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IRON BASED LAYERED DOUBLE HYDROXIDE AND ITS CALCINED DERIVATE AS EFFICIENT PHOTOCATALYSTS IN PHENOL REMOVAL

BY

ELENA-FLORENTINA GROSU* **and GABRIELA CARJA**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Chemical Engineering and Environmental Protection

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Abstract. We report here the fabrication of novel semiconductor photocatalysts with high efficiency in the advanced oxidation reactions. Layered double hydroxides (LDHs) are nontoxic and environmental friendly anionic clays studied due to their photoresponses under UV, visible and solar irradiation. In this work ZnFeAlLDH and the derived mixed oxides obtained after calcination, denoted as ZnFeAl750 were synthesized and used for the first time in the process of phenol photodegradation under irradiation with a solar simulator. The structure and the optical properties of the catalysts were studied by XRD, FTIR and UV-Vis techniques. The photocatalytic tests were done using a solar simulator. The results demonstrate that ZnFeAlLDH has a specific hydrotalcite structure that transformed into highly homogeneous mixed oxides after calcination at 750°C. The tested catalysts are able to absorb light starting from the red region of the spectrum. Results show that the maximum photodegradation of phenol was reached with ZnFeAl750, which removed 70% from the initial concentration of the phenol pollutant after 6 h of irradiation with solar light.

Keywords: LDHs; photocatalyst; mixed oxides; pollutant; phenol; solar photodegradation.

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*Corresponding author; *e-mail*: elena_grosu89@yahoo.com; gcarja@ch.tuiasi.ro

1. Introduction

The increases of pollution and resources problems are not only a permanent danger for humans, but also for all the leaving species which populate our planet. In this context, recycling, reuse and reduction concepts must be supported by methods which will allow eliminating different toxic pollutants before they will be discharged in municipal or, even worst, directly in fresh water sources.

Layered double hydroxides are known for over 150 years and the first discovered mineral with this structure was hydrotalcite (Mingos, 2006), reported by Hochstetter in 1842 and synthesized 100 years later by Feitknecht (Bravo-Suárez *et al*., 2004). The structure of this compound is related to that of brucite in which part of Mg^{2+} cations are replaced by Al^{3+}. Carbonate anions are intercalated between the layers to maintain electroneutrality of material. The presence of hydrotalcite in nature is reduced. For this reason, the synthesis of LDHs was investigated and was concluded that many transition metals in the first series can be used to obtain new materials with layered structure (Forano *et al*., 2006). These materials are also investigated due to their special properties and have technological importance in catalysis, photocatalysis, separation technology, optics, medical science and nanocomposite material engineering (Nalawade *et al*., 2009).

Layered double hydroxides own a basic character and a great ability to intercalate anions in their structure (Basu *et al*., 2014). They have many of the physical and chemical properties of the mineral clay, being capable of ion exchange (Forano *et al*., 2006).

The general formula of LDHs materials is: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$ where M^{II} = divalent cation (Mg^{2+}, Ca^{2+}, Zn^{2+}, etc.); M^{III} = trivalent cation (Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, etc.); A^{n-} = interlayer anion with charge n^- (Cl^-, CO_3^{2-}, NO_3^-, etc.); x represents the molar ratio of [M (III) /(M (II) + M (III))]; y = number of water molecules located in the interlamelar space (Basu *et al.*, 2014).

Although the general formula involves only the presence of divalent and trivalent cations materials having a similar structure, but containing monovalent ions of lithium (Gupta *et al*., 2012) were also synthesized. In addition, was shown that it is possible to incorporate tetravalent ions in LDH structures. Thus, have been synthesized anionic clays containing a tetravalent metal like: Zr^{IV} (Chaparadza and Hossenlopp, 2011), Sn^{IV} (Velu *et al.*, 1999), Ti^{IV} (Mingos, 2006). In a review published in 2004 by Bravo-Suárez are reported many other metals that have been incorporated in LDH layers (Bravo-Suárez *et al*., 2004).

