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ZnTiLDH and the derived mixed oxides as mesoporous nanoarchitectonics with photocatalytic capabilities

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Keywords

Layered Double Hydroxides, thermal treatment, mixed metal oxides, phenol, photodegradation

Abstract

Layered double hydroxides (LDHs) containing zinc and titanium with the cationic ratio of 3 were synthesized by the co-precipitation method at constant pH. The mixed metal oxides (ZnTi-MMO) obtained by the calcination of ZnTi-LDH at different temperatures were characterized together with the precursor material by X-ray diffraction (XRD), N₂ sorption, scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) and ultraviolet-

visible (UV-vis) spectroscopy techniques. The photocatalytic activity was studied for the phenol degradation in aqueous solution under UV light irradiation. The results point out that the structural transformations of the layered porous clay to the ZnTi-mixed oxides, as a function of the calcination treatment, have an important impact on the photocatalytic performances of the phenol degradation. These results may open new perspectives in tailoring the semiconductor-based capabilities of ZnTi-LDHs based nanoarchitectonics.

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Abstract

Layered double hydroxides (LDHs) containing zinc and titanium with the cationic ratio of 3 were synthesized by the co-precipitation method at constant pH. The mixed metal oxides (ZnTi-MMO) obtained by the calcination of ZnTi-LDH at different temperatures were characterized together with the precursor material by X-ray diffraction (XRD), N₂ sorption, scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) and ultraviolet-visible (UV-vis) spectroscopy techniques. The photocatalytic activity was studied for the phenol degradation in aqueous solution under UV light irradiation. The results point out that the structural transformations of the layered porous clay to the ZnTi-mixed oxides, as a function of the calcination treatment, have an important impact on the photocatalytic performances of the phenol degradation. These results may open new perspectives in tailoring the semiconductor-based capabilities of ZnTi-LDHs based nanoarchitectonics.

Keywords

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1 Introduction

The removal of the organic pollutants is nowadays a very challenging aspect of environmental technology. This requires the development of new photocatalysts with specific semiconductor properties, able to promote advanced oxidation reactions [1]. Phenol and phenolic compounds are considered some of the major organic pollutants. These pollutants are very persistent, have high toxicity even at low concentrations, partially biodegradable and tend to accumulate in the environment [2, 3]. Titania (TiO₂) is one of the most used semiconductor photocatalyst [4-7]. Due to its high chemical stability, non-toxic and cheap, the commercially available P-25 Degussa appears to be superior for the photocatalytic degradation of various organic pollutants. However, the use of pure P25 can also bring difficulties in separation from suspensions when it is used in aqueous systems and also tends to agglomerate into larger particles especially at high concentrations reducing the photocatalytic performances.

Nowadays there is an increasing research interest for tailoring LDHs nanoarchitectonics with improved photoresponsives capabilities [2, 3, 8-14]. Xia et al. just reported $MxOy/ZnTiLDHs$ as efficient photocatalytic formulations for acid 14 decomposition [15]. Further Garcia group recently introduced the novel concept of doped semiconductors based on LDHs by preparing a series of hydrotalcite zinc oxide and studying their activity for Vis-light catalytic oxygen generation [16]. The aim of this work is to study for the first time how the photocatalytic abilities of $ZnTiLDHs$ are evolving during the structural evolution, by the controlled thermal treatment, to the corresponding $ZnTiMMO$.

Layered double hydroxides (LDHs) are a family of naturally occurring anionic clays. Their structure derives from the one of brucite, in which a part of the divalent cations are replaced with trivalent or tetravalent cations in an octahedral configuration, generating positive brucite-type layers. The cationic layers are held together by interlayer counter anions forming the interlayer gallery together with the water molecules. They are represented by the empirical formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{q-}_{x/q}) \cdot nH_2O$, where: M^{2+} are divalent cations (Mg^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , etc.), M^{3+} are trivalent cations (Al^{3+} , Fe^{3+} , Ga^{3+} , Mn^{3+} , etc) and A^{q-} are interlayer anions (CO_3^{2-} , NO_3^- , etc). Calcination of these anionic clays at temperatures between 250°C and 750°C leads to the formation of mixed metal oxides (MMOs) with specific properties [17, 18, 19, 20]. Our previous research reveals that the layered double hydroxide materials can supply a good dispersion of the metal cations within the layers which may act as charge separation centers enhancing their efficiencies in catalytic applications. [2, 21, 22].

