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 Scientific report for he research activities developed during 2013-2014

In 2013, the research project activities aimed the developing and optimizing the parameters of experimental procedures regarding the manufacture of new photocatalytic formulations of nanoarchitectures self-assembled type Me / LDHs of MexOy / LDHs.

The new catalyst formulations were designed and fabricated by structural self-assembly of metals nanoparticles (Me) or metal oxides (MexOy) with mesoporous matrices of layered double hydroxide-type (LDHs) using a specific synthesis method.

The experimental steps of this method are simple and economical. The method uses the property of structural memory that defines the usually stratified LDHs-type matrices, permitting obtaining of nanoparticles (NPs) type Me (e.g: Ag, Au) and / or MexOy (E.g: Cr_2O_3, Fe_2O_3, CeO_2, NiO) and their assemblation within the LDHs structure in the absence of any organic product.

The method was developed within our team work in collaboration with Japanese specialists from Tokyo Institute of Technology, its use - in order to obtain complex photocatalytical nanoarchitectures - is possible under conditions of development of specific photo-response properties to each component of the nanostructured assembly, namely NPs of Me or MexOy, and LDHs-type matrix. Research activities developed presumed the study of the experimental procedure as a function of optimizing the parameters involved.

The method for obtaining complex photocatalytical nanoarchitectures – developed within our team work in collaboration with Japanese specialists from Tokyo Institute of Technology - is applicable if each component of the nanostructured assembly, namely NPs of Me or MexOy and the LDHs-type matrix, possesses/evidences specific photo-response properties. The investigations also involved optimization of all parameters used in the experimental procedure.

In 2014, under the drastic reduction of the required funds demanded in the approval phase of project financing, the project activity plan of the project and consequently the developed research activities have focused on establishing and optimizing experimental procedures of photocatalytic testing of Me / LDH and MexOy / LDH nanoarchitectures using photocatalytic reactions test (e.g., phenol degradation).

From the project funds we were able to purchase a UNNASOL-US800-type (Germany) sunlight simulator (equipped with separating filters for different wavelengths of light radiation), permitting to adjust the illumination intensity projected onto a controlled surface.

The new equipment allowed testing of the photo-response characteristics of the catalysts as a function of various wavelengths of light radiation. Specific experimental tests for monitoring the concentration of the pollutant in the photocatalytic process have been performed and optimized.

The influence of structural and compositional formulations of new nanostructured assemblies (e.g., heat treatment) on the properties of photocatalytic response has been also studied, the results obtained being disseminated at national and international level. The developed research activities implied the direct participation the conjoint work with research teams from University of Antwerpen Belgium, Tokyo Institute of Technology and Chiba University, Japan.

Diseminations of the results obtained between 2013-2014 highlight the acceptance of the project results by the international scientific comunity.

Papers published in ISI indexed journals with Impact Factors

1. Applied Catalysis B: Environmental, 164 (2015) 251 –260, (I.F. = 6,007), (ELSEVIER PRESS)
   Authors: *E. M. Seftel (**Postdoctorand** Antwerpen University Belgium), M. C. Puscasu (Ph.D. student), M. Mertens (researcher VITO Institute, Belgium), P. Cool (professor Antwerpen University, Belgium) G. Carja (profesor, director de proiect – autor de corespondenta).*
   Title: *Fabrication of CeO_2/LDHs self-assemblies with enhanced photocatalytic performance: a case study on ZnSn-LDH matrix;*
2. Applied Catalysis B: Environmental, 150– 151 (2014) 157– 166 (I.F. = 6,007), (ELSEVIER PRESS)
   Authors: E. M. Seftel (Postdoc Antwerpen University, Belgium), M. C. Puscasu (Ph.D.student), M. Mertens (cercetator VITO Institute Belgium), P. Cool (profesor Antwerpen University, Belgium) G. Carja (profesor, director de proiect – autor de corespondenta).
   Title: Assemblies of nanoparticles of CeO_2–ZnTi-LDHs and their derived mixed oxides as novel photocatalytic systems for phenol degradation;
3. Catalysis Communications, 54 (2014) 39–44 (I.F. = 3.320), (ELSEVIER PRESS)
   Authors: M. Mureşeanu (conferentiar, membra a echipei proiectului) , I. Georgescu, L. E. Bibire, G. Carja (director de proiect)
   Title: CU^{II} (Sal Ala)/MgAlLDH and CU^{II} (Sal-Phen)/MgAlLDH as novel catalytic systems for cyclohexene oxidation by H_2O_2;
4. International Journal of Current Research in Chemistry and Pharmaceutical Sciences, 1(7):155-163. (2014) I.F. = 0.632.)
   Authors: M. Mureseanu (conferentiar, membra a echipei proiectului), C. Babeanu, L. E. Bibire, G. Carja (director de proiect)
   Title: Novel artificial superoxide dismutase (sod) based on CU^{II} (Sal-Ala)/MgAlLDH and CU^{II} (Sal-Phen)/MgAlLDH hybrids;
5. *Journal of Inorganic and Organometallic Polymers and Materials, DOI: 10.1007/s10904-014-0132-y, (I.F. = 1,007), (SPRINGER PRESS)*

Authors: C. M. Puscasu (**doctorand, membra a echipei proiectului, prim autor si autor de corespondenta**), E. M. Seftel, M. Mertens, P. Cool, G. Carja (director de proiect, autor de corespondenta)
Title: *ZnTiLDH and the Derived Mixed Oxides as Mesoporous Nanoarchitectonics with Photocatalytic Capabilities.*

6. Catalysis Today, (I.F. = 3,309), (ELSEVIER PRESS)- accepted for publication

Authors: E. M. Seftel (Postdoc Antwerpen University, Belgium), M. C. Puscasu (membra a echipei proiectului, doctorand), M. Mertens (cercetator VITO Institute Belgium), P. Cool (profesor Antwerpen University, Belgium) G. Carja (profesor, director de proiect – autor de corespondenta).
Title: Photo-responsive behavior of γ-Fe_2O_3 NPs embedded into ZnAlFe-LDH matrices and their catalytic efficiency in wastewater remediation

7. Prepared for being submitted to publication la Applied Catalysis A: General, (I.F. = 3,674), (ELSEVIER PRESS)

Authors: Shogo Kawamura, M.C. Puscasu, Yusuke Yoshida, Yasuo Izumi, and Gabriela Carja (autor de corespondenta)
Title: Tailoring assemblies of plasmonic silver/gold and zinc-gallium layered double hydroxides for photocatalytic conversion of carbon dioxide using UV-visible light,

Alte publicatii: *Mihaela Birsanu, Dragos Mardare, Magda Puscasu, Kiyoshi Okada and Gabriela Carja, AuNPs/LDHs Assemblies as Nanoarchitectures: Fabrication, Properties and Specific Application as Photocatalysts,* (2014), in *New applications of nanomaterials*, Editura Academiei, 9-18; ISBN 978-973-27-2311-1 , Editori: A. C. Ion, Dan Dascalu, G. Carja, M. L. Ciurea

Total *IF* a revistelor in care apar publicatiile= 6.007X2+3.320+0.632+1.007+3.309= 20.289 (fara lucrarea no 7).