The interlamellar space of LDHs is occupied by anions, water molecules and sometimes other neutral or charged moieties (De Roy *et al*., 2001). The linkage of these species is carried out by a complex network of hydrogen bonding. The connection between the layers and interlamellar space involves a combination of electrostatic effect and hydrogen bonding. Because of layered structure of LDHs, the anions must to satisfy excess positive charge on both of the octahedral layers, which are electrically balanced by two neighboring interlayers. The interaction between the layers and interlayer galleries are realized particularly by strongly polarized hydroxyl groups which are bonded to trivalent cations and interact with the interlayer anions (Mingos, 2006).

Being semiconductor materials, LDHs nanocomposites were used many times in the photodegradation of different harmful compounds using UV, visible or solar irradiation (Chen *et al*., 2014; Carja *et al*., 2011; Mikami *et al*., 2016). However, the most used LDHs, ZnAlLDH and MgAlLDH are able to adsorb only the UV irradiation, and because of the large band gap, a fast recombination of photogenerated electron-pairs species take place, and the photocatalytic performance of these materials is weak. To solve this issue, in the LDHs matrix can be introduced cations able to produce a shift to the red region of the absorption spectrum (Ma *et al*., 2015). Also, it was proved that the surface separation created at the interface of two semiconductors or a semiconductor and a metal can lead to an increasing of the time life of the charge carriers (Ingram and Linic, 2011; De Oliveira and Silva, 2011). Starting with LDHs, hybrid formulation between NPs supported on clays surface (Mikami *et al*., 2016), or combination between metal oxide and spinel phase created via calcination up to 700°C can be obtained (Zhao *et al*., 2010), with the propose of enhancing the photoresponse of initial materials (Puscasu *et al*., 2015).

The aim of this paper is to synthetize ZnFeAlLDH and its derived mixed oxides by calcination at 750°C (ZnFeAl750) and to use these materials in the photodegradation of phenol, a very harmful pollutant, under solar irradiation. As far as we know, ZnFeAlLDH and the derived mixed oxides were used for the photodegradation of methylene blue under visible light (Xia *et al*., 2015) and 2,4-dichlorophenoxyacetic acid under UV irradiation (Mantilla *et al*., 2009). Also, Fe_2O_3/ZnFeAl and ZnFeAlLDH were used for phenol, 4-nitrophenol and 2,4-dinitropheno UV photodegradation (Seftel *et al*., 2015). However, ZnFeAlLDH and its calcined derivate never were used for the photodegradation of phenol under solar light.

2. Experimental

2.1. Preparation of the Catalysts

ZnFeAlLDH ($Zn^{2+}/Fel^{3+}/Al^{3+}=2/0.5/0.5$) was prepared by co-precipitation method (Cavani *et al*., 1991). For this, a solution containing $Zn(NO_3)_2.6H_2O$, $Fe_2(SO_4)_3$ 7 H_2O and $Al(NO_3)_3.9H_2O$ was slowly added to an aqueous solution of $NaOH/Na_2CO_3$ in such a way that the final pH remained at a constant value of 8. The resulting precipitate was stirred 24 h at 25°C. The final product was recovered by filtration and dried at 90°C. The obtain catalyst was calcined at 750°C and the resulting derived mixed oxides is denoted as ZnFeAl750.

2.2. Characterization of the Catalysts

Structural characteristics and the optical proprieties of our catalysts were investigated using a D8 ADVANCE XRD diffractometer at a Bragg angle (θ_B) of $2\theta_B = 3^o–60^o$ with a scan step of 0.01° and a scan rate of 5 s per step. The measurements were performed at 40 kV and 40 mA using Cu Kα emission and a nickel filter. Further structural investigation was studied by FTIR analysis using a PerkinElmer FTIR Spectrum 100 spectrometer while the optical responses under light irradiation was studied using an UV-VIS Jasco V550 spectrophotometer equipped with an integration sphere for solids.

2.3. Photocatalytic Experiments

The photoresponse ability of our materials was investigated in the photodegradation of a phenol solution, 25 mg/L. For this, 1 g catalyst/L pollutant solution was firstly kept in the dark to establish the adsorption desorption equilibrium, afterwards the first sample was taken and the solar irradiation started. In order to prove that the pollutant is not degraded only by the light, a blank test was made during two hour when the phenol was irradiated without using any catalysts and no degradation was observed. The sampling was made at determined times and the photodegradation was appreciated using UV-VIS spectrometry measurements. The samples were irradiated by our solar simulator, UNNASOL US 800 (Product Instrument, Germany), 180 W.

