



Research paper

Photocatalytic degradation of phenol using MgAlSn hydrotalcite-like compounds

Sonia Mancipe^{a,*}, Francisco Tzompantzi^a, Hugo Rojas^b, Ricardo Gómez^a^a Universidad Autónoma Metropolitana-Iztapalapa, Depto. De Química, Área de catálisis, grupo ECOCATAL, Av. San Rafael Atlixco No 189, México, D.F. 09340, México^b Universidad Pedagógica y Tecnológica de Colombia, Escuela de Química, Facultad de Ciencias, Grupo de Catálisis (GC-UPTC), Av. Norte, Tunja, Colombia

ARTICLE INFO

Article history:

Received 8 March 2016

Received in revised form 4 May 2016

Accepted 5 May 2016

Available online 25 May 2016

Keywords:

Hydrotalcite

Phenol degradation

SnO₂ segregated

Electron-hole pair

ABSTRACT

MgAl Layered Double Hydroxides (LDH) with molar ratio Mg/Al = 3 and MgAlSn containing 5, 10 and 15wt% of tin were synthesized by the co-precipitation method. The solids were characterized by X-ray diffraction (XRD), N₂ sorption, infrared spectroscopy (FTIR), Scanning Electron Microscopy coupled to a detector for energy dispersive X-ray spectroscopy microanalysis (SEM/EDS), Transmission Electron Microscopy (TEM) and UV–Vis spectroscopy (UV–Vis) in order to determine the crystalline structure, textural properties, vibrational modes of the LDH, morphology and tin content, as well as the band gap of the solids. The photocatalytic behaviors of synthesized materials were tested in phenol degradation under UV irradiation. The results showed that MgAlSn 15% present the highest activity with 80% degradation of the contaminant molecule after 3 hours of exposure to light.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Industrial processes generate wastewater that often contains toxic organic compounds that are not susceptible in direct treatments to be eliminated causing severe environmental problems (Luan et al., 2012; Vallet et al., 2012). In this way the presence of phenolic compounds has heightened concerns in recent years, due to their high toxicity and bio-recalcitrant nature (Ahmed et al., 2011). Several methods, including ultrasound/H₂O₂ or ozone (Sano et al., 2007), UV/H₂O₂ (Han et al., 2004), ozone/H₂O₂ and photo-Fenton processes (Huang et al., 2010) for dealing these compounds have been applied successfully. However, catalytic advance oxidation processes (AOP) have been proposed as alternative method improving the treatment of wastewater containing phenolic pollutants (Mohapatra and Parida, 2012). Among the AOP the photocatalytic degradation of organic compounds using semiconductors like TiO₂ (Bayarri et al., 2013), ZnO (Chakrabarti and Dutta, 2004), Fe₂O₃ (Pradhan et al., 2013), ZnS (Torres-Martínez et al., 2001), and FeO (Nezamzadeh-Ejhieh and Shirzadi, 2014) has been reported as very efficient method for the oxidation and total mineralization of dyes, drugs and a large variety of phenolic compounds. The photoactivity of semiconductors is explained by the electron-hole pair generated when the semiconductor is irradiated with a light source with energy equal or higher than his band gap generating an electron in the conduction band and a hole in the valence band. The photo-generated holes react with surface H₂O molecules or with HO[•] forming

HO[•] radicals which are reported as excellent oxidizing species in the photocatalytic oxidation reactions (Seftel et al., 2008).