This work presents how the photocatalytic capabilities for phenol photodegradation of $ZnTi$ -layered anionic clay are evolving during the tailored structural evolution of the clay (by the controlled thermal treatment) to the derived mesoporous $ZnTi$ -based mixed metal oxides.

2 Experimental

2.1 Synthesis of $ZnTi$ -LDH sample

The $ZnTi$ -LDH sample with the cationic ratio of 3 was prepared by a co-precipitation method at constant pH [2, 13] as follows: the sample was synthesized by the slow addition of a mixed $Zn(NO_3)_2 \cdot 6H_2O$ (Acros Organics, 98%) and $TiCl_4$ (Aldrich, 99.9%) solution (1 M in total) to a Na_2CO_3 ($2 \cdot 10^{-3}$ M) solution under magnetic stirring. During the synthesis the pH value was kept constant at 7.5 by adding suitable amounts of 1 M NaOH solution. The resulting slurry was aged about 24 h at room temperature. The final product was recuperated by filtration, washed several times with distilled water and dried at room temperature over night. The sample was denoted as $ZnTi$ -LDH. After calcinations at different temperatures: 250°C, 400°C,

600°C and 750°C, for 8h, the catalysts obtained was also denoted as: ZnTi-MMO(250), ZnTi-MMO(400), ZnTi-MMO(600) and ZnTi-MMO(750).

2.2 Photocatalytic experiments

The photocatalytic activity was evaluated for the photodegradation of phenol in aqueous solution under ultraviolet irradiation. In a batch-type reactor, 0.5 g/L catalyst dose was added together with an aqueous solution of phenol with the concentration of 50 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 mixture was stirred under UV light irradiation for several hours (7.5h) using a Pen-Ray-Power Supply lamp (UVP Products) at room temperature. From time to time, 4 mL of solution were sampled and filtered in order to remove the solid phase. The phenol mineralization was controlled using UV-vis analysis following the absorbance at 270 nm, characteristic to phenol.

2.3 Characterization techniques

XRD power diffraction patterns of ZnTi-LDH and of the derived mixed metal oxides were recorded with a PANalytical XPert PRO MPD diffractometer with filtered $\text{CuK}\alpha$ radiation. Measurements were done in the 2θ mode using a bracket sample holder with a scanning speed of 0.04/4s in continuous mode. UV-vis spectra were obtained at room temperature with a Jasco V-550 Spectrophotometer with integration sphere. Thermoanalytical measurements were performed using a Perkin Elmer Pyris Diamond TG/DTA thermobalance. Samples were heated at a heating rate of 10°C/min under air flow. Fourier transform infrared (FTIR) spectra, in a KBr phase, were recorded on a Perkin Elmer Spectrum 100 spectrophotometer in the frequency range of 400–4000 cm^{-1} , at a resolution of 4 cm^{-1} . The surface area and porosity of the photocatalysts were determined on a Quantachrome Quadrasorb SI automated gas adsorption system with an AS-6 degasser. Prior to the measurements, the ZnTi-LDH sample was outgassed at room temperature for 16 h whereas the ZnTi-MMO samples were degassed at 200°C for 16 h. Afterwards N_2 -sorption was carried out at -196°C . The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area. The pore size distribution (PSD) was obtained from the adsorption branch of the isotherm using BJH (Barrett–Joyner–Halenda) method. The volume adsorbed at the relative pressure $p/p_0 = 0.97$ was used to determine the total pore volume. Scanning electron microscopy (SEM) images were recorded on a Mira TescanType Mira II LMU Electronic Microscope.

3 Results and discussion

3.1 Structural characterization of the catalysts

X-ray diffraction patterns of the a-synthesized sample ZnTi-LDH and the corresponding mixed metal oxides are shown in Fig. 1.

Fig. 1

The XRD pattern of the parent ZnTi-LDH material shows the formation of very small LDH-type crystallites of around 5 nm, as calculated using the Scherrer equation [22].