Ph.D.Thesis Reported: Layered double hydroxides as advanced materials with specific properties and applications, Ph.D. student M. C. Puscasu

Diseminations of the results by participation at the international conferences:

E. Seftel, M. Dobromir, M. Puscasu, M. Mertens, P. Cool, G. Carja, Fe_2O_3/ZnO-$ZnCr_2O_4$, Bi_2O_3/ZnO-$ZnCr_2O_4$ as novel photocatalytic systems with enhanced photoresponsive abilities, 8th EUROPEAN MEETING ON SOLAR CHEMISTRY AND PHOTOCATALYSIS: Environmental Application, 25-28 June, 2014, Thessaloniki, Grecia.

1) E. Seftel, M. Puscasu, M. Mertens, P. Cool, G. Carja, Photo-responsive behavior of Fe_2O_3NPs embedded into ZnFeLDHs and ZnAlFeLDH matrices and their catalytic efficiency in wastewater remediation, 8th EUROPEAN MEETING ON SOLAR CHEMISTRY AND PHOTOCATALYSIS: Environmental Application, 25-28 June, 2014, Thessaloniki, Grecia.

2) Magda Puscasu, Gabriela Carja, Carmen Zaharia
Titlu MgFeZnLDHS nanoarchitectonics for photocatalytic removal of some organic pollutants under solar irradiation, ModTech International Conference, Modern Technologies in Industrial Engineering, 13-16 July, 2014, Gliwice, Polonia.

3) C.M. Puscasu, E. M. Seftel, M. Mertens, P. Cool, G. Carja, ZnTi-LDH and the derived mixed oxides as photocatalysts for phenol degradation at room temperature, European-MRS 2014 FALL MEETING, 15-19 september, Warsaw University of Technology, Polonia.

4) M. Puscasu, K.I. Katsumata, S. Boariu, G. Carja, NPs of Fe_2O_3 on $ZnCrO_4$ matrices as wide spectrums photocatalysts for light energy conversion, 2nd International Conference on Chemical Engineering, November 5 – 8, 2014, Iasi, Romania.

5) L.E. Bibire, M. Bercea, M. Puscasu, G. Carja, Hybrid nanoarchitectures based on polymers/layered double hydroxides for applications in innovative technologies, 2nd International Conference on Chemical Engineering, November 5 – 8, 2014, Iasi, Romania.

6) Mihaela Mureşeanu, Irina Georgescu, Livia Elena Bibire, Nanohybrids copper(ii) Schiff base complex immobilized into mesoporous silica for efficient catalytic oxidation, E-MRS 2014 FALL MEETING, 15-19 september, Warsaw University of Technology, Polonia.

8. M. Puscasu, E.M. Seftel, M. Mertens, P. Cool, G. Carja
Self-Assemblies of nanoparticles of Cr2O3-ZnTi LDHs and the derives mixed oxides as novel photocatalysts for phenol removal
Conference for Young Scientists in Ceramics; The Tenth Students' Meeting, SM-2013; The Third ESR Workshop, COST MP0904 - Oral Presentation.

9. Au/anionic clays nanoarchitectonics as novel photocatalysts for hydrogen generation from water, under solar irradiation
Mihaela Birsanu, Hermenegildo Garcia, Kiyoshi Okada, Magda Puscasu, Gabriela Carja
CONFERINTA: Nano and Advanced Materials Workshop and Fair, NAMF 2013 September 16-19, – Oral Presentation.

10. Gabriela Carja, Ken-ichi Katsumata, Magda Puscasu, Kiyoshi Okada
Nanosized gold/anionic clay matrices as a controlled release system of gold nanoparticles
CONFERINTA: E-MRS 2013 SPRING MEETING, Symposium - Oral Presentation.

Objective of the 2013 single stage: Development and optimization of the parameters used in the experimental procedures for the manufacture of MeLDHs and MexOy / LDHs nanoarchitectonics.

Research activities developed for accomplishing the objective for the year 2013:

- Establishment of the experimental parameters for the synthesis of the LDHs matrix as a function of compositional diversity of cations from the clay layers (*e.g.*, Zn, Mg, Al, Ti).

- Optimization of the manufacturing parameters used in the experimental procedure of the Me / LDHs and MexOy / LDHs-type nanoarchitectonics, as a directly dependent function on the nature of NPs, Me and/ or MexOy-types, using the structural memory effect property of the LDHs matrix.

- Experimental studies regarding the structural characteristics of MexOy / LDHs nanoarchitectonics by XRD structural analysis. XRD analysis was performed in collaboration with specialists from Antwerp University, Belgium.

- Experimental studies concerning the photo-response characteristics of MexOy / LDHs nanoarchitectonics by UV-VIS analysis.

The results obtained in this stage assumed sending a paper for publication and communications at 3 international conferences. Research activities were carried out in cooperation with a team of researchers from the University of Antwerp, Belgium.

Synthesis and optimization of the photocatalytic formulations and a partial physicochemical study of theirs were also conducted, whereas the structural characterization through XRD

analysis and photocatalytic tests was performed by researchers from the Belgian university. The nanostructured Cr2O3 / ZnTiLDHs self-assembly which is the subject of the paper - issued in 2014 in the journal ***Applied Catalysis B, Environmental no. 150-151, 5 May 2014, Pages 157-166*** - is actually the result of the compositional optimization performed using a variety of catalyst samples (no.: 27).

Obtaining an effective catalytic composition required optimization of the synthesis parameters as a function of clay composition and of the compositional nature of the Cr_2O_3 nanoparticles (NPs) organized on the surface of the LDHs matrix. Clay compositional formulation was also studied, as a function of the cationic Me2 + / Me3 + rate from the LDHs layers and of the nature of cations from the layers.

Equally, the effect of introducing some POMs-type anions among the clay layers and how this operation/action might influence the structural clay reconstruction process were also studied. Among the tested LDHs-type compositional formulations tested by the co-precipitation method, mention should be made of: ZnLDH, TiZnLDH and MgAlLDH. Double-layer hydroxides, such as: ZnCrLDH, ZnCeAlLDH and MgFeAlLDH have been also obtained by co-precipitation of aqueous dilute solutions at low pH values applied during the synthesis.

A second solution of precipitates was slowly added in order to form LDHs with a stratified structure for subsequent utilization as a support. Another important stage of the research conducted in 2013 was *optimization of the experimental procedure for obtaining photocatalytic formulations in co-relation with manifestation of the structural memory effect of the LDHs matrix*. This process is shown schematically in Figure 1. It is interesting to note that, in the specific aqueous media of the $Me^{+}X^{-}$-type solutions, manifestation of the structural memory effect of the LDHs matrix is also a function of clay compositional formulation optimization, as well of the nature and features of NPsMe or NPsMexOy. Equally important is that not all compositional formulations of LDHs present the structural memory effect in aqueous media of inorganic salts. Moreover, obtaining of Me and MexOy-type nanoparticles depends on a proper optimization of the working parameters (temperature, stirring speed, pH, concentration) during structural re-formation, after the previous destruction of the LDHs layered structure.

