Applied Clay Science 95 (2014) 41–49

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Hydrotalcite-like compounds: A way to recover a hazardous waste in the aluminium tertiary industry

R. Galindo [a], A. López-Delgado [a,*], I. Padilla [a], M. Yates [b]

[a] National Centre for Metallurgical Research, CSIC, Avda./Gregorio del Amo, 8, 28040 Madrid, Spain
[b] Institute of Catalysis and Petrochemistry, CSIC, C./Marie Curie, 2, 28049 Madrid, Spain

ARTICLE INFO

Article history:
Received 18 December 2013
Received in revised form 19 March 2014
Accepted 22 March 2014
Available online 21 May 2014

Keywords:
Hydrotalcite
Layered double hydroxide (LDH)
Non-conventional aluminium source
Hazardous waste

ABSTRACT

Magnesium–aluminium hydrotalcite-like compounds at ratios of 2:1, 3:1 and 4:1 were prepared using a non-conventional aluminium source, the hazardous wastes from the aluminium tertiary industry. The method consisted in a conventional coprecipitation at constant pH 10 with magnesium chloride hexahydrate and stable solutions of Al^{3+} from dispersions of the fine powder from the sleeve filter suction system in the aluminium slag milling process. The characterisation of the resulting materials indicated that hydrotalcites were strongly dependent on the presence of iron in the layers, as well as the carbonate and chloride content in the interlayer which affected the final properties. XRD and SAED indicated low crystallinity for these materials. Furthermore, as can be seen by SEM, the formation of disordered tiny nuclei was significant causing small spherical agglomerates. The infrared spectra showed a change of symmetry in the interlayer for the different ratios and the textural data suggested the "ink-bottle shaped" mesopores and type IIb isotherms, similar to the results obtained for pillared clays, and the transition to H2 type in the hysteresis loops as a function of the higher ratio.

1. Introduction

Hydrotalcite-like compounds are a valuable and widely reported group of materials with complex structures that are composed of positively charged brucite-like layers $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$, where M^{2+} and M^{3+} are divalent and trivalent cations distributed among octahedral positions, alternating with disordered and negatively charged interlayers $[A_{x/n}]^{n-}$ formed for instance by inorganic ions, heteropolyacids, organic acids, etc. [Miyata, 1983; Cavani et al., 1991] which present a formula of type $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A_{x/n}]^{n-}\ mH_2O$. The presence of the different anions located in the interlayer region leads to distinct interlayer thicknesses which play an important role when ion exchange is desired. Furthermore, under thermal decomposition, these materials can produce stable non-stoichiometric mixed metal oxides which possess homogeneous dispersion of the elements, high specific surface areas and strong basic properties. Moreover, the "memory effect" allows the reconstruction, under mild conditions, of the original hydrotalcite structure when the calcined product contacts with a solution containing anions. These special features enable a huge number of applications with high added-value in several fields such as heterogeneous catalysts, adsorbents, flame retardants, ion exchangers, drug releasers, and anticorrosives [Choudary et al., 2000; Costantino et al., 2008; Yang et al., 2013]. Nowadays, many methods have been described in the literature for preparing these materials. In general, they refer to conventional coprecipitation by slow addition, and simultaneously under stirring, of metal nitrates/chlorides as well as precipitants (sodium hydroxide, ammonia, urea, etc.) at a fixed pH (usually from 8 to 13), or increasing the basicity of the metal solution to the corresponding pH value, followed by a long ageing time (about 1 day or more) and/or hydrothermal treatment in order to improve the crystallinity at temperatures from 60 to 140 °C; or unconventional procedures, like ultrasound assisted coprecipitation methods or ageing for instance by microwave radiation [Climent et al., 2004; Okamoto et al., 2007; Yang et al., 2007]. Since the control of textural characteristics such as particle size, porosity or degree of crystallinity leads to satisfy new requirements, other authors also have reported sol–gel synthesis, doping with other elements, use of surfactants and studies with microemulsions or micelles [Othman et al., 2006; Pérez Bernal et al., 2009; Bellezza et al., 2012; Schulze et al., 2001] with the objective of establishing a better control on the synthesis parameters and improving the resulting properties for these materials.

The slag milling process performed by the aluminium tertiary industry generates hazardous wastes whose handling is regulated by the Directive 2008/98/EC in the European Union. Briefly, the scope of this Directive is to prevent or reduce waste generation and promote the recovery as well as its use. Particularly, it considers that a hazardous waste may not be considered as non-hazardous, only by dilution to levels below the threshold values, and encourages the study of innovative re-using ways. Thus, a significant number of investigations have dealt with the recycling of hazardous wastes in order to increase their value in a whole range of activities and fields. In regard to these points, only a few papers have focused on the aluminium tertiary industry.

* Corresponding author.
E-mail address: alopezdelgado@cenim.csic.es (A. López-Delgado).

http://dx.doi.org/10.1016/j.clay.2014.03.022
0169-1317/

Table 1
P6 and P9 waste compositions (main components) obtained by XRF expressed as oxides, and contents of aluminium nitride present.