ZnTi-LDH catalyst has a rhombohedral 3R symmetry; based on Bragg's law the unit cell parameters a and c were calculated [18]. The unit cell parameter c reflects the stacking of the brucite-layers one on top of each other. The unit cell parameter a represents the cation–cation distance within the brucite-like sheets. Values of 0.31 nm and 2.12 nm for these parameters show that the obtained clay has the characteristic lamellar structure and the incorporation of Ti^{4+} in the brucite-like network was successful [10]. When exposed to a heat treatment, the ZnTi-LDH starts to decompose at $\sim 250^\circ\text{C}$; this is also revealed by thermogravimetric analysis (not shown). Thus, the XRD pattern recorded on the ZnTi-MMO(250) sample indicates the formation of zinc oxide nanoparticles with a wurtzite-type structure, the titanium species being in amorphous form. It shows the participation to a solid state reaction when the temperature increases up to 600°C giving rise to Zn_2TiO_4 with spinel crystal structure [2]. At 750°C full crystallization occurs and the XRD analysis clearly points the formation of ZnO/ Zn_2TiO_4 system.

The textural properties of the catalysts were analysed using adsorption - desorption isotherms of N_2 at -196°C and Scanning Electron Microscopy (SEM) techniques. The Figure 2 shows the N_2 sorption isotherm and the SEM micrograph of the parent ZnTi-LDH clay.

Fig. 2

The N_2 adsorption - desorption isotherm for the parent anionic clay is of Type II with a H_3 hysteresis loop. This type of isotherm is characteristic for mesoporous materials containing slit-shaped pores [12]. From the SEM image it can be observed that the ZnTi-LDH has a clear plate-like morphology characteristic for this type of materials. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The Brunauer-Joyner-Hallenda (BJH) method was applied to calculate the pore size distribution (PSD) from the adsorption branch of the isotherm. These values are included in Table 1.

Table 1

Fig. 3

Generally, a high specific surface area facilitates a good adsorption of the pollutant and enhances the generation of electron-holes pairs. Moreover, a better distribution of the pores of the catalyst favours the transport and diffusion of the species [5, 23]. Fig. 3 shows the N_2

sorption isotherm for MMO-type materials after calcination of the parent clay at different temperatures. ZnTi-MMO catalysts clearly display a type II adsorption-desorption isotherm with a H_3 hysteresis loop indicating the mesoporous features of the catalysts [24]. No limiting adsorption at higher pressure was observed, indicating the existence of macropores [9]. The PSD profiles indicate differences in the porous features between ZnTi-LDH and the derived MMO pointing out these mesoporosity features accentuated after the thermal treatment. The parent ZnTi-LDH material is characterized by smaller pores as compared with the corresponding calcined materials. The PSD profiles indicate the increase in the pore diameter up to 8.4 nm upon calcination until 400°C. This observation may be associated with the loss of the carbonate anions (cavitation) and dehydroxylation of the layers which leads to the increase in the pore size. Further calcination up to 750°C indicates less accentuated porous texture of the MMO which may be correlated with the structural transformation into the spinel-like materials with very low porosity features, increased the crystallite size and agglomeration of the particles [25].

FTIR technique is used to identify the type of anions present between the brucite-like layers of the catalysts. Fig. 4 presents the infrared spectra of the as-synthesized and the calcined samples.

Fig. 4

The band observed in the range of 3400-3450 cm^{-1} may be assigned to the characteristic vibration mode of the -OH groups in the brucite-type layers as well as to the -OH groups of the physisorbed water molecules [9, 26]. The band observed at $\sim 1620 \text{ cm}^{-1}$ is generally attributed to the bending vibration of the water H-O-H bonds between the layers [22]. The ν_3 stretching vibration appears at 1384 cm^{-1} indicating the presence of the carbonate anions between the brucite-type sheets. The $\sim 820 \text{ cm}^{-1}$ absorption band can be assigned to the stretching mode of the CO_3^{2-} in the interlayer galleries of ZnTi-LDH in a C_{2v} symmetry [21]. For the non-calcined clay, the carbonate anion can be identified also at 1500 cm^{-1} , 1030 cm^{-1} and 670 cm^{-1} . These bands are assigned to the ν_3 , ν_1 and ν_4 vibration mode, respectively [22, 26] which appears due to the increased affinity of LDHs for this anion. The lattice vibrations appear as weak bands in the region 500 – 420 cm^{-1} [19]. Upon thermal treatment, the bands corresponding to the interlayer anions decrease in intensity. At 750°C the IR spectrum does not show any characteristic bands corresponding to carbonate anions and only the vibrations of the M-O and M-O-M bonds in the mixed oxides can be observed. The FTIR results are in good agreement with the XRD results pointing out the structural transformation from the LDH-layered structure into the mixed metal oxide nanocomposites.