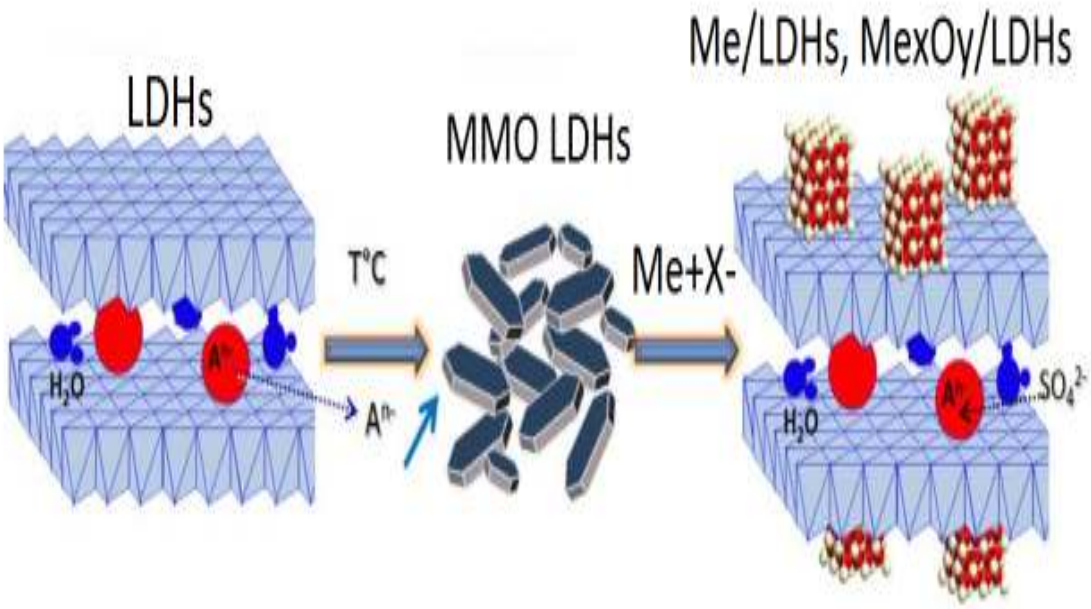

Figure 1. Schematic presentation of the experimental protocol of Me / LDHs or MexOy / LDHs-type nanostructured self-assemblies manufacturing

Much work is still necessary to gain sufficient knowledge regarding the formation process of NPs on clay surface during reconstruction. For now, neither we nor our partners in Belgium, Spain and Japan can answer the question: why cations from the reconstruction medium are self-organizing as nanoparticles on the clay surface during its reconstruction in specific inorganic media? Why are they not crowded as microparticles, for example? How is the nano-dimension of NPs on the clay surface preserved?

How can we use the basic properties of the LDHs matrix for particles organisation?

Another aspect still to be optimized refers to the experimental parameters, which would allow a uniform textural distribution of metal or metal oxide NPs.

And, even more specifically, we cannot control the size uniformity of the Me and MexOy-type NPs, nor their organization, independently on the cationic composition of the clay layers.

Furthermore, the influence of the anion nature from the Me^{+} X^{-}-type solution has not been studied in detail.

The results obtained in this phase were communicated in 3 international conferences.

We would like to emphasize the involvement of the young researchers, PhD students, Magda Puscasu and Mihaela Barsanu in these conferences.

Also initiated in the first phase of the project was the study of the photo-response characteristics of the Me/LDHs and MexOy/LDHs-type nanoarchitectures obtained by UV-Vis analysis, bringing together researchers from Japan, Spain and Belgium. Most of the results obtained in this phase are discussed in papers not yet published or waiting to be accepted for publication. Therefore, we will present them only after their publication. One of the most interesting examples to be discussed in the following refers to the photo-response characteristics of nanoarchitectonics type Fe_2O_3/FeLDH - both for precursor clay FeLDH and for the reconstructed clays noted in figure 2 as: Fe/FeLDH1, respectively Fe/FeLDH2 (see *Figure 2*). The UV-Vis spectra for clays containing Fe3 + in the clay layer show two absorption bands around 270 nm and in the 300-450 nm range, associated with charge transfer in MeO6 octahedrons of lamellar structure. The band appearing in the 450-560 nm range indicates the presence of Fe3+ ions as large particles. For Fe/FeLDHs assemblies, the absorption band around 400 nm occurs due to the d-d transitions of the Fe3 + ions. The absorbance at wavelengths above 500 nm is due to the d-d transitions of the Fe2O3 particles formed on the surface of the FeLDH precursor clay.

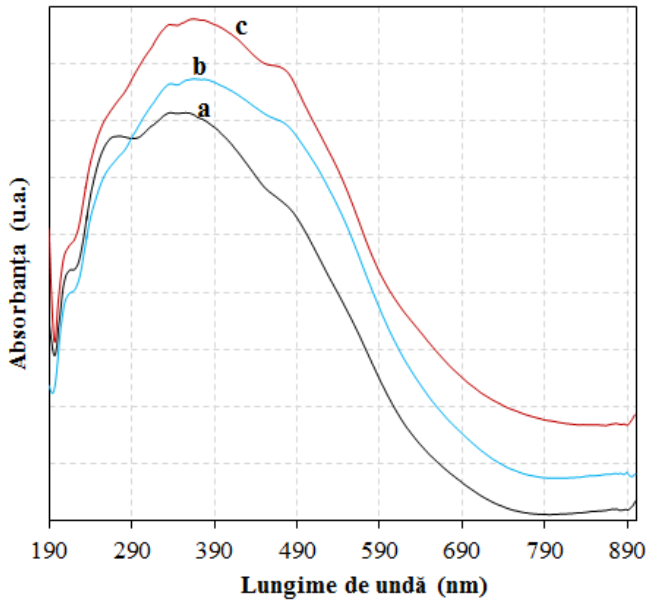

Figure 2. UV-Vis absorption spectra for the precursor and reconstructed clay samples; a) FeLDH; b) Fe2O3 / FeLDH1; c) Fe2O3 / FeLDH2

Single stage Objective 2014: Establishment and optimization of the experimental procedure parameters for photocatalytic testing.

Research activities performed for achieving the objective proposed for the year 2014:

- acquisition of reagents, consumables and equipment necessary for setting an equipment of photocatalytic testing under the action UV lamp irradiation (UV lamp), visible light (Vis lamp + filter) and sunlight, solar simulator (photoreactor and solar simulation lamp) HR UV-Vis and photoluminescence spectrophotometers and accessories, UV-VIS filters.
- Experimental studies for establishing the optimal parameters that define the experimental photocatalytic test procedure of the self-assembled nano architectonics type MexOy/LDHs and/or Me/LDHs (*e.g.*, thermal treatment of the catalyst).
- Photocatalytic tests of some organic and inorganic substances using the self-assembled nanoarchitectures type MexOy/LDHs and/or Me/LDHs. The activity was developed by international collaboration.
- acquisition of reagents, consumables and equipment necessary for setting a device of photocatalytic testing under the action UV lamp irradiation, visible and sunlight, solar simulator, UV-Vis accessories and photoluminescence spectrophotometers and UV-VIS filters.

