Journal of Hazardous Materials 263P (2013) 67–72

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Photocatalytic degradation of 2,4-dichlorophenol with MgAlTi mixed oxides catalysts obtained from layered double hydroxides

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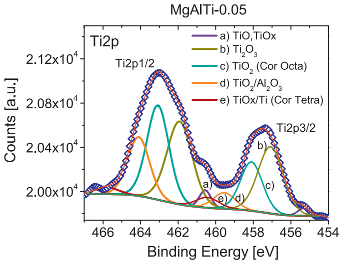
HIGHLIGHTS

- MgAl and MgAlTi mixed oxides were obtained from LDH materials synthesized by the sol–gel method.
- Ti^{4+} was incorporated to the LDH structure at low content of M^{4+}.
- MgAl and MgAlTi mixed oxides were evaluated as photocatalysts in the photodegradation of 2,4-dichlophenol.
- Very higher photodegradation of 2,4-DCP was reached with MgAl and MgAlTi mixed oxide catalysts than with P-25 TiO_2.

GRAPHICAL ABSTRACT

Two different types of Ti coordination, octahedral and tetragonal, are observed by XPS analysis of the MgAlTi mixed oxides; the presence of tetragonal coordination indicates an interaction between Ti and Al_2O_3, improving their photocatalytic properties and efficiency for the mineralization of phenol.



ARTICLE INFO

Article history:
Received 17 January 2013
Received in revised form
19 September 2013
Accepted 20 September 2013
Available online 1 October 2013

Keywords:
MgAlTi mixed oxide photocatalysts
2,4-Dichlorophenol photo-degradation
MgAlTi LDH sol–gel synthesis
MgAlTi photocatalysts
XPS analysis

ABSTRACT

MgAl and MgAlTi mixed oxides were obtained from the thermal treatment of LDH materials synthesized by the sol–gel method; these materials were characterized by N_2 physisorption, XRD, UV–vis, XPS, EDS-SEM and TEM techniques. According to the results, Ti was incorporated in the LDH layer when content in the material was low. The MgAl and MgAlTi mixed oxides were evaluated in the photo-degradation of 2,4-dichlorophenol (2,4-DCP) in the presence of UV light. A superior efficiency in the photo-degradation of 2,4-DCP, in comparison with the Degussa P-25 TiO_2 reference catalyst was observed, reaching a total decomposition of the 2,4-DCP molecule in less than 60 min. According to the results, Ti was incorporated in the LDH layer when the content in the material was low. The MgAl and MgAlTi mixed oxides were evaluated in the photo-degradation of 2,4-dichlorophenol (2,4-DCP) in the presence of UV light. A superior efficiency in the photo-degradation of 2,4-DCP with the MgAl and MgAlTi mixed oxides, in comparison with the Degussa P-25 TiO_2 reference catalyst was observed, reaching a total decomposition of the 2,4-DCP molecule in less than 60 min.

1. Introduction

Phenol and its derivatives are very toxic compounds which contribute significantly to water pollution. There are several methods reported to remove organic compounds from water: physical, chemical, biological and the denoted as Advanced Oxidation Process (AOP), which degrade these compounds using semiconductor photocatalytic materials in the presence of a light source [1–3].

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http://dx.doi.org/10.1016/j.jhazmat.2013.09.047

Most of the semiconductor materials reported in the literature as photocatalysts for the AOP are based on TiO_2 [4,5].

Nowadays, the use of mixed oxides prepared by the thermal treatment of LDH materials, as photocatalysts active for the elimination of organic compounds in aqueous medium has received considerable attention. Layered double hydroxides (LDH) also named hydrotalcites, are materials obtained from the partial replacement of Mg^{2+} by Al^{3+} ions in the brucite structure (MgOH). This substitution results in a layered structure with positive charge, which is compensated by the presence of anions as $CO_3{}^{2-}$, $NO_3{}^{-}$, $SO_4{}^{2-}$, Cl^-, OH^-, etc. and water in the interlayer space [6,7]. The formula of LDHs is $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}[A^{n-}{}_{x/n}]\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations and A^{n-} is the compensation anion. Calcination of LDHs at temperatures between 300 °C and 600 °C (depending on the cation of the LDH), leads to the formation of mixed metal oxides (MMOs), which exhibit porous structure and high thermal stability [8–10]. Because of the versatility of the chemical composition of these mixed metallic oxides as well as the high dispersion reached, LDH and MMO materials have been widely used as catalysts supports, basic catalysts, adsorbents for environmental remediation and photocatalysis [8,11–17].

Although the replacement of M^{2+} by M^{3+} ions is the most usual method to improve the catalytic properties of LDHs, it has been scarcely reported that the partial substitution of M^{2+} by M^{4+} or M^{3+} by M^{4+} with similar ionic radius [18–20], produce important changes in the photo-catalytic properties of the material. In this way, some authors report the integration of Ti on LDH materials by different methods like biotemplated synthesis [8], titanium embebed [21], impregnation [22], mechanical mixtures [23], etc. and its use as efficient photocatalysts with good results.

Keeping this in mind, the obtaining of MgAlTi mixed oxides by the thermal treatment of MgAlTi LDH materials synthesized by the sol–gel method and the evaluation of its photocatalytic properties in the photodegradation of 2,4-dichlorophenol, is presented in this paper.