3. Results and Discussions

3.1. Catalysts Characterization

The X-ray diffraction patterns of ZnFeAlLDH ($Zn^{2+}/Fel^{3+}/Al^{3+}$ =2/0.5/0.5) and the mixed oxides derived from it are displayed in Fig. 1. The diffractogram of the parent LDH exhibits the diffraction lines typical for a hydrotalcite-like structure, in which a series of sharp and symmetric basal reflections of the (00ℓ, ℓ=3, 6, 9) planes and broad, less intense, reflections for the nonbasal (01ℓ, ℓ=2, 5, 8) planes are easily recognized (Cavani *et al.*, 1991).

These reflections are missing in the diffractograms of the calcined catalyst pointing out that the calcination process carried in order to obtain the derived mixed oxides leads to a collapse of the layered structure during the thermal treatment. New reflections, sharper and more intense are detected showing that a homogeneous mixture of $ZnFe_2O_4$ and ZnO is clearly identified, after ZnFeAlLDH calcination.

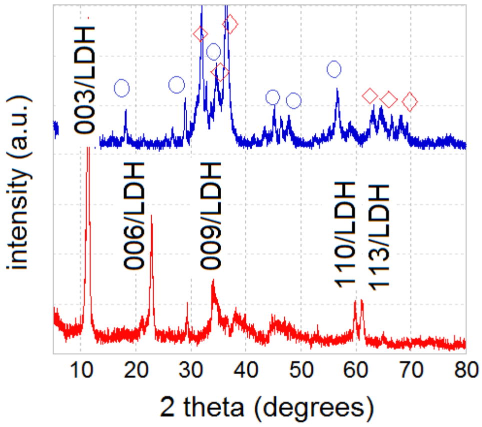

Fig. 1 – The XRD spectra of the studied catalysts. O ZnFe2O4; ◊ ZnO;

FTIR analysis was used to further investigate the specific catalysts structure of our the synthesized ZnFeAlLDH. As it can be seen in Fig. 2, around 3400 a large absorption band can be observed, which is assigned to the hydroxyl groups from the clay lamella. Further, the interlayer water H-O-H molecules, which are linked to the anions molecules via hydrogen bonds, are represented by a small shoulder around 1630 cm^{-1} (Ahmed *et al.*, 2012). The three signals at 1510, 1390 and 833 cm^{-1} are corresponding to the antisymmetric and symmetric stretching modes of carbonate anions (Chubar *et al.*, 2013; Wang *et al.*, 2014). The metal oxides from the material structure have vibration bands between 400-800 cm^{-1} (Ahmed *et al.*, 2012).

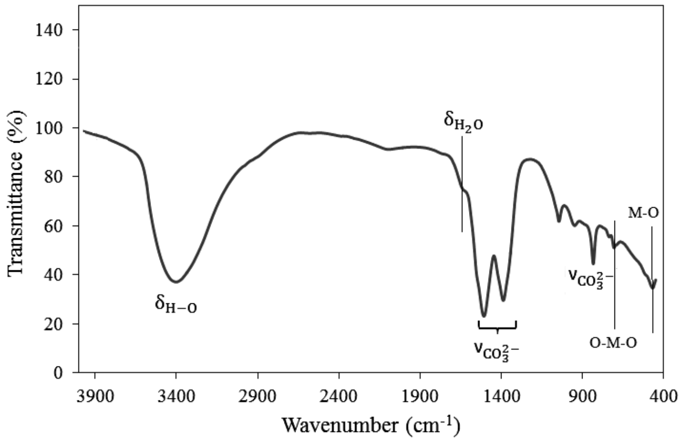

Fig. 2 – FTIR spectrum of ZnFeAlLDH layered double hydroxide.

