



Synthesis and characterisation of hydrotalcites produced by an aluminium hazardous waste: A comparison between the use of ammonia and the use of triethanolamine



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ABSTRACT

Hydrotalcite-like compounds were co-precipitated with diluted sodium hydroxide from an unconventional aluminium source: the aluminium waste generated by the tertiary aluminium industry, with the assistance of ammonia and triethanolamine at pH 10. These products were characterised by several techniques (XRD, FT-IR, UV-vis-NIR, SEM, DTA-TG and BET methods) to compare results. The characterisation of products confirmed significant differences depending on basic reagent selected. Products co-precipitated with ammonia showed less crystal growth, a more significant iron content in the structure and higher internal surface area. Products from triethanolamine showed the entry of organic molecules into the layered structure. These findings were important for the improvement of methods based on waste treatment, transforming an aluminium hazardous waste into a value added product as layered double hydroxides.

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1. Introduction

Hydrotalcites belonged to a general group of materials called Layered Double Hydroxides (LDHs). LDHs were recognised as valuable materials in multiple fields as catalysts, adsorbents, flame retardants, ion exchangers, drug releasers, anticorrosives, etc. (Orthman et al., 2003; Costantino et al., 2008; Alcântara et al., 2010; Behrens et al., 2010; Rives et al., 2013; Zeng et al., 2014). In addition, examples reported in the literature concerning environmental applications increased the interest in these materials to obtain adsorbents of pollutant gases (SO₂ (Cantú et al., 2005), CO₂ (Wang et al., 2011)), catalysts for environmentally benign synthesis (Schulze et al., 2001; Sahu et al., 2013) or quasi-solid state electrolytes for dye-sensitised solar cells (Wang et al., 2013). These compounds had a general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[A_{x/m}]^{n-} \cdot m\text{H}_2\text{O}$ where M²⁺, M³⁺ were di- and trivalent cations and Aⁿ⁻ could be an inorganic anion, heteropolyacids, etc. (Cavani et al., 1991). The structure was formed by layers that were built up by the condensation of octahedral MO₆ units, as in brucite. The hydroxyl groups pointed towards the interlayer space and were shared by three octahedral cations (Morales-Serna et al., 2013). In this sense, LDHs exhibited a high specific surface area (SSA), considerable anion-exchange capacity (AEC), and a variable basal spacing to accommodate a wide range of anionic species with different sizes (Abellán et al., 2012). The co-precipitation method

was the simplest way to prepare these materials because of its reproducibility and low cost. In this method, a strong enough alkali source was usually used to precipitate the mixed solution of cations at the appropriate pH such as sodium hydroxide, ammonia, urea, triethylamine, etc. Furthermore, a considerable number of investigations were reported in the literature based on a better control of the product uniformity and particle size which could result in being key factors for final uses and applications. These studies described variations in the synthesis process from the point of view of precursors and synthesis conditions, such as the production of hydrotalcites with microwaves (Rivera et al., 2006; Benito et al., 2008), sono-assisted preparations (Climent et al., 2004; Chang et al., 2011) or sol-gel methods (Lopez et al., 1996).

The use of ammonia in hydrotalcite synthesis instead of the use of strong alkali sources such as sodium hydroxide was reported in several papers. The main advantages, when this co-precipitant agent was used, were the following: formation of compact particles because of the lower effective hydroxyl concentration, favouring the crystal growth; and ammonium ions prevented the intercalation of carbonate (Olanrewaju et al., 2000; Olf s et al., 2009). The triethanolamine molecule (TEA or TEOA, C₆H₁₅NO₃) has been reported in the literature in applications such as template, surfactant, pH modifier (basic), CO₂ adsorber or anti-corrosive. With respect to this organic molecule, very few examples based on the synthesis of hydrotalcites were documented. In this sense, this chelating agent with surfactant properties was used as auxiliary reagent that permitted the synthesis of a highly crystalline micrometric-sized hexagonal-shaped $[\text{Ni}_{1-x}\text{Fe}_x(\text{OH})_2](\text{CO}_3)_{x/2}$ ($x =$

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0.25) LDH at pH 8 and its subsequent exfoliation in formamide (Abellán et al., 2010).

The process of slag milling in the aluminium tertiary industry generated dust, which was trapped in filter sleeves used in the corresponding suction systems. Directive 2008/98/EC referred to it as hazardous waste (labelling code 100321 by the European Waste Catalogue) as a consequence of the small particle size and the release of gases such as ammonia and hydrogen. Currently, this undesired by-product must be disposed of in secure landfills due to the absence of proposals for its treatment. The synthesis of Mg/Al hydrotalcites by co-precipitation of solutions with this hazardous waste and sodium hydroxide as base was analysed recently by the authors in order to promote a feasible recovery by means of manufacturing profitable products for anticorrosive coatings (Galindo et al., 2014). In this paper, the authors evaluated a simple way to produce these materials and performed the characterisation of products. The obtained hydrotalcites suggested the presence of basal spaces made up with mixtures of chloride (predominant) and carbonate anions (minority), with textural properties in accordance with absorbent materials (type IIb isotherms) but showed extremely low particle size and high disorder in their morphology. Moreover, the use of the aluminium source prepared with the hazardous waste incorporated low amounts of iron in the products. Other attempts to analyse the synthesis of hydrotalcites with similar wastes and sodium hydroxide as co-precipitant agent indicated huge possibilities for uses such as toxic metal absorbers, specifically for arsenic (Murayama et al., 2006). However, no studies were found in the literature that dealt with the use of other co-precipitant agents, or modifiers, and their corresponding effects on the resulting products. These studies are a key factor to determine better conditions of synthesis that would allow introducing and developing new improvements for the industrial treatment of the waste.