2. Experimental

2.1. Synthesis of MgAl and MgAlTi LDHs

MgAl LDHs with a molar ratio Mg/Al = 3 were synthesized by the sol–gel method using $Mg(EtO)_2$, $Al(t\text{-}SecBuO)_3$ alkoxides (Aldrich) as metallic precursors and n-butanol as solvent. Subsequent preparations maintaining the same Mg/Al molar ratio were carried out by adding $Ti(n\text{-}BuO)_4$ to the precursor solution to obtain a molar concentrations of Ti^{4+} of 0.05, 0.1 and 0.3 (MgAlTi-0.05, MgAlTi-0.1 and MgAlTi-0.3, respectively). The precursor solutions were heated at 70 °C under continuous stirring during 4 h and then an aqueous solution of urea (NH_2CONH_2) with a H_2O/urea molar ratio = 2 was added to the precursor solution to carry out the hydrolysis. The solution was then kept in reflux at 90 °C during 36 h. The obtained solids were washed and filtered with distilled water at 90 °C and then dried at 80 °C for 12 h. Finally, the materials were annealed at 450 °C for 6 h at a heating rate of 1 °C per min, in order to obtain the corresponding mixed oxides.

2.2. Characterization of MgAl and MgAlTi materials

XRD powder diffraction patterns of MgAl and MgAlTi LDH synthesized materials and the respective mixed oxides were recorded at room temperature with a Siemens D500 diffractometer, using a CuKα source ($\lambda = 0.154$ nm). The diffraction intensity as a function of the angle 2θ was measured between 5° and 70°, with a 2θ step of $0.03°\,s^{-1}$. Identification of the diffraction peaks from the XRD patterns was carried out using the JCPDS database. The band gap values (E_g) of MgAl and MgAlTi mixed oxides were calculated by using a UV-Vis CARY 100 SCAN spectrophotometer with diffuse reflectance integrating sphere attachment. Specific surface area was determined from the nitrogen adsorption isotherms using the Brunauer–Emmet–Teller (BET) equation. X-ray photoelectron spectroscopic (XPS) analyses were performed using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a monochromatized AlKa X-ray source (1487 eV). The position of the O 1s peak at 531.0 eV was monitored on each sample to ensure that no binding energy shift due to charging had occurred. Narrow scans were collected at 60 eV analyzer pass energy and a 400 μm spot size. The samples were deposited on film to minimize the effects of load. The materials were analyzed by Transmission Electron Microscopy (TEM) using a JEOL JEM-2100F equipment equipped with a field emission gun, operating at 200 kV and the chemical composition of the particles was determined by Energy-Dispersive X-ray spectroscopy (EDS) using an Oxford equipment; the samples were mounted on a cooper grid coated with a carbon film.

2.3. Photocatalytic behavior evaluation

The photocatalytic activity of MgAl and MgAlTi mixed oxides and Degussa P-25 TiO_2 was evaluated using a glass homemade batch-type reactor (250 mL) with internal diameter 1.75 inch and 7.0 inch in length covered with a jacket cooling. The source of irradiation was a Pen-Ray UV lamp (254 nm and 4400 $\mu W/cm^2$), protected with a quartz tube having an outer diameter of 0.5″ and 0.35″ as inner diameter, which was immersed in the reactor. The photodegradation of 2,4-dichlorophenol in aqueous solution was carried out according to the following procedure: 0.613 mmol L^{-1} of 2,4-dichlorophenol (2,4-DCP-Aldrich) equivalent to 100 ppm was dissolved in deionized water under airflow of 1 mL s^{-1} for 1 h. An aliquot of 200 mL of this solution was put into the reactor followed by the addition of 200 mg of the mixed oxides. The reaction mixture was stirred under the airflow (1 mL s^{-1}) and then the system was irradiated using a Pen-Ray UV power supply lamp (UVP products) protected with quartz tube, with a typical wavelength of 254 nm and intensity of 4400 $\mu W/cm^2$. In order to determine the photolysis effect, the mixture of 2,4-dichlorophenol aqueous solution and catalyst was stirred during 1 h and an aliquot was sampled after this period. Then, the lamp was turned on and aliquots were sampled every 10 min during 2 h. The 2,4-dichlorophenol content in the samples was analyzed by measuring the maximum adsorption band ($\lambda = 304$ nm) using a VARIAN CARY 100 spectrophotometer equipment. The amount of organic carbon present in the solution after reaction was determined with a TOC-V CSH/CSN Shimadzu Analyzer (catalytic oxidation on Pt at 680 °C). Calibration runs were performed injecting known amounts of potassium phthalate.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD patterns of MgAl and MgAlTi LDH materials synthesized by the sol–gel method. From this figure, it is observed that MgAl, MgAlTi-0.05 and MgAlTi-0.1 LDHs show typical structures of pure MgAl layered double hydroxides; no diffraction peaks corresponding to titanium are observed in the XRD patterns suggesting that Ti^{4+} cations are well dispersed into the MgAl LDH crystalline lattice. The basal spacing parameters “a” and “c” obtained by the Bragg equation, assuming a hexagonal staking, are presented in Table 1. As it has been established by several authors [14,15], the incorporation of Ti^{4+} in the layers of LDH can be assessed from changes in the lattice parameters a and c, since, in the case of the parameter a, part of Al^{3+} (with ionic radius