The optical proprieties of the “as synthesized” and calcined catalysts were investigated using UV-VIS spectroscopy. Fig. 3 reveals the absorption profile of our materials. The nanocomposites present absorption bands in both UV and visible regions of the spectrum. The absorption bands of ZnFeAlLDH at 215, 270 and 480 nm are assigned to Fe^{3+} ions octahedral coordinated in the clay structure, while the large adsorption edge between 300 and 360 nm is attributed to the ZnO nanoparticles (Heredia *et al*., 2011). The calcined product ZnFeAl750 has an adsorption band at 360 nm characteristic to the small size ZnO nanoparticles and also the adsorption threshold edges assigned to the spinel $ZnFe_2O_4$ at around 680 nm (Ahmed *et al*., 2014).

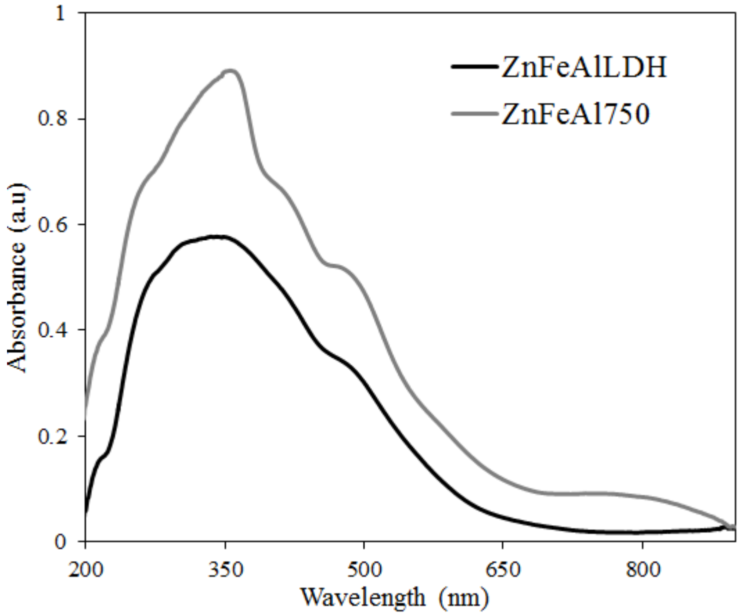

Fig. 3 – The UV–Vis absorption spectra of the studied catalysts.

3.2. Photocatalytic Mechanism

Two processes are involved in pollutants photodegradation. First, the pollutant has to be adsorbed on catalyst surface, and second, the electron-holes pairs photogeneration under an appropriate irradiation source. When a semiconductor material is excited using electromagnetic irradiation, whose energy is higher than the material’s band gap, the electrons from the valence band will be transferred in the conduction band where they can move freely. The electrons and the holes react with the dissolved oxygen and water and in this way hydroxyl radicals will be created and involved further in the degradation of pollutant compounds (Eqs. (1)-(5)) (Paredes *et al*., 2011; Chen *et al*., 2014).

$$\text{Catalyst} + h\nu \rightarrow \text{Catalyst}\,(e_{CB^-} + h_{VB^+}) \tag{1}$$

$$\text{Catalyst}\,(h_{VB^+}) + H_2O \rightarrow \text{Catalyst} + OH^{\bullet} + H^+ \tag{2}$$

$$OH^{\bullet} + \text{Pollutant} \rightarrow \text{Degradation products} \tag{3}$$

$$\text{Catalyst}\,(e_{CB^-}) + O_2 \rightarrow \text{Catalyst} + O^{\bullet -} \tag{4}$$

$$O^{\bullet -} + \text{Pollutant} \rightarrow \text{Degradation products} \tag{5}$$

3.3. Photocatalytic Activity

ZnFeAlLDH and ZnFeAl750 nanocomposites photoresponse was appreciated in the photodegradation of phenol (λ = 270 nm), under a solar source of irradiation. In Fig. 4 are presented the degradation profiles obtained when the fresh and the calcined samples were used.