	XRF (% in mass)								Kjeldahl method (% in mass)
	Al_2O_3	MgO	Fe_2O_3	TiO_2	SiO_2	CaO	BaO	Others	AlN
P6	80.49	1.32	0.93	8.30	2.93	1.64	0.08	4.31	23.6
P9	76.85	4.14	0.38	3.21	2.56	1.96	1.38	9.52	16.0

Furthermore, authors have been concerned with recovery capabilities as aluminium precursors to obtain added-value materials, and have described waste as a complex and heterogeneous blend of several components such as corundum, spinels, aluminium nitride (in high content, from 10 to 25% in mass), metallic aluminium, quartz, calcite, and iron oxide, and also other minor oxides and salts [López-Delgado and Tayibi, 2012; López-Delgado et al., 2012]. The high content of aluminium nitride, and the presence of sulphide, can initiate a simple reaction with moisture in air, releasing ammonia and hydrogen sulphide as toxic by-products in the environment [Krnel et al., 2004].

In this context, few examples for procedures of the hydrotalcite obtained by using wastes as precursors are documented in the literature. For instance, Kuwahara et al. (2010) described appropriately the use of blast furnace slags (BFSs) as a source for the synthesis of hydrotalcite-like compounds, and zeolites. Thus in relation to this substance, authors referred BFS as a commercial waste, however, they alert about new ways of recycling due to the high increasing production which is more intense than its consumption. In fact, a lot of countries, including the European Union, consider the blast furnace slag as a by-product instead of an inert or hazardous waste [COM (2007) 59 final, 2007]. Murayama et al. (2006) prepared hydrotalcite from aluminium dross which were discharged in an aluminium secondary industry and evaluated its catalytic properties. The use of bauxite residue, a by-product of the Bayer process, as a precursor for the synthesis has also been reported [Santini and Fey, 2012].

Therefore, the aim of this work was to acquire a better understanding about the preparation and characterisation of hydrotalcites by the coprecipitation method using an alternative aluminium source as wastes. The synthesis was developed at constant and controlled pH 10. For this purpose, two samples of hazardous wastes, generated by the aluminium slag milling process in the tertiary industry and destination to secure landfill, were treated separately to provide stable aluminium solutions. These solutions were employed as precursors combined with magnesium chloride in order to obtain Mg–Al-hydrotalcites with a variable ratio. The resulting materials were characterised by several techniques such as XRD, FT-IR, DTA–TG, SEM and TEM. The specific surface area (SSA), zeta-potential and isoelectric points were also determined to complete the textural characterisation of samples.

2. Experimental

2.1. Reagents

The Mg/Al chloride–carbonated hydrotalcites produced in this study were based on Mg/Al ratios of 2:1, 3:1 and 4:1. In order to prepare these materials, magnesium chloride hexahydrate (Mg^{2+} precursor, reagent grade), and 1 mol/l sodium hydroxide (precipitant reagent) supplied by Panreac S.A. were used. The demanded Al^{3+} was provided by hazardous aluminium waste (samples denoted as P6 and P9) from a tertiary industry (Metalquex, S.L. — Zaragoza, Spain). This waste was the fine powder which came from the sleeve filter suction system in the aluminium slag milling process. Thus, the Al^{3+} precursor consisted of an aluminium solution which was obtained by the process described by Gonzalo-Delgado et al. (2011). Briefly, a 20 g sample of powdery waste was dispersed in a 200 ml hydrochloric aqueous solution (10% v/v) for 3 h at 80 °C under vigorous stirring. Then, solution was separated from solid by filtering on a GTTP Millipore filter of 0.22 μm at 5 bar. The resulting solution was adjusted to 500 ml with distilled water. Solutions were colourless or yellowish depending on the presence of other minor components such as iron. At the end, metal concentrations, Mg^{2+} as well as Al^{3+}, were analysed by atomic absorption spectroscopy (AAS), on a Varian SpectrAA 220 FS, to calculate the theoretical concentrations required for the three different ratios. Furthermore, aluminium chloride hexahydrate (reagent grade) as precursor, supplied by Panreac S.A., was used to prepare blank materials for comparison (samples denoted as BL).

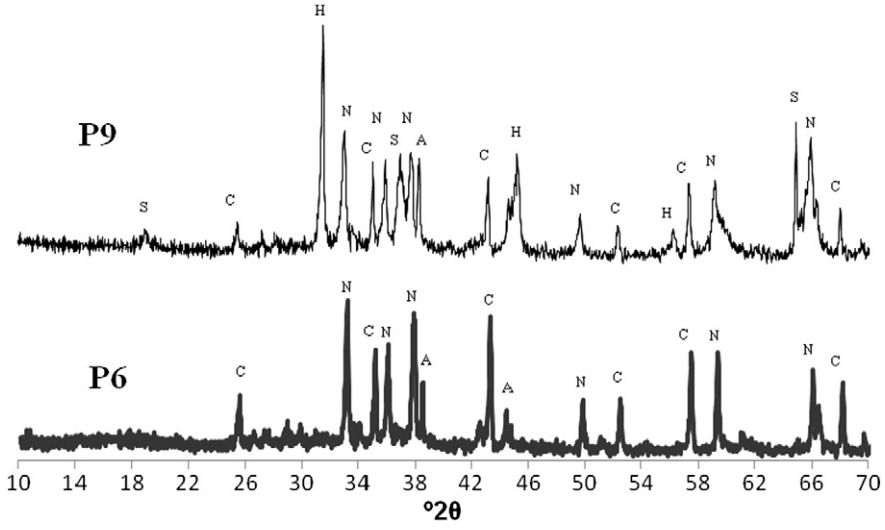

Fig. 1. XRD obtained for wastes P6 and P9 (where A = Al^0; C = Al_2O_3; N = AlN; H = NaCl; and S = $MgAl_2O_4$).