A sunlight simulator equipped with filters that allow separation of radiation as a function of wavelength was purchased from UNNASOL Company (Germany), as well as a US800-type solar simulator that allows adjustment of the radiation intensity applied, a UV lamp VL-8LM, 365/312 nm, 8W, along with a SLV-6 support for the quartz photoreactor with water jacket were purchased from Jasco Company, Cluj. We also purchased reagents and calculation tehnique. Experimental studies were performed for establishing the optimal parameters that define the photocatalytic-test experimental procedure of self-assembled nanoarchitectonics type MexOy/LDHs and/or Me/LDHs (e.g. thermal treatment of the catalyst). The ever more numerous environmental problems caused by water pollution with industrial pollutants explain the considerable efforts made by researchers dedicated to the degradation of pollutants using one of the cheapest energy of our planet, the energy of light. Phenols and phenolic compounds are major sources of pollution of the aquatic environment. Phenol can occur in the aquatic environment due to its large use in agriculture, petrochemicals, textiles, paint, plastic and chemical pesticides. Characterized by a high carcinogen and mutagen potential, phenol presents

at high risk for mammals and aquatic life. Due to its stability and solubility in water, the removal from contaminated waters at a safe level (0.1 - 1.0 mg / L) is an extermely important aspect, approached by scientists all over the world. The scientific results published in recent years have shown an increasing interest in developing new photocatalysts able to use the light energy in order to generate strong oxidants, such as hydroxyl radicals (• OH), which oxidize not only phenol but also other organic pollutants from wastewaters. In this respect, searching in databases shows that hundreds of scientific articles have been published only in the last 7 years on this topic.

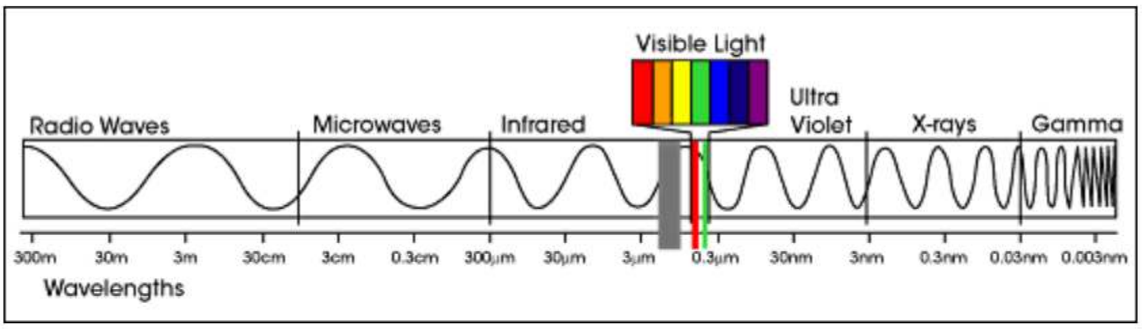

Figure 3. Sections of the electromagnetic spectrum as a function of the electromagnetic radiation wavelength

The use of photocatalysts obtained by assembling nanostructures of various nano-components - in order to initiate photo-catalytic reactions - generated a great interest due to their unique physicochemical properties caused by sharing the specific properties of various nano-structured components. The experimental installation used in this application considers first the use of different types of radiation (illustrated in Figure 3) for testing the new photocatalytic assemblies in degradation processes. To this end, a UV-Vis lamp reactor with UV Pen-Ray-Power Supply lamp (UVP Products, TQ 718, 700W) and a sunlight simulator purchased this year, from the project funds (shown in Figure 4), have been purchased. Another aspect under study for setting the experimental photocatalytic-test procedure of the self-assembled nanoarchitectonics type MexOy/LDHs and/or Me/LDHs referred to monitoring of pollutant concentrations considered in the catalytic-test reaction, namely phenol concentration monitoring during the photocatalytic testing in the photoreactive type built in - UV-lamp (see Figure 4 B)

Pen-Ray-Power Supply lamp (UVP Products, TQ 718, 700W). Complementary methods for monitoring phenol concentration were applied, such as:

Figure 4. Aspects of the research activities highlighting the use of solar simulator (A), reactor with UV-Vis irradiation lamp (B), determining the optical response by UV-Vis spectrometry (C), and preparation of various catalytic samples with controlled compositional formulations type Me/LDHs and MexOy/LDHs (D).

- Concentration monitoring by spectrophotometric calibration with a Jasco 550 UV-Vis spectrophotometer.- modified spectrophotometric colorimetric method, used in spectrophotometric determination of phenol and described briefly in *Applied Catalysis B: Environmental 152-153 (2014) 202-211*.- Phenol mineralization has been traced by COD (chemical oxygen demand) monitoring, using commercial kits (Machery Nagel, Duren, Germany).

The thermal treatment of the catalyst has been also analyzed in correlation with the catalytic performance procedure in the studied degradation processes. The thermal treatment of nanoarchitectonics type NPs / LDHs, the implications of the photo-response changing characteristics of the catalysts and the optimization of their catalytic efficiency were studied as a function of:

A) the structural modifications appearing in the LDHs type matrix during thermal treatment, in the reversible modification process from the stratification type LDH to the state of mixed oxides and return by memory effect, to the state of layered porous matrix type LDHs.

B) increasing the size of dispersed NPs on the clay surface, maintaining them to sizes below 20 nm and also reducing the level of agglomeration process that occurs after the thermal treatment.

- Photocatalytic testing of some organic or inorganic substances using self-assembled nanoarchitectures type MexOy/LDHs and/or Me/LDHs. This activity was developed by international collaboration.

The present chapter will present briefly some of the best catalytic formulations that were tested. One should emphasize that the current optimization of composition and texture of nanoarchitectonics type Me/LDHs (eg Me: Ag, Au) and MexOy/LDHs (eg MexOy: Cr_2O_3, CeO_2, Fe_2O_3, ZnO, Bi_2O_3 etc.) was reached after hours of work and detailed experimental testing both in our laboratory and in the laboratories of our partners.

A compositional and textural effective formula of a new catalyst system designed for a specific process is established as a result of catalyst optimization according to the energy needs of the catalytic process studied. This research can take years of effort and experimental tests. In our case, from the experimental results of the project, we chose to disseminate only the most effective catalysts, obtained in a limited number. We would like to mention that the effective compositional and textural formulations have involved the optimization of tens of catalytic samples, which were prepared, characterized and tested experimentally as a function of a variety

of experimental parameters. In this report and in the dissemination of results we present very briefly only the effective catalytic formulations. They represent no more than 20% of all experimental results that have been obtained. For exemple, we had difficulties with the reconstruction through memory effect of the matrix type ZnSnLDH. About 3 months of work were necessary until the structural reconstruction process of the matrix ZnSnLDH in aqueous solution of CeSO4 led to a nano-structured catalyst type CeO_2 / ZnSnLDH with an optimal degree of NPs CeO2 loading on the ZnLDHs surface. Further on, we present some of these results.

