Mixed oxides derived from layered double hydroxides as novel catalysts for phenol photodegradation

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Abstract. The removal of organic pollutants is nowadays a very challenging aspect of the environmental research. There are strong interests to develop novel semiconducting photocatalysts able to efficiently promote advanced oxidation reactions. The development of photocatalysts based on the mixtures of mixed oxides derived from layered double hydroxides (LDHs) - a family of naturally occurring anionic clays - might offer novel environmentally-friendly solutions for the cost-effective removal of organic pollutants. This work presents ZnO/ZnAl₂O₄, ZnO/Zn₂TiO₄ and ZnO/ZnCr₂O₄ as novel photocatalytic formulations for phenol degradation under UV irradiation. They were obtained by the controlled thermal treatment of the layered double hydroxides matrices (LDHs), as precursors materials, type ZnM-LDH (M = Al³⁺, Cr³⁺ or Ti⁴⁺). The LDHs were synthesized by the co-precipitation method at a constant pH. Controlled calcination at 650°C gives rise to solutions of mixed metal oxides. The structural and nanoarchitectonics characteristics of the studied catalysts were described by: XRD, SEM/TEM and TG/DTG techniques. Results show that in the photocatalytic process of the phenol degradation from aqueous solutions, ZnO/ZnCr₂O₄ and ZnO/ZnAl₂O₄ showed the best performance degrading ~98% of phenol after 3.5 hs and 5 hs, respectively; while ZnO/Zn₂TiO₄ has degraded almost 80 % after 7.5 hs of UV irradiation. These results open new opportunities in the development of new cost effective photoresponsive formulations able to facilitate the photo-degradation of the organic pollution as "green" solution for removal of dangerous pollutants.

1. Introduction
One of the environmental concerns of entire humanity is the continuous decreasing of natural clean water amount in the entire world, and consequently the increasing interest to remove harmful organic pollutants from water resources and wastewaters [1],[2]. Moreover, for minimization of environmental impact produced by untreated wastewater discharge in natural receptor nearby, or reduction of hazardous toxic species in terms of cumulative effects when are...
mixed together with different wastewaters in sewage system, the industrial wastewater must be treated before final discharge by efficient procedures [3],[4], such as advanced homogeneous, heterogeneous, or hybrid oxidative methods, adsorptive ones, among others.

Photocatalysts with semiconductor properties are considered important in key remediation processes as water photolysis, photodegradation, photooxidation of toxic compounds, photoelectrochemical conversion [5], where are acting as efficient eco-friendly materials for removal of hazardous species. Thus, these materials are able to use the natural sunlight, or artificial illumination energy to produce efficient oxidants, HO• radicals, which are the key factors in organics decomposition [1],[6]. Recent scientific reports were demonstrated that nano-photocatalysts can be successfully applied to eliminate toxic organics from aquatic environments, mainly because of their unique size-dependent transport properties related to photons able to establish specific photoresponsive functions which cannot be achieved by their bulk counterparts [7]. Therefore, manipulation of photocatalytic properties by selective control of catalyst nanoarchitectonics and use of collective properties of nanoassembly systems is a continuous challenge in designing of catalysts nanoarchitectonics [8].

The development of semiconductor photocatalysts based on the layered double hydroxides (LDHs) matrices have attracted great attention due to their interesting properties in anion exchangeability, compositional flexibility, biocompatibility [9],[10], and structural ‘memory effect’, the last one permitting synthesis of nanoparticles of metal oxides-LDHs (M2O/LDHs) as self assemblies. Tailoring catalysts nanoarchitectonics implies to optimize nano-sizes and shape of the catalysts but also to design the particles interconnection patterns. LDHs are layered porous matrices belonging to the class of anionic clays. They are represented by general formula [MII1-xMIIIx(OH)2]x+y·A^m-n·mH2O, where, the divalent MII and trivalent MIII cations may be Mg2+, Zn2+, Ni2+, Cu2+, Al3+, Fe3+, etc, and the A^m can be almost any organic or inorganic anion. LDHs own also the memory effect of their structure; this means they are able to rebuild their layered structure by using contacting anions solution as interlayer anions, adsorbing also metal cations and organizing them as nanosized metal oxides on its surface [11]. A large compositional diversity of the mixed oxides can be designed by modifying either the nature of metal cations of LDHs layers and/or nature of M2O nanoparticles together with control of collective compositional properties for generation of specific photocatalytic characteristics [5]. Further the controlled thermal treatment of the LDHs materials destroys the lamellar structure giving rise to mixtures of mixed oxides. Hence, the unique features of these anionic clays make LDHs interesting candidates as precursors of powerful complex photocatalysts with combined active sites.