Since these authors observed a great number of queries with no response about the preparation of hydrotalcites from waste such as: the implementation of more complex co-precipitation techniques as those aforementioned in order to produce products with better properties (crystallinity, textural, etc.) and boost the industrial treatment of the hazardous waste; effect of using bases (ammonia, TEA) with high complexing capacity in the production of high quality materials despite the high likelihood of formation of undesired by-products as a consequence of the great number of impurities associated with this waste; the implementation of easy and inexpensive modifications to obtain more purified products; the possibility of a better understanding on properties concerning the presence of impurities in hydrotalcites and evaluate the composition of the resulting material. Therefore, the working hypothesis was focused on the implementation and study of other basic reagents in the co-precipitation of hydrotalcites from hazardous waste with sodium hydroxide to obtain an easy, affordable and optimal control in products, specifically purity, crystal morphology and textural properties.

The general aim of this work was to characterise Mg/Al hydrotalcites that were prepared from an aluminium hazardous waste by co-precipitation at pH 10 with sodium hydroxide and the assistance of basic modifiers. These modifiers were aqueous solutions of ammonia 30% (m/m) and TEA 15% (v/v) that were incorporated when metals were introduced. Similar to our previous work, the aluminium source was obtained from different solutions prepared after treating the hazardous waste collected in filter sleeves from the aluminium tertiary industry (Galindo et al., 2014). Several techniques were performed to understand the benefit of these modifiers and study the presence of impurities in hydrotalcites: X-Ray Diffraction (XRD), Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), Fourier-Transformed Infrared Spectroscopy (FT-IR), Ultraviolet-visible-Near Infrared spectroscopy (UV-vis-NIR), Scanning Electron Microscopy (SEM), Differential Thermal Analysis and Thermogravimetric Analysis (DTA-TG). A secondary goal was to produce blank materials with a conventional aluminium source

(aluminium chloride) to compare results and evaluate similarities and differences among samples. This goal was useful, specifically, for the improvement of the knowledge about the production of hydrotalcites with triethanolamine due to the scarce references reported in the literature.

2. Experimental

2.1. Reagents

Magnesium chloride hexahydrate (Panreac S.A.) was the main Mg^{2+} source for the preparation of Mg-Al hydrotalcites at molar ratios of 2:1, 3:1 and 4:1. The required Al^{3+} was extracted from the hazardous waste provided by the industry of tertiary aluminium (Metalquex, S.L. – Zaragoza, Spain). This waste corresponded to the fine powders collected in filter sleeves used in the milling process of aluminium slag. Thus, the Al^{3+} precursor consisted of aluminium solutions which were obtained, and subsequently characterised, by means of the process described by the authors in our previous work (Galindo et al., 2014). The co-precipitant assistants used were both aqueous ammonia 30% (m/m) (Panreac S.A.) and aqueous solutions of triethanolamine (15% v/v) (Panreac S.A.). Furthermore, aluminium chloride hexahydrate (Panreac S.A., reagent grade) as precursor was used to prepare blank materials for comparison (samples denoted as BL).

2.2. Hydrotalcite synthesis

Hydrotalcites were synthesised by a co-precipitation method for 2 h at 80 °C under a nitrogen atmosphere (2.5 bar) and 1 h of ageing. The drop-wise addition of precursors and co-precipitant agents was carried out by means of a peristaltic pump with two separated channels. In the first channel, a 200 ml mixed aqueous solution of Al^{3+} and Mg^{2+} at the appropriate Mg/Al molar ratio was placed. In the second one, the co-precipitant agent was introduced. Both channels were pumped into a basic aqueous solution, composed of 400 ml distilled water and 1 mol/l NaOH, at constant pH 10 with vigorous stirring. When the addition of both metals and basic solutions was finished, pH measurement for co-precipitation with ammonia was 9.25 and 8.50 for TEA; therefore, more quantities of diluted sodium hydroxide and water were added to attain both constant pH 10 and final volume of 800 ml. In the meantime, a fine precipitate was observed, whose colour ranged from white to orange depending on the increasing ratio of aluminium. For products obtained with TEA, the colour intensity lowered considerably in comparison to ammonia samples. The resulting solid material was separated by filtration under pressure (at 5 bar) on GTTP Millipore filter of 0.22 µm and washed thrice with 500 ml of basic distilled water (pH 9–10) to remove the excess of chloride ions and other unreacted substances. The washing waters also presented pH 10 due to the excess of co-precipitant agent added and the transformation of ammonium ions released by waste into ammonia. These sewage waters could be reused in subsequent syntheses to reduce the required ammonia amount. Finally, the cake was dried under vacuum at 125 mbar and 80 °C for 8 h, and milled manually with a mortar. The ICP-OES analysis was performed to confirm the final Mg, Al and Fe molar ratios in all samples (measurement of 0.1 g of hydrotalcite synthesised in 100 ml aqueous HCl 10% v/v) on a Perkin Elmer Optima 3300 DV. Samples were denoted with the following codes: BL = sample prepared with aluminium chloride; W = sample prepared from waste; 2, 3, 4 = Mg/Al molar ratio proposed; NH₃ = co-precipitation assisted with ammonia; TEA = co-precipitation assisted with triethanolamine.

2.3. Sample characterisation

Samples were characterised as follows: XRD was carried out using a Bruker D8 Advance diffractometer with Cu K α radiation, from 4 to 70 °2 θ , at a scan rate of 0.02 °2 θ , 8 s per step, 40 kV and 30 mA; FTIR spectra were recorded under vacuum on Bruker IFS 66v/S in the range of

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