Photocatalytic activities for ZnTi-LDH, CeO2 / ZnTi-LDH phtocatalysts and for the mixed oxides derived by calcination at different temperatures are presented for the photodegradation process of phenol in aqueous solution. Suitable amounts of the catalyst were dispersed in a solution of phenol of concentration 50 mg / L, in a reactor, at an optimal dose of catalyst of 0.5 g / L. Temperature was kept constant at 25 ° C, and the solutions were stirred at dark for 30 minutes, to establish the adsorbtion- desorption equilibrium between pollutant and the catalyst surface. The solutions were irradiated with UV light for 7 hours using a UV Pen-Ray power source placed in a quartz tube, which was immersed in the solution. The photodegradation profile of phenol was monitored by measuring the UV-VIS absorption spectra with a spectrophotometer type Jasco V-550 or/and colorimetric method described in detail in *Applied Catalysis B and: Environmental 152-153 (2014) 202-211*. Photocatalytic degradation of phenol - with catalysts type ZnTi-LDHs - is shown in Figure 5. Initially, the solution of phenol with a concentration of 50 mg / L was stirred without UV light for 30 minutes, in order to establish the adsorption-desorption equilibrium between the phenol and the catalyst surface. After this time, no change in the absorption profile of phenol solution was observed. Initially, the sample ZnTi-LDH contains octahedrons of ZnO6 and TiO6 that share the edges forming the characteristics of the layered-type brucite in double layered hydroxides.

The changes in the composition of phenol solution are shown in colors in the Figures that illustrate the photocatalytic tests. The calcined derivatives samples are a combination of ZnO/Zn2TiO4 having a semiconductor-like behavior which produces a hyperchromic shift in the UV spectrum with concomitant electronic changes in the phenol molecule; these results indicate the formation of intermediate species with different chromophore groups. Therefore, in the first minutes of the reaction, all phenol molecules are readily converted to catechol, which may

degrade to biodegradable aliphatic acids. The apparent concentration increases (Figure 6b and 6c), which can be interpreted as a complete transformation in catechol. The degradation process continues by opening of the catechol aromatic ring, leading to the formation of the corresponding aliphatic acids. The main aliphatic acids observed in the absorption profile are oxalic and formic acids, that present a maximum absorption at 198 nm, respectively 195 nm. The ZnTi-LDH sample is the most effective catalyst. The proposed degradation mechanism is illustrated in

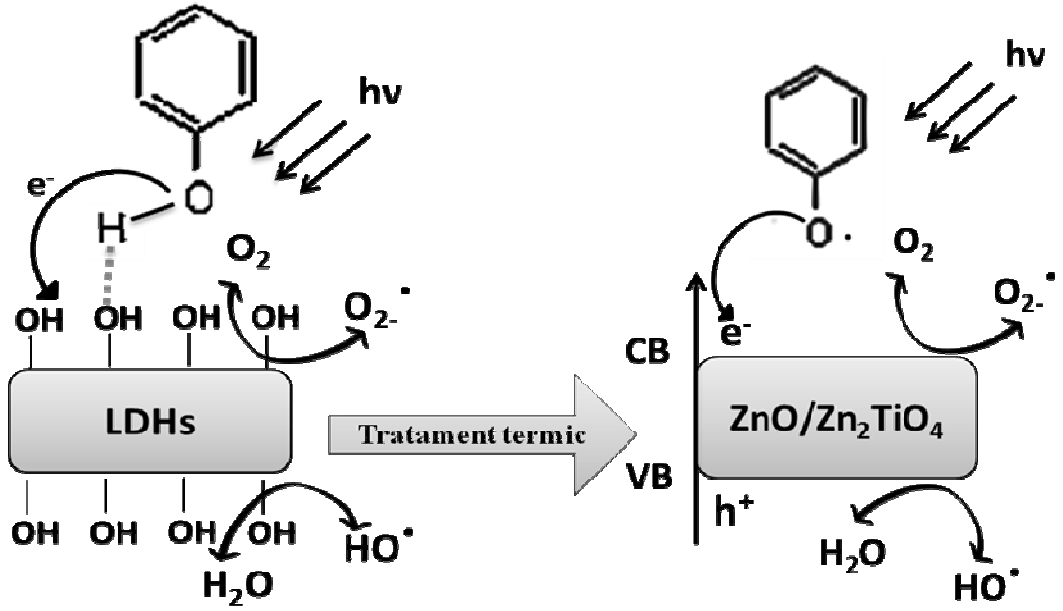

Figure 5. Photocatalytic degradation of phenol using nanostructured assemblies type CeO_2/ZnTi-LDH are illustrated in Figure 7. For this series of samples, phenol photodegradation occurs differently, which may be associated with the presence of CeO2 nanoparticles on the surface of LDHs. For the uncalcined sample type CeO_2 / ZnTi-LDH, the adsorption step occurs normally, without significant changes in the absorption profile.

Under UV irradiation, formation of a mixture of aliphatic and aromatic fractions, occurs, such as: hydroquinone, catechol, muconic acid and oxalic acid. Thus, according to the schematic representation of the degradation process, part of the initial phenol molecules opens the aromatic ring and degrades to aliphatic acid, muconic acid, oxalic and formic, and finally to CO_2 and H_2O. The hydroquinone fraction undergoes rapid changes in p-benzoquinone, which is a very stable molecule. Only a small part of the molecule is degraded until the end of the photocatalytic test.

Differences persist when the samples are calcined at different temperatures. As shown by the TG / DTG technique, this sample undergoes various phase transformations, comparatively with the ZnTi-LDH sample. A further loss of weight was observed up to 400 ° C, which probably did not caused a major structural change of the photocatalytic system. To prove this, an additional photocatalytic test was conducted using a calcined sample at 400 ° C (see Figure 7).