We present in this work ZnO/ZnAl2O4, ZnO/Zn2TiO4 and ZnO/ZnCr2O4 as novel photocatalytic systems obtained by thermal treatment of the precursor ZnM-LDH type materials (where M = Al3+, Ti4+ and Cr3+).

2. Experimental

2.1. Catalysts synthesis

ZnM-LDHs with M = Al3+, Ti4+ or Cr3+ denoted as ZnAlLDH, ZnTiLDH and ZnCrLDHs with carbonate anion in the interlayer gallery were synthesized by the co-precipitation method as reported in other work [12],[13],[14]; each 400 mL of the aqueous solutions of metal salts as precursors: Zn(NO3)2•6H2O/Al(NO3)3•9H2O or Zn(NO3)2•6H2O/Cr(NO3)3 or Zn(NO3)2•6H2O/TiCl4 and the aqueous solution of NaOH/Na2CO3 precipitants (1M in total) were added dropwise together in the reaction medium at the constant pH of 8.5 ± 0.1. The resulting slurries were aged about 24 h at room temperature and denoted as ZnAlLDH, ZnCrLDH and ZnTiLDH, respectively. The final product was recuperated by filtration, washed several times with distilled water and dried under vacuum overnight. In order to obtain the mixtures of mixed oxides
systems, the as-prepared ZnM-LDHs were thermally treated at a temperature of 650°C for 24 hours; the resulted samples were denoted as ZnO/ZnAl$_2$O$_4$, ZnO/Zn$_2$TiO$_4$ and ZnO/ZnCr$_2$O$_4$.

2.2. Characterization techniques
Structural characteristics, crystallinity and purity information were recorded by X-ray diffraction (XRD). The XRD power diffraction patterns of the samples were recorded using a Shimadzu XRD 6100 diffractometer with monochromatic ($\lambda = 0.1541$ nm), operating at 40 kV and 30 mA over a 2θ range from 5º to 80º. Transmission electron microscopy (TEM) observation was performed on a Hitachi H900 transmission electron microscope operating at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were recorded on a Mira Tescan Type Mira II LMU Electron Microscope. Thermoanalytical measurements were performed using a Perkin Elmer Pyris Diamond TG/DTA thermobalance; samples were heated at a heating rate of 10ºC/min under air flow and the UV-Vis spectra were obtained at room temperature with a Jasco V-550 spectrophotometer.

2.3. Photocatalytic activity
The photocatalytic activity of the mixtures of mixed oxides systems derived from calcined ZnM-LDHs was tested for the process of phenol removal from aqueous solutions under UV irradiation. Phenol is known as major pollutant for aquatic life and also human carcinogen even at low concentration [6]. Photocatalysis experiments were carried out by using 0.1 g/L of catalyst in 250 mL of phenol solution with an initial concentration equal with 0.05 g/L. Prior to the catalytic experiments, the phenol solution and catalyst were stirred in the dark for about 30 min (for establishing adsorption-desorption equilibrium), until phenol concentration remained constant (no influence of adsorption processes in further phenol removal). A UV Pen-Ray Power Supply lamp (UVP Products) placed in a quartz tube which was immersed in the solution, was used for irradiation. 4 mL of aliquots were taken at different time intervals and centrifuged to remove the catalyst. The phenol removal was evaluated by UV-VIS analysis monitored the decreasing of phenol concentration determined by absorbance (A) measurement at 270 nm.

3. Results and discussion

3.1. Characterization of ZnM-LDH matrices and the derived mixtures of mixed oxides
The crystalline structure and the crystal phases of the synthesized catalysts were firstly characterized by XRD analysis. X-ray diffraction patterns of the as-synthesized samples and the corresponding mixed metal oxides are depicted in Figure 1. For the ZnM-LDH anionic clays (a, b, c) all the peaks that are observed in the 2θ range from 2 to 70 degrees are typically for a structure of regular clay materials with sharp and symmetric basal reflections for the (003), (006), (110) and (113) planes and broad asymmetric peaks for the (012), (015) and (018) non-basal planes [15, 16, 17, 18].

When exposed to a controlled thermal treatment, ZnAILDH, ZnTilLDH and ZnCrLLDH start to decompose mixtures of mixed oxides. The thermogravimetric analyses of the ZnM-LDH are depicted in Figure 2. It clearly indicates transformation of the layered structure of LDHs. The chromium, titanium and aluminium species are in amorphous forms. This first stage might be associated with the loss of adsorbed and/or intercalated water molecules and the removal of OH groups bonded to the brucite-like sheets.
Figure 1. XRD patterns of ZnM-LDH samples: (a) ZnTiLDH, (b) ZnAlLDH and (c) ZnCrLDH, together with the diffractograms of ZnM-LDH samples calcined at 650°C (ZnO/ZnTiO₄, ZnO/ZnCr₂O₄, ZnO/ZnAl₂O₄).