However, recently it has been reported that solids which are not classified as semiconductors showed important photocatalytic properties. Among them layered double hydroxides (LDH) or anionic clays attract attention of various scientists. LDH as MgZnAl (Valente et al., 2009), Zn–Cr (Mohapatra and Parida, 2012), Zn–Ti (Shao et al., 2011), and NiZnAl (Wang et al., 2014) have been reported as efficient photocatalysts for the photodegradation of 2,4 dichlorophenoxyacetic acid, xanthene dyes, methylene blue and orange G respectively. LDH, also known as hydrotalcite-like materials are described by the general formula [M^{II}_{1-x}M^{III}_x(OH)₂]^{x+} [(Aⁿ⁻)_{x/n}YH₂O]^{x-}, where M^{II} is the divalent metal as Mg, Fe, Cu, Ni, Co, Zn, etc., M^{III} is the trivalent metal as Al, Fe, Cr, etc., and Aⁿ⁻ is exchangeable anion that compensates the charge (e.g., CO₃²⁻, NO₃⁻, Cl⁻, SO₄²⁻, F⁻) (Albertazzi et al., 2004; Mandal et al., 2012; Chen et al., 2014). The structure of the layered double hydroxides consists of brucite-like layer (coordinated octahedrally by hydroxyl groups) in which a part of M²⁺ is substituted isomorphously by M³⁺, so the excess of positive charge of the layers is compensated by anions between them for maintain electroneutrality, also water molecules can occupy a space in the interlayer region (Das and Samal, 2004; Kameda et al., 2007). The x value can vary in a wide range from 0.17 to 0.33, generating isostructural materials with different physicochemical properties. The charge density can be controlled by varying the molar relation M²⁺/M³⁺ and moreover the anion most employed commonly is carbonate. The base material of anionic clays is the natural hydrotalcite Mg₆Al₂(OH)₁₆CO₃·4H₂O (Goh et al., 2008). In addition to divalent and trivalent cations, a wide range of cations such as Zr⁴⁺, Ti⁴⁺, and Li⁺ may be accommodated in the octahedral sites of close-

* Corresponding author.

E-mail address: sonia.mancipe@hotmail.com (S. Mancipe).

packed configuration of OH⁻ ions in the layers of the LDH (Zhang et al., 2008). Generally, LDHs are used as photocatalyst, catalyst, ion exchangers, ceramic precursors, functional materials, active nanocomposites, precursors of metallic oxides and adsorbents (Tsai et al., 2014). These solids can be considered promising materials due to their high versatility, easy synthesis, low cost and wide range of composition.

The LDH are obtained by direct and indirect synthesis. Direct anion exchange, anion exchange by elimination of the interlamellar precursors susceptible to acid attack and structural regeneration by re-hydration of calcined LDH are indirect techniques, while, the co-precipitation, hydrothermal synthesis and sol-gel methods belong to the direct synthesis (Benício et al., 2015). The co-precipitation and anion exchange methods have often been used for the formation of LDH composite (Tsai et al., 2015).

In the present work the preparation of MgAl and MgAlSn LDH with different contents of tin (5, 10 and 15 wt%) to be used in the photo-oxidation of phenol is reported. The synthesized solids were characterized by X Ray Diffraction, Nitrogen physisorption, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy/ Energy Dispersive X-Ray Spectroscopy (SEM/EDS), Transmission Electron Microscopy (TEM) and UV-Vis spectroscopy. A mechanism describing the segregation of SnO₂ from the MgAl LDH forming strong OH (radical) species during the irradiation is proposed.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite-like compounds (Mg²⁺/Al³⁺ molar ratio = 3) containing tin were synthesized by the co-precipitation method. A mixed aqueous solution of Mg(NO₃)₂·6H₂O (0.43 mol), Al(NO₃)₃·9H₂O (0.14 mol) and SnCl₄·5H₂O (5, 10 and 15 wt%) in order to obtain MgAlSn in the selected composition was put under stirring at room temperature, then an amount of urea (2.61 mol) was added. Samples were hydrolyzed at 373 K for 10 h. Afterwards, the pH was adjusted to 9.5 with 2 M solutions of NaOH and Na₂CO₃. The resulting suspension was then kept at 433 K for 36 h. The precipitate was filtered and washed several times with deionized water and dried at 353 K for 12 h. The obtained materials were labeled as MgAlSn 5%, MgAlSn 10% and MgAlSn 15% depending on the tin content. The MgAl reference LDH was prepared in the same way as for the preparation of the MgAlSn materials without adding the tin precursor. A solid SnO₂/MgAl with 15 wt% was prepared by impregnation and was compared with the LDH materials.

2.2. Characterization

X-ray Diffraction patterns were measured on a Bruker D-2 Phaser with Cu K α radiation, a crystal graphite monochromator and data were collected in a scan range from 5° to 80° with a 2 θ step of 0.01 s⁻¹. Crystallite size was calculated using the Scherrer equation $\beta = (k * \lambda) / (FWHM * \cos\theta)$ where k is a numerical factor, λ is the wavelength of the X-rays, FWHM is the full-width at half maximum of the X-ray diffraction peak in radians and θ is the Bragg angle. The diffraction patterns have been treated with Rietvel refinement method using the Topas program.