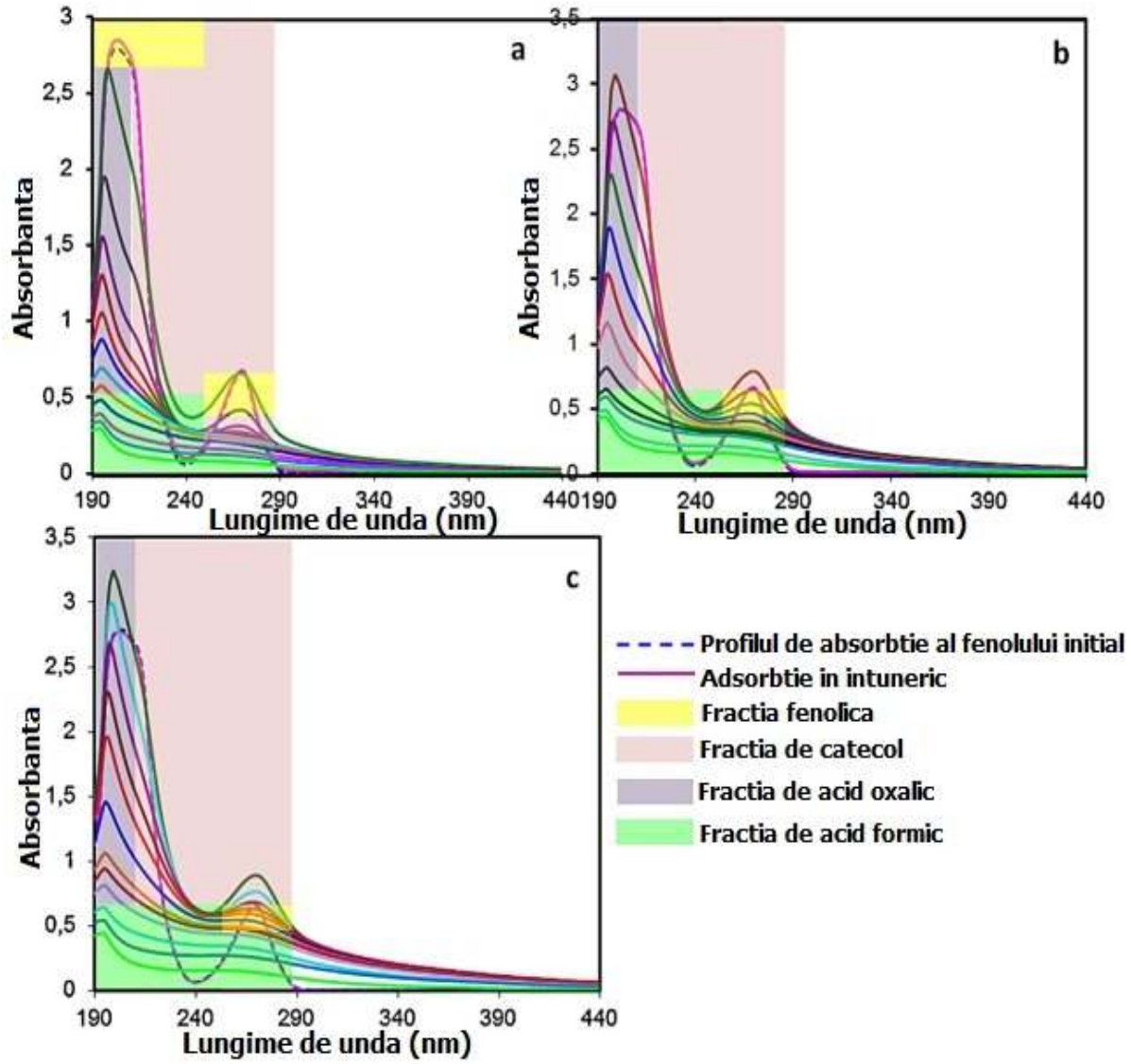

Figure 6. UV-VIS spectra of the photodegradation process of phenol in the presence of the samples (a) ZnTi-LDH, (b) ZnTi-600 ° C and (c) ZnTi-750 ° C

For the sample CeO_2 / ZnTi-600 ° C, after the absorption step in the absence of light, it can been observed that the apparent concentration increases; this can be interpreted by the formation of different chromophore groups, with the formation of a catechol and hydroquinone mixture, with subsequent transformation in muconic acid, oxalic acid and formic acid and p-benzoquinone. The results obtained in testing CeO_2 / ZnTi-400 ° C show the same behavior, suggesting non-structural transformation from 400 ° C to 600 ° C. On the contrary, when the sample is calcined at 750 ° C, the photocatalytic test shows a different mineralization path.

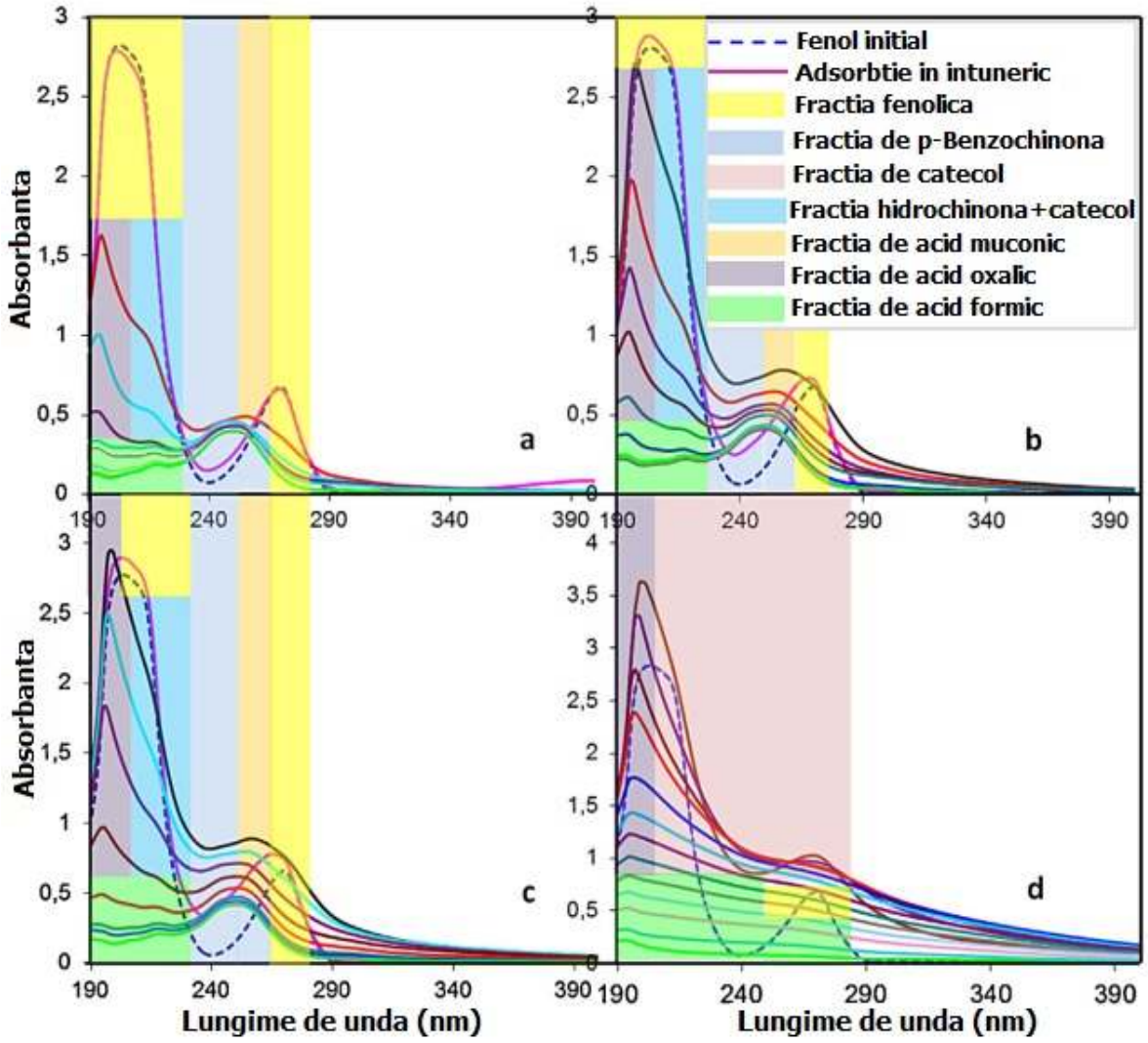

Figure 7. UV-VIS spectra of the photodegradation process of phenol in the presence of samples (a) CeO2/ZnTi-LDH, (b) CeO2/ZnTi-400°C, (c) CeO2/ZnTi-600°C si (d) CeO2/ZnTi-750°C

This can be closely linked with that formation of the nanocomposite system CeO_2 / Zn_2TiO_4, that manifests a different behavior of semiconductor. These changes can be well correlated with the Raman and UV-VIS observations indicating differences in the energy band gap of the nanoarchitectonics type MexOy studied.