Figure 2. Thermoanalytical curves TG-DTG profile of (a) ZnTiLDH, (b) ZnAlLDH and (c) ZnCrLDH.
The largest percentage of weight loss generally occurs in the second stage; this step occurs in the temperature range of 200 - 450ºC and is associated with transformation through dehydroxylation and decarbonisation of the layered structure. After this temperature the solid state diffusion of cations with the formation of mixtures of mixed oxides and further the spinel-type structure occurs [19]. Therefore, when the temperature increases up to 650ºC the spinel-type structure is formed. This is further confirmed by XRD analysis where it can be seen that calcination at 650ºC lead to the formation of ZnO and also the spinel-type Zn₂TiO₄, ZnAl₂O₄ and ZnCr₂O₄ with high crystallinity (Figure 1). Thus, controlled calcinations of ZnCrLDH, ZnTiLDH and ZnAlLDH at 650ºC gives rise to a complex formulations type of solid solutions of ZnO/ZnCr₂O₄, ZnO/Zn₂TiO₄ and ZnO/ZnAl₂O₄, respectively.

The results of SEM/TEM analyses can be correlated very well with the XRD results regarding the uniformity and high crystallinity of the mixed metal oxides systems obtained. Figure 3 illustrates a representative SEM image for ZnO/Zn₂TiO₄. It can be seen that the mixed metal oxides system are in a disordered arrangement of small crystallites of ZnO interconnected with nanocrystallites of Zn₂TiO₄. On the other hand, TEM image of the ZnCrLDH sample after calcination at 650ºC (Figure 4) highlights amazingly well mixed metal oxides system formation.

Figure 3. Representative SEM image of ZnO/Zn₂TiO₄.

Figure 4. Representative TEM image of ZnO/ZnCr₂O₄.
3.2. The results of photocatalytic tests
The photocatalytic activities of the mixed mixtures of zinc based metal oxides type ZnO/ZnCr$_2$O$_4$, ZnO/Zn$_2$TiO$_4$ and ZnO/ZnAl$_2$O$_4$ were tested in the phenol photodegradation process from aqueous solutions, under UV irradiation. The general representation of the photodecomposition mechanism is illustrated in Figure 5. In a photocatalytic process, generally, the semiconductor particles absorb photons with energy equal or greater than the band gap energy width, promoting an electron from the valence band (VB) to the conduction band (CB) generating a hole (h$^+$) in the valence band. However, the majority of photogenerated charge carriers undergo recombination, either in the particle bulk or on the particle surface, rather than reacting with absorbed species to generate free radicals [20]. The photodegradation mechanism is strongly related with the reactive species involved in the phenol degradation process. It was found that the phenol did not significantly degrade itself without any catalyst (only ca. 5% of phenol removal). Therefore, the catalytic tests were realized at a catalyst dose of 0.1 g/L and UV-Vis spectrophotometry was used to monitor the evolution of the phenol concentration at 270 nm.

Prior, the mixtures of catalyst and phenol solution were stirred in dark for 30 minutes. When the UV irradiation is turned on differences in the absorption profiles are observed (Figure 6). For the ZnO/Zn$_2$TiO$_4$ and ZnO/ZnAl$_2$O$_4$, phenol is transformed rapidly in catechol (shows absorption maxima in the same wavelength range as phenol) which also can be degraded to biodegradable aliphatic acids. In the case of ZnO/Zn$_2$TiO$_4$ the initial increase of the phenol concentration represents a complete transformation of phenol molecules in catechol. However the phenol degradation process in this case is much slower and in a lower percentage than phenol degradation when using ZnO/ZnAl$_2$O$_4$ system. This difference in the photocatalytic activity of the mixed metals oxides systems are due to the influence of the nature of the cations within the LDH network on the phase composition of the nanosystems obtained by calcinations at 650°C of the ZnM-LDHs precursors.
Figure 6. Kinetic profile and the UV-VIS spectra of phenol photodegradation process in the presence of ZnO/Zn$_2$TiO$_4$, ZnO/ZnAl$_2$O$_4$ and ZnO/ZnCr$_2$O$_4$ catalysts.