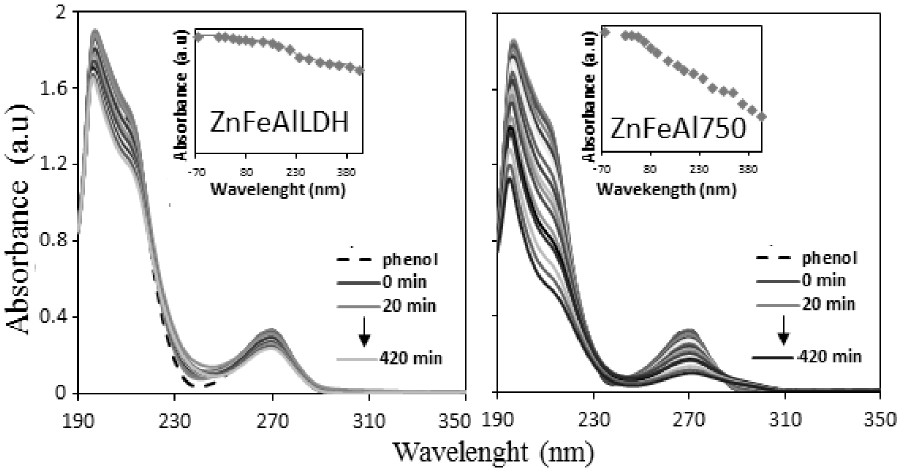

Fig. 4 – UV–vis spectra of phenol during the photodegradation process in the presence of the ZnFeAlLDH and ZnFeAl750.

During the time, the pollutant characteristic absorbance decreases due to its elimination from the system. It can be easily observed that the thermal treatment of the ZnFeAlLDH leads to the formation of a material which has a higher photodegradation ability comparted with its precursor. This result can be explained by the formation of a two semiconductors nanocomposite, where the spinel phase is homogeneously dispersed in the metal oxide matrix. This new calcined material is able to generate under irradiation a transfer of electrons from the conduction band of $ZnFe_2O_4$ to the conduction band of ZnO, and a transfer of holes from oxide phase to the spinel phase (Zhao *et al.*, 2012). In this way the lifetime of charge carriers is increased. The total removal of phenol obtained in case of ZnFeAl750 was 70%, while ZnFeAlLDH only 29%.

4. Conclusions

In this study, novel photoresponsive materials were tested in the process of phenol degradation. ZnFeAlLDH was synthetized in an easy and simple way, using the co-precipitation method. To enhance the photocatalytic performance of the fresh layered double hydroxide, ZnFeAlLDH was calcined at 750ºC and a derived mixed oxide was formed. The photocatalytic results obtained after the photodegratadion of phenol show an activity increase in the case of ZnFeAl750 compared with its precursor (from 27% to 70%). In the calcined catalyst, an efficient electrons-holes transfer between their interfaces might be possible influencing the problem of the charge carrier fast recombination.

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HIDROXID DUBLU LAMELAR PE BAZĂ DE FIER ȘI DERIVATUL SĂU CALCINAT CA FOTOCATALIZATORI EFICIENȚI PENTRU ELIMINAREA FENOLULUI

(Rezumat)

Noi descriem în acest manuscris fabricarea de semiconductori cu proprietăți fotocatalitice ce sunt capabili să genereze reacții de oxidare în prezența radiației solare. Hidroxizii dublu lamelari (LDHs) sunt argile anionice netoxice și prietenoase cu mediul înconjurător fiind studiate datorita fotorăspunsului pe care pe care îl oferă atunci când sunt stimulați cu radiație UV, vizibilă sau solară. În această lucrare, ZnFeAlLDH și oxizii săi micști derivați denumiți ZnFeAl750 au fost folosiți pentru prima dată în fotodegradarea fenolului sub lumină solară. Structura și proprietățile optice ale catalizatorilor au fost investigate prin FTIR și spectrometria UV-VIS. Pentru testele fotocatalitice s-a folosit un simulator solar. Rezultatele au arătat faptul că ZnFeAlLDH, prezintă o structură caracteristică hidrotalcitului, ambele materiale fiind capabile să absoarbă radiație din regiunea roșie a spectrului. Dintre cei doi catalizatori, materialul calcinat are cea mai bună activitate, degradând 70% din cantitatea inițială de poluant după 6 ore de iradiere.