

Photoassisted Degradation of 4-Chlorophenol and *p*-Cresol Using MgAl Hydrotalcites

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ABSTRACT: MgAl hydrotalcites, or layered double hydroxides (LDHs), with different Mg/Al molar ratios were synthesized by the coprecipitation method. The structure of the solids was collapsed by thermal treatment at 723 K obtaining MgAl mixed oxides with high specific surface areas (264–318 m²/g). When these oxides were put in contact with aqueous solutions containing 4-chlorophenol and *para*-cresol (80 ppm:0.62 and 0.73 mmol, respectively) the layered structure was recovered by rehydration of the material showing the named “memory effect” of LDH materials. Mg/Al LDHs were active for chlorophenol and *p*-cresol degradation under UV irradiation, being more active and selective to the mineralization of the pollutants than TiO₂ P-25 photocatalysts. Since Mg/Al hydrotalcites are not semiconductors their high photoassisted activity was surprising; this activity was explained by a photo excitation which produces mobility of charges in the lamellar structure, inducing the formation of photoactive defects.

INTRODUCTION

Chemical and petrochemical industries generate a wide variety of highly toxic organic pollutants. Phenol and its halogenated derivatives, especially chlorophenol and *para*-cresol (*p*-cresol) used in the manufacture of herbicides, bactericides, refrigerants, and other chemical products are some of the most hazardous and pollutant compounds generated by the chemical and petrochemical industrial processes.^{1,2}

There are several studies concerning the removal of these organic pollutants. Most of these works are focused on the development of new catalysts that can be used in removing pollutants from contaminated water and the oxidation of the contaminant molecules by using Advanced Oxidation Processes (AOPs).^{3–5} AOP technologies use the high reactivity of OH[·] radical in driving the oxidation process to achieve complete mineralization of the organic pollutant. The oxidant reagents can be oxygen, ozone, hydrogen peroxide, or air, and the process can be combined with UV-light.^{6–9}

In this way, among the new catalysts developed for use in removing pollutants by AOP process, hydrotalcites (or layered double hydroxides (LDHs)) seem to be good alternatives. LDHs have been recently reported as active solids for the decomposition of organic pollutants like benzene,¹⁰ phenolic compounds,^{11–13} or pesticides such as 2,4-D.¹⁴ LDHs or hydrotalcites have the general formula [M_x²⁺M_{1-x}³⁺(OH)₂xAm · zH₂O]; these materials consist of positive charged layers of brucite-like in which the M²⁺ ions are replaced by M³⁺ ions, with anions like CO₃²⁻ in the interlayer space which are responsible of compensate the positive charge. When they are calcined above 673 K, the layered structure of these compounds is collapsed and they are transformed in mixed oxides; this temperature depends on the M²⁺ and M³⁺ and ratio in the LDH material. When the calcined hydrotalcites are rehydrated they show the named “memory effect”, which consists in the recovery of its original layered

structure (Figure 1); this memory effect gives LDH materials excellent adsorptive properties of anionic compounds in aqueous solution.^{15–17}

In the present work, Mg/Al hydrotalcites with different Mg/Al molar ratios were synthesized and evaluated in the *p*-cresol and chlorophenol photodecomposition bubbling air in aqueous solution (AOP). Characterization of the solids was made by XRD, TGA-DTA, and nitrogen adsorption.

EXPERIMENTAL SECTION

Catalysts Synthesis. LDH materials with three different M²⁺/M³⁺ molar ratios were prepared by the coprecipitation method. Solutions of Mg(NO₃)₂ · 6H₂O and Al(NO₃)₃ · 9H₂O in appropriated amounts to get 40 g of each catalyst, were added dropwise in a 1-L glass reactor vessel containing 800 mL of bidistilled water; the resulting mixture was stirred vigorously using a magnetic stirrer. The pH of the final solution was adjusted to 9 by adding NH₂CONH₂ as precipitant agent. The solution was stirred during 4 h at 363 K and maintained under reflux for 36 h. The obtained materials were washed with deionized water. The solids were dried at 373 K (dried samples) for 12 h.

Finally, the materials were annealed at 723 K for 12 h in air flux 2 mL/sec (calcined samples).

Characterization of Catalysts. The specific surface areas and mean pore size diameters were obtained by the BET and BJH methods, respectively, from the nitrogen adsorption isotherms, using a Quantachrome Autosorb-3B equipment. The X-ray

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