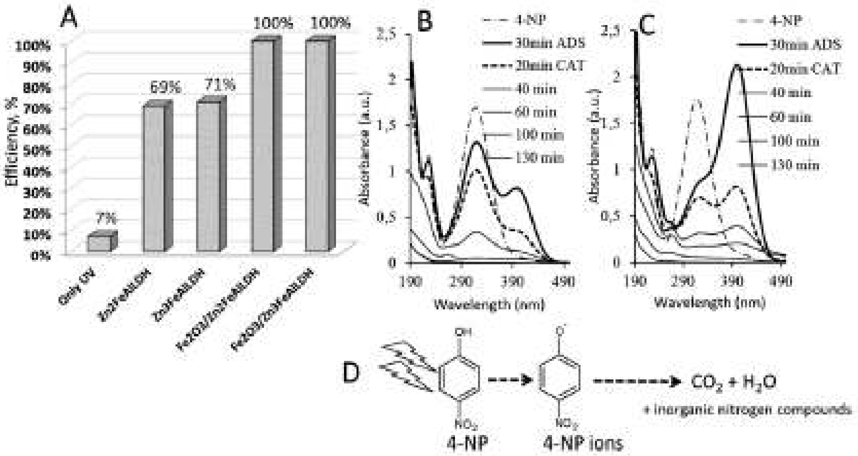

Fig. 3 Photocatalytic results for the degradation of 4-NP: (A) photo-bleaching and photo-degradation efficiency of 4-NP in the presence of Fe_2O_3/Zn_xAlFe-LDH and compared with the parent Zn_xAlFe-LDH samples (4-NP: 25 mg/L; catalyst dose 0.5 g/L; time: 130 min); (B, C) UV-Vis absorption spectra of the 4-NP solution during the photocatalytic tests in the presence of Fe_2O_3/Zn_2AlFe-LDH and Fe_2O_3/Zn_3AlFe-LDH, respectively, and (D) schematic representation of the photodegradation pathway.

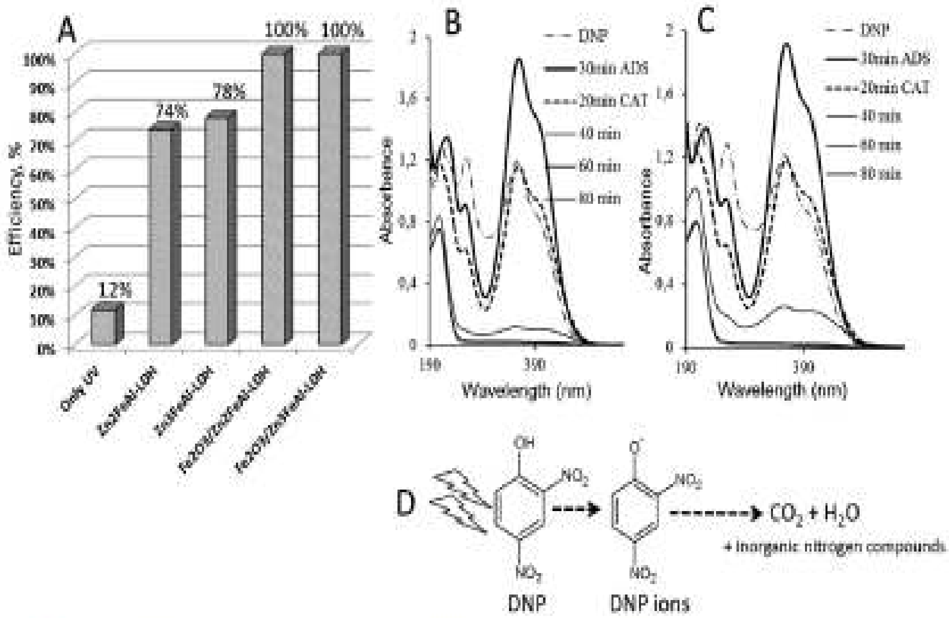

Fig.4 Photocatalytic results for the degradation of DNP: (A) photo-bleaching and photo-degradation efficiency of DNP in the presence of Fe_2O_3/Zn_xAlFe-LDH and compared with the parent Zn_xAlFe-LDH samples (DNP: 25 mg/L; catalyst dose 0.5 g/L; time: 80 min); (B, C) UV–vis absorption spectra of the DNP solution during the photocatalytic tests in the presence of Fe_2O_3/Zn_2AlFe-LDH and Fe_2O_3/Zn_3AlFe-LDH, respectively, and (D) schematic representation of the photodegradation pathway.

<u>International recognition of the results of research carried out within the Project 75/2013 through citations in ISI quoted journals:</u>

The published papers that acknowledge the financial support of the project 75/2013 were already appreciated by the scientific community being cited by highly quoted journals as:

Chemical Society Reviews (Royal Society of Chemistry) 43 (20), pp. 7040-7066, 2014

Catalytic applications of layered double hydroxides: Recent advances and perspectives
Fan, G., Li, F., Evans, D.G., Duan, X.

Structure and Bonding 166, pp. 105-136

Layered double hydroxide materials in photocatalysis
Shao, M., Wei, M., Evans, D.G., Duan, X.

We can conclude that the research objectives and goals of the project 75/2013 for the year 2015 were fully fulfilled. Moreover, we want to underline that the sum of ISI impact factor of the journals where papers were published is equal to 20.151. In the conditions that the results of the research activities developed inside this project is described in 6 published manuscripts in 2015 more details regarding the obtained results might be find in the published manuscripts.