BET specific surface areas were calculated from the N₂ adsorption-desorption isotherms using a Quantachrome Autosorb-3B equipment. The solids were degassed in vacuum (10⁻⁵ Torr) at 373 K for 12 h before the analysis. The FTIR spectra were recorded in the spectral range of 4000 cm⁻¹ to 400 cm⁻¹ with a Shimadzu IR Affinity-1 spectrometer.

SEM images of the catalysts were performed in a JEOL equipment 7600F model coupled to a detector for energy dispersive X-ray spectroscopy microanalysis (SEM/EDS) to 30KV. Transmission Electron Microscopy (JEOL JEM – 2100F) equipped with a field emission gun, operating at 200 KV was used for the observation of the catalysts structure. The UV-Vis absorption spectra for the different samples were

obtained with a Cary – 100 Varian spectrophotometer equipped with an integration sphere. The E_g values of the samples was calculated by extrapolating the reflectance to the X-axis curve for $y = 0$.

2.3. Photodegradation activity

The photodegradation of phenol was studied using a solution containing 0.425 mmol/L of the pollutant in bi-distilled water. 200 mL of the solution was put in contact with 0.1 g of photocatalyst at room temperature in a made home glass container and kept under stirring. Before exposure to light the suspension was maintained in dark for 30 min to achieve the adsorption desorption equilibrium of the pollutant, after the solution was irradiated with a 254 nm Pen-Ray Lamp (4.4 mW/cm²) contained in a quartz tube immersed in the solution for 4 h. During the reaction aliquots of 4 mL was taken from the irradiated solution every 30 min using nylon filters. The evolution of the concentration of phenol as a function of time under irradiation was followed by UV-Vis spectroscopy, using a Cary 100 spectrophotometer following the absorption band at 268 nm for phenol. Total Organic Carbon analysis of the irradiated samples, was made employing a Shimadzu TOCV CSH. Photo-degradation of phenol with TiO₂-P25 and SnO₂/MgAl under the same reaction condition was carried out for comparison.

3. Results and discussion

3.1. X-ray diffraction

Diffraction patterns of the samples are showed in Fig. 1. The materials present hydrotalcite-like phases. The diffraction peaks can be observed in a hexagonal lattice with an R-3m rhombohedral symmetry (Palomares et al., 2008; Dvininov et al., 2010). In the Figure characteristic reflections (003) and (110) at 2 θ = 11.6 and 60.7 corresponding to the basal spacing and the distance between cations respectively can be seen. The lattice parameters were calculated from the position for the first basal peak appearing around 2 θ = 11 as $c = 3d_{(003)}$ and a lattice parameter was calculated from the position of the first peak of the doublet appearing around 2 θ = 60 as $a = 2d_{(110)}$ (Kishore and Rodrigues, 2007). The c parameter defines the distance of the interlamellar space related to the size of the anion and to the degree of hydration, while a lattice parameter corresponds to the distance between cations. Also in the diffractograms it can be seen the formation of segregated tin (SnO₂) which increases with the tin content in the hydrotalcite phase. In the MgAlSn 10% material it can be seen peaks at 2 θ around 13, 15 and 30; these reflections correspond to formation of hydromagnesite that is the most commonly available magnesium hydroxycarbonate (Botha and Strydom, 2001). This may be because the hydroxycarbonate

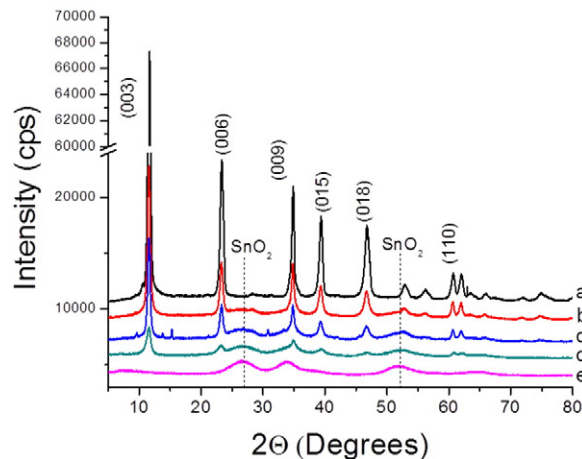


Fig. 1. X-ray diffraction patterns of LDH with different tin content: MgAl hydrotalcite (a), MgAlSn 5% (b), MgAlSn 10% (c), MgAlSn 15% (d) and SnO₂ (e).

Download English Version:

<https://daneshyari.com/en/article/1694025>

Download Persian Version:

<https://daneshyari.com/article/1694025>

[Daneshyari.com](https://daneshyari.com)