Figure 7d shows that, after the adsorption step at dark, no change in the electronic structure of the phenol molecule was observed, the UV-VIS absorption profile coinciding with the measured profile of the initial phenol solution. Once launched the UV radiation, the electronic structure changes immediately, due to the hyperchromic effect, alongwith increasing of apparent concentration. This can be interpreted by the complete transformation in catechol, that allows opening of the aromatic ring and complete decomposition of phenol.

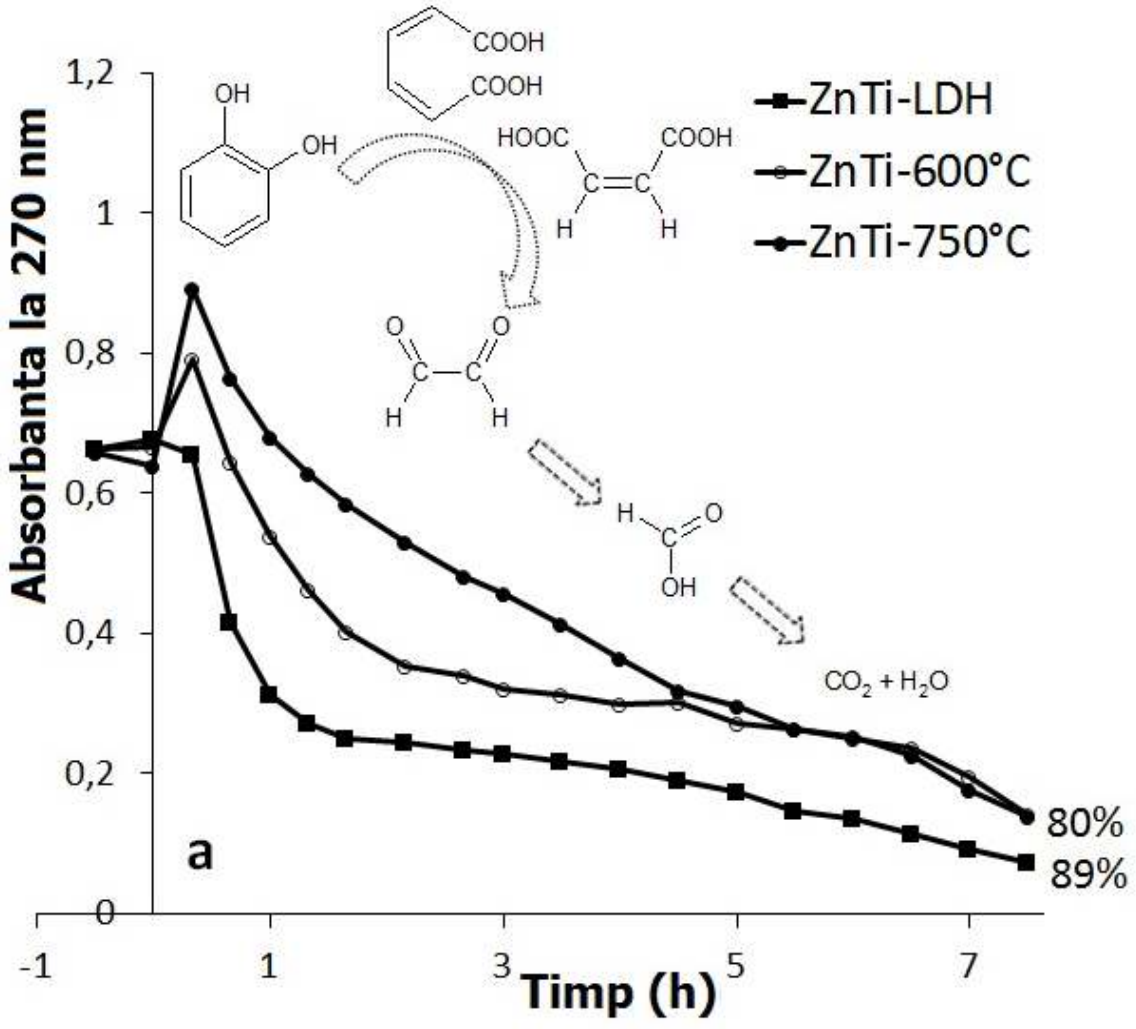

Figure 8. Degradation of phenol under UV irradiation for photocatalysts ZnTi - LDH, ZnTi - 600 °, and ZnTi -750 ° C.

An overview of the photodegradation process of phenol is shown schematically in Figure 8. It can be seen that the decrease in absorbance at 270 nm is graphically plotted as a function of time. The results demonstrate that the highest degradation efficiency of phenol is obtained on the nanostructured assembly CeO_2/ZnTi-LDH and the derived mixed oxides (Figure 9). Moreover, it can be seen that 90% of phenol is completely eliminated in the presence of CeO_2 / ZnTi-750 ° C catalyst. Although the process takes longer, compararively with samples CeO_2 / ZnTi-600 ° C and CeO_2 / ZnTi-LDH, the obtained mixture does not contain traces of p-benzoquinone, the degradation products being CO2 and water.