Information regarding the environment and the coordination state of the Zn and Ti atoms in the Zn–Ti-LDH and calcined samples were obtained using the UV–vis diffuse reflectance spectroscopy (Fig. 5).

Fig. 5

The absorption band up to 330 nm might be attributed to the ligand-to-metal charge transfer involving Zn and Ti atoms in octahedral coordination within the layered network [2, 12, 21]. Furthermore, the heat treatment at increased temperatures leads also to modifications in the spectral features of the obtained materials. It can be observed that the increase of the calcination temperature leads to a shift of both absorption maxima and edges leading to the specific differences in the band gap energies as is presented in Fig. 5 (B).

4 Photocatalytic evaluation

The photocatalytic capabilities of mesoporous semiconductor-type catalysts have been tested in the degradation process of phenol in aqueous solution under the UV radiation. The general mechanism of the studied degradation process is presented in Scheme 1. The intermediate products of degradation were identified during the test and are catechol (aromatic compound), oxalic acid and formic acid (aliphatic compounds). Considering that these intermediates might be also detected by UV-vis spectroscopy, we analysed the pure intermediate products in order to elucidate the phenol photodegradation pathway. Fig. 6 shows the shape of the absorption spectra of these intermediate products (pure reagents) at concentration of 50 mg/L.

As we previously reported [2, 13] the photodegradation reaction can be described in general as follows: phenol is converted to catechol through the phenoxy radical. The formation of this radical, in a higher or lower percentage, is depending on the characteristics of the catalyst (Fig. 7 (A)). Further, the formed catechol opens its aromatic ring and passes into oxalic acid and then formic acid. The final degradation products are CO₂ and water.

Scheme 1

Fig. 6

Before the UV irradiation of the catalysts the phenol solutions and the catalyst were vigorously stirred in dark for 30 min. This affords to establish the adsorption – desorption equilibrium between the pollutant and the catalyst surface before the catalytic process. For all the photocatalytic experiments, the catalyst dose was set at 0.5 g/L and a fixed phenol concentration of 50 mg/L was used. The UV-vis Spectrometry was employed to rationalize the phenol photodegradation process. Fig. 7 displays the UV-vis spectra of the phenol photodegradation process in the presence of ZnTi-LDH and ZnTi-MMO (A), the kinetic profile (B) and the amount of degraded phenol (C).

Under the UV irradiation the specific thermal treatment of ZnTiLDH influences the nanoarchitecture characteristics and the photocatalytic behaviour of the obtained ZnTi-MMO (Fig. 7 (A)). An increase of the intensity at 270 nm in the absorption spectra may be observed when the thermal treatment temperature increases and this may be assigned to the initial formation of the phenoxy radicals, followed by the formation of catechol which is gradually mineralized to CO₂ and H₂O. This phenomenon called hyperchromic shift was also reported by Valente et al [10] and has the character of false increased concentrations as can be seen from Fig. 7 (A). Moreover, the thermal treatment at increased temperatures leads to a decrease of the photocatalytic activity of the obtained ZnTi-MMO nanoarchitectonics (Fig. 7 (B)) which may be correlated with the loss of the -OH groups of the surface of the ZnTi-layered double hydroxides while increasing of the calcination temperature. As it was previously reported [2, 10, 13] the presence of highly hydroxylated surfaces in the ZnTi-matrix favours the photocatalytic degradation of phenol molecules and this is schematically illustrated in Scheme 2.

Scheme 2

As it can be observed from Scheme 2 for the parent ZnTi-LDH the ligand to metal-charge transfer mechanism (LMCT) is governing the phenol photodegradation mechanism; this follows the formation of the phenolate-type connections between the ligand, e. g. phenol, and the -OH groups of the LDH surface. The phenolate linkage promotes the absorption of radiation and thus the phenol photodegradation. For ZnTi-LDH catalyst the catalytic efficiency increases; this might be due to the presence on the surface of the -OH groups. Further, the irradiation of the thermal treated ZnTi-MMO catalysts, promotes the formation of the electron - hole pairs thus facilitates the formation of the radical oxidative species (HO[•] and [•]O₂⁻) which are responsible for the photodegradation of the phenol molecules [27, 28].