For ZnO/ZnCr$_2$O$_4$, when the UV irradiation is on the aromatic ring of phenol there are immediately open the phenolic rings and the muconic acids are obtained. This direct formation of muconic acid produces changes in the absorption profile. The absorption maxima are shifting from 270 nm to 265 nm which is characteristic to muconic acid [21]. The presence of Cr$^{3+}$ in the layered structure of ZnCrLDH precursor and moreover the formation of ZnCr$_2$O$_4$ spinel cup led in ZnO/ZnCr$_2$O$_4$ system changes clearly the degradation mechanism of phenol until CO$_2$ and H$_2$O. It was found that the ZnO/ZnCr$_2$O$_4$ and ZnO/ZnAl$_2$O$_4$ had the best performance degrading ~98% of phenol after 3.5 hs and 5 hs respectively, while ZnO/Zn$_2$TiO$_4$ had degraded almost 80% after 7.5 hs of UV irradiation.

4. Conclusions
It was synthesized new Zn$^M$-LDH (M = Cr$^{3+}$, Al$^{3+}$, Ti$^{4+}$) clays as precursors using a simple and efficient ‘low cost’ procedure. The mixed metals oxides catalysts - ZnO/Zn$_M$M$_y$O$_z$ was obtained after a thermal treatment at 650°C of ZnAlLDH, ZnTiLDH and ZnCrLDH, respectively. The structural and morphological characteristics of the ZnO/Zn$_M$M$_y$O$_z$ together with LDHs precursors are investigated using XRD, SEM/TEM and TG/DTG techniques. The specific composition of the mixed metals oxides developed from Zn$^M$-LDHs contributes to establish the best photocatalytic properties for degradation of phenol, e.g. degradation performance up to
98% for ZnO/ZnCr₂O₄ and ZnO/ZnAl₂O₄ after 3.5 hs and 5 hs respectively, and only 80% for ZnO/Zn₂TiO₄ after 7.5 hs of UV irradiation.

These results might open new possibilities to design better photocatalysts for the phenol photodegradation by tailoring the specific compositions of the mixed metals oxides developed from LDHs layered network.

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6. References
[1] Puscasu C M, Carja G and Zaharia C 2015 Int. J. Materials and Product Technology 51 228
[2] Parida K M and Mohapatra L 2012 Chem. Eng. J. 179 131
[3] Zaharia C, Amarandei V and Muresan A 2014 Adv. Mater. Res. 1036 58
[4] Zaharia C, Suteu D and Muresan A 2012 Environ. Eng. Manag. J. 11 493
[5] Carja G, Dartu L, Okada K and Fortunato E 2013 Chem. Eng. J. 222 60
[6] Seftel E M, Puscasu M C, Mertens M, Cool P and Carja G 2014 Appl. Catal. B: Environmental 150-151 157
[7] Tong H, Ouyang S, Bi Y, Umezawa N and Oshikiri M Ye 2012 J. Adv. Mater 24 229
[8] Grzeleczak M, Vermant J, Furst E M and Liz-Marzana L M 2010 ACS Nano 4 3591
[9] Gomes Silva C, Bouizi Y, Fornes V and Garcia H 2009 J Am Che. Soc 131 13833
[10] Seftel E M, Popovici E, Mertens M, De Witte K, Tendeloo G V, Cool P and Vansant E F 2008 Micropor Mesopor Mater 113 296
[11] Carja G, Husanu E, Gherasim C and Iovu H 2011 Appl Catal B: Environmental 107 253
[12] Carja G, Kameshima Y and Okada K 2008 Microporous and Mesoporous Mater. 115 541
[13] Carja G, Nakajima A, Dranca S, Dranca C and Okada K 2010 J. Phys. Chem. 114 14722
[14] Carja G, Kameshima Y, Nakajima A, Dranca C and Okada K 2009 Int. J. Antimicrob. Ag. 34 534
[15] Zaharia C 2014 Environmental chemistry. Laboratory tests and problems (Iasi: Performantica Ed., Romania) 135
[16] Carja G and Niiyama H 2005 Mater. Let. 59 3078
[17] Dartu L, Zaharia C and Carja G 2014 Adv. Mater. Res. 837 271
[18] Sahu R K, Mohanta B S and Das N N 2013 J. Phys. Chem. Solids 74 1263
[19] Meng W, Li F, Evans D G and Duan X 2004 J. Porous Mater. 11 97
[20] Wang C, Xu B Q, Wang X and Zhao J 2005 J. Solid State Chem. 178 3500
[21] Seftel E M, Puscasu M C, Mertens M, Cool P and Carja G 2015 Appl. Catal. B: Environmental 164 251