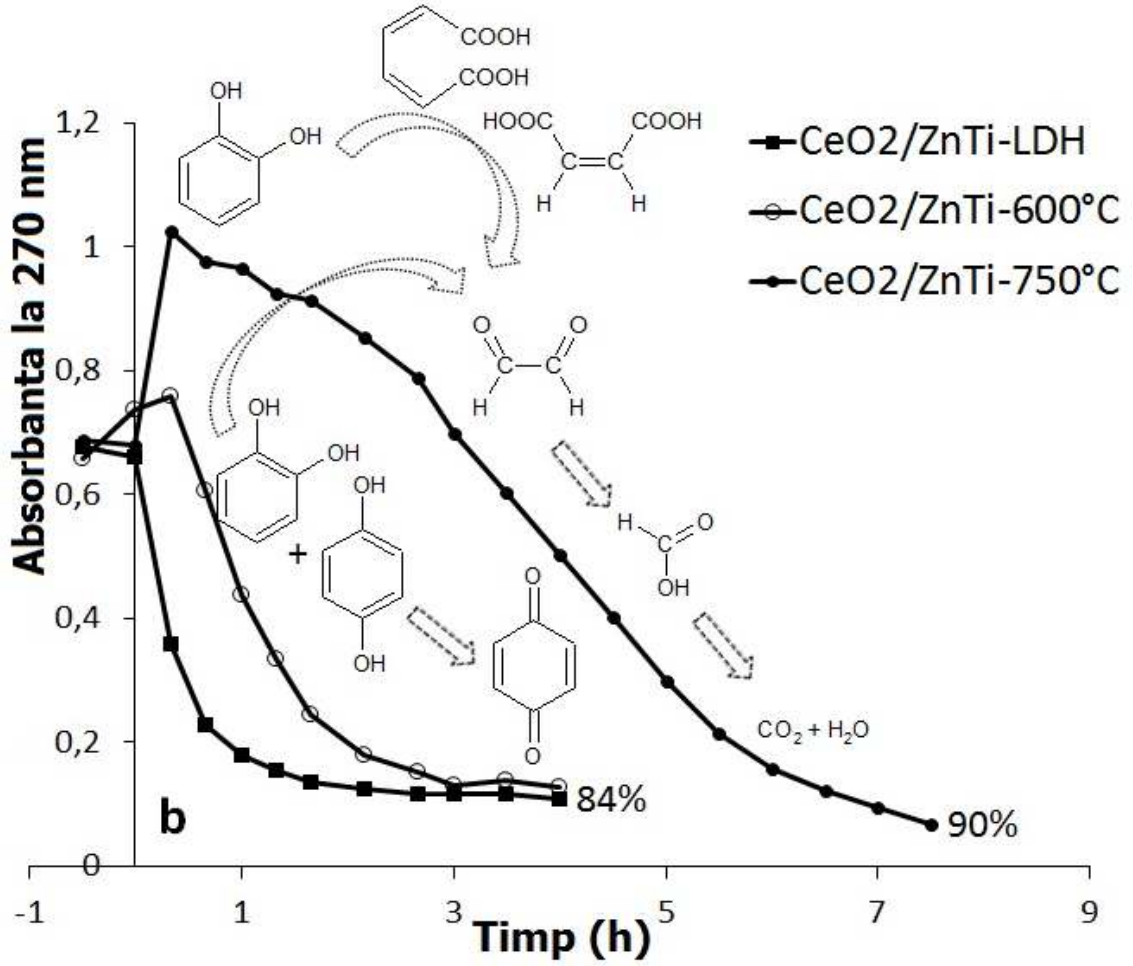

Figure 9. Degradation of phenol under UV irradiation for the catalytic samples: CeO2 / ZnTi-LDH, CeO2 / ZnTi-600 ° C and CeO2 / ZnTi-750 ° C.

http://www.msl.titech.ac.jp/
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Professor Gabriela CARJA
Technical University "Gh. Asachi" of Iasi
Iasi, Bd. D. Mangeron no 71, 700050
Romania

January 29, 2014

Dear Professor Gabriela Carja

We are pleased to invite you to Materials and Structure Laboratory (MSL) of Tokyo Institute of Technology, Japan as a Visiting Researcher for one month from the 2 th of March to the 29nd of March 2014.

We will provide you with the opportunity to pursue your research work on "Self-Assemblies of Nanoparticles of Metal Oxides–Layered Double Hydroxides as Novel Formulations for Photocatalytic Applications ". Your research plan will be carried out in association with Professor Nobuhiro Matsushita and Dr. Ken-ichi Katsumata of Materials Science Laboratory of Tokyo Institute of Technology, Japan inside the UEFISCDI project PCE IDEI 75 / 2013. Your expenses for daily life and accommodation in Japan will be supported by PCE IDEI 75 / 2013.

We look forward to seeing you soon at MSL. Please feel free to contact us for further details, if necessary.

Sincerely Yours,

Nobuhiro Matsushita

Associate Professor
Nobuhiro Matsushita
Tokyo Institute of Technology, Japan

Universiteit
Antwerpen

Antwerp, June 12th 2014

Dear Professor Gabriela Carja,

I am pleased to invite you in the Laboratory of Professor Pegie Cool, Department of Chemistry of University of Antwerp, Belgium from the 25th of September till the 7th of October 2014.

During this period we will provide you the opportunity to pursue some research work and to discuss and analyze the results obtained during our collaboration inside the research project entitled: "Self-Assemblies of Nanoparticles of Metal Oxides–Layered Double Hydroxides as Novel Formulations for Photocatalytic Applications". Your activity in our laboratory will be carried out in association with Professor Pegie Cool and Dr. Elena Seftel, from the University of Antwerp, inside the UEFISCDI project PCE IDEI 75/2013. Based on this, all of your expenses for this research work meeting will be supported by PCE IDEI 75/2013.

We look forward to seeing you soon at Antwerp University. Please feel free to contact us for further details, if necessary.

Yours, sincerely,

UNIVERSITY OF ANTWERPEN
CAMPUS DRIE EIKEN
LABORATORY OF ADSORPTION
AND CATALYSIS
DEPARTMENT OF CHEMISTRY
Universiteitsplein 1
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BELGIUM

E-MRS 2014 Fall MEETING

Warsaw University of Technology, Poland
15-18 September, 2014

We hereby certify that

Gabriela Carja

served as Chairman of Symposium C "Inorganic nanoarchitectonics: from design and fabrication to sustainable solutions".

We are pleased to thank her for her outstanding efforts in organizing the symposium and maintaining the scientific level of the E-MRS 2014 Fall Meeting.

Thomas K. Lippert
President of E-MRS

Andrzej Mycielski
Conference Chairperson

Warsaw, September 2014

E-MRS FALL MEETING

Warsaw University of Technology, Poland

Warsaw, 17 September 2014

We hereby certify that Mihaela Mureseanu attended the E-MRS 2014 Fall Meeting held at the Warsaw University of Technology from 15th to 19th of September 2014.

Mihaela Mureseanu presented two posters "FeNPs -Ti-SBA-15 nanoarchitectonics for Vis-light photocatalytic degradation of organic compounds" and „Nanohybrids copper(ii) schiff base complex immobilized into mesoporous silica for efficient catalytic oxidation".

On behalf of the Conference Organisers

Agnieszka Rafel

E-MRS FALL MEETING

Warsaw University of Technology, Poland

E-MRS
European Materials Research Society
23, rue du Loess - B.P. 20
67037 STRASBOURG Cedex 2 (France)

Warsaw, 15 September 2014

We hereby certify that Gabriela Carja attended the E-MRS 2014 Fall Meeting held at the Warsaw University of Technology from 15th to 18th of September 2014.

Gabriela Carja served as a Chairman of Symposium C "Inorganic nanoarchitectonics: from design and fabrication to sustainable solutions" and gave a talk entitled "NPs of CuO on ZnO/ZnAl2O4 matrices as wide spectrums photocatalysts for light energy conversion" at Symposium L.

On behalf of the Conference Organisers

Agnieszka Dyfet

CERTIFICATE OF ATTENDANCE

ICCE 2014

This is to certify that

Mrs./Mr. **Magda Puscaşu**

from **"Gheorghe Asachi" Technical University of Iaşi, Iaşi, Romania**

attended the 2ND **INTERNATIONAL CONFERENCE ON CHEMICAL ENGINEERING** held in IAŞI, ROMANIA, 05th -08th November, 2014.

Chairman:
Professor Teodor Măluţan

2014