Fig. 7

An overview of the phenol photodegradation process can be visualized in Fig. 7 (B) and (C), where the absorbance recorded at the phenol characteristic wavelength as well as the percentages of phenol that could be decomposed can be observed. The results show that the ZnTi-LDH is endowed with the highest photocatalytic activity which might be directly a consequence of the presence of the hydroxylated groups on the catalytic surface.

5 Conclusion

The ZnTi-layered double hydroxide was prepared by the co-precipitation method at constant pH. ZnTi-MMO obtained by the controlled thermal treatment at different temperatures and also the clay matrix precursor have been characterized by various techniques in order to

investigate the physical chemical features and the photocatalytic capabilities of the studied nanocatalysts. ZnTi-LDH thermal treatment, as a function of the temperatures, alters the structural and textural properties of the catalysts and changes the energy band levels. The photocatalytic activity was tested in the process of phenol photodegradation of aqueous solutions. Results show that ZnTi-LDH owns the best efficiency for the phenol photodegradation; this might be due to the presence on the surface of OH groups and their involvement in the catalytic process. The photocatalytic performances of ZnTi-MMO are a function of the characteristics of thermal treatment that implies specific surface and structural modification of the catalysts.

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Table caption

Table 1 Textural properties, band gap energy and the total weight loss for the as-synthesized and calcined samples.

Scheme caption

Scheme 1 The schematic representation of the degradation mechanism of phenol.

Scheme 2 Schematic representation of the photodegradation mechanism.

Figure caption

Fig. 1 The XRD patterns of the (a) ZnTi-LDH, (b) ZnTi-MMO(250), (c) ZnTi-MMO(400), (d) ZnTi-MMO(600) and (e) ZnTi-MMO(750) samples

Fig. 2 Textural properties of the ZnTi-LDH sample: (a) N₂ adsorption/desorption isotherm and pore size distribution (inset picture) and (b) representative SEM image

Fig. 3 (A) N₂ adsorption/desorption isotherms and (B) pore size distribution for ZnTi-MMO(250), ZnTi-MMO(400), ZnTi-MMO(600) and ZnTi-MMO(750) samples

Fig. 4 The FTIR spectra of (a) ZnTi-LDH, (b) ZnTi-MMO(250), (c) ZnTi-MMO(400), (d) ZnTi-MMO(600) and (e) ZnTi-MMO(750) samples

Fig. 5 The UV-vis spectra (A) and plots of $(\alpha h\nu)^2$ vs. $h\nu$ (B) for (a) ZnTi-LDH, (b) ZnTi-MMO(250), (c) ZnTi-MMO(400), (d) ZnTi-MMO(600) and (e) ZnTi-MMO(750) samples

Fig. 6 The absorption spectra of the intermediate products (pure reagents) at a concentration of 50 mg/L

Fig. 7 (A) UV-vis spectra of phenol photodegradation process in the presence of ZnTi-LDH, ZnTi-MMO(250), ZnTi-MMO(400), ZnTi-MMO(600), ZnTi-MMO(750), (B) the kinetic profile and (C) the amount of degraded phenol

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

HQ - Hydroquinone Cat - Catechol Res - Resorcinol p-BQ - p-Benzoquinone o-BQ - o-Benzoquinone

Scheme 1

Scheme 2

Table 1 Textural properties, band gap energy and the total weight loss for the as-synthesized and calcined samples

Sample	$S_{\text{BET}}(\text{m}^2/\text{g})$	$\text{TV}_\text{P}(\text{cm}^3/\text{g})$	D_p (nm)	E_g (eV)	TWL (%)
ZnTi-LDH*	147	0.3141	5.4	3.21	25.90
ZnTi-MMO(250)	121	0.3345	8.4	3.10	8.32
ZnTi-MMO(400)	84	0.2726	8.4	3.10	5.81
ZnTi-MMO(600)	31	0.1256	-	3.14	2.53
ZnTi-MMO(750)	13	0.0341	-	3.17	2.07

* by elemental analysis: Zn (wt%= 61.17), Ti (wt%=16.1%).

S_{BET} – specific surface area calculated using the BET method, TV_p – total pore volume measured at p/p_0 of 0.97, D_p - calculated using the Scherrer equation [20], E_g – band gap energy calculated based on UV-VIS analysis, TWL – total weight lost calculated from TG/DTG measurements