

Preparation, physicochemical characterisation and magnetic properties of Cu–Al layered double hydroxides with CO_3^{2-} and anionic surfactants with different alkyl chains in the interlayer

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Abstract

Layered double hydroxides with the hydrotalcite-like structure, containing Cu(II) and Al(III) in the layers, and different alkyl sulphonates in the interlayer, have been prepared and characterised by powder X-ray diffraction, FT-IR spectroscopy, differential thermal analysis and thermogravimetric analysis. Their magnetic properties have been also studied. Except for the sample containing octadecanesulphonate in the interlayer, for which an excess of sulphonate exists, pure crystalline phases have been obtained in the other cases. Upon heating, combustion of the organic chain takes place at lower temperature than for the corresponding sodium salts. A two-dimensional antiferromagnetic behaviour is observed at 200 K in all samples containing intercalated sulphonate. The χT value is lower for the samples containing interlayer sulphonates (with layer–layer distances in the 21–31 Å range), than for a carbonate-containing analogue (basal spacing 7.51 Å).

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1. Introduction

Layered double hydroxides, LDHs, have as general formula $[\text{M}_1^{2+}_x\text{M}_2^{3+}_{3-x}(\text{OH})_2(\text{A}^{n-})_{x/n}] \cdot y\text{H}_2\text{O}$. These materials are also called anionic clays or hydrotalcite-like compounds. The structure of these solids is derived from a brucite structure in which trivalent cations partially substitute divalent ones. This substitution gives rise to positively charged layers balanced with interlayer anions; water molecules also exist in the interlamellar region [1]. LDHs are able to host both inorganic and organic anions with different sizes in the interlayer space, and their swelling ability makes them suitable as pristine materials to prepare nanocomposite solids. The synthesis of organic–inorganic hybrid materials has been widely studied in recent years, and new methods of preparation for this kind of materials have been developed [2,3]. The organophyllic

nature of the LDHs interlayer space with surfactants as interlayer anions makes them suitable materials for the adsorption of other organic molecules or the intercalation of C_{60} molecules into the hydrophobic interlayer [4]. Among other uses, these kinds of materials are used as catalysts and as catalyst precursors after calcination at different temperatures.

Copper-containing hydrotalcites represent a rather peculiar system in this family of compounds, probably due to the well-known tendency of copper to form distorted octahedra because of a Jahn–Teller effect. Consequently, much effort has been made to prepare hydrotalcites containing copper, to be used for different purposes. So, copper hydrotalcites with carbonate as the interlayer anion have been used by Corma et al. [5] as catalyst precursors for the catalytic removal of SO_x and NO_x . The catalytic production of hydrogen by steam reforming of methanol has been carried out over several Cu-containing layered double hydroxides [6]. Cu–Al or Cu– M^{2+} –Al hydrotalcites have been also tested as catalyst

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precursors in the liquid-phase hydrogenation of cinnamaldehyde [7]. In addition, several authors have investigated the magnetic interactions within the layers in copper(II) hydroxides with different interlayer organic and/or inorganic anions, finding a dependence of the magnetic properties on the nature of the anionic species [8,9]. However, despite the growing interest of LDHs in recent years, up to our best knowledge, such a study has not been carried out on Cu-containing hydrotalcites. In this paper we report on the synthesis, characterisation and magnetic properties of a series of layered Cu–Al hydroxides intercalated with alkylsulphonates. These solids differ from each other in the length and nature of the hydrocarbon chain of the interlayer anion, and four different sulphonates have been used to prepare these materials, two of them containing an aromatic ring in the hydrocarbon chain.

2. Experimental

2.1. Synthesis of the samples

The solids were prepared by direct synthesis through coprecipitation, using NaOH as precipitation agent. All chemicals were from Fluka (Switzerland) and were used as received. Four samples containing a surfactant anion in the interlayer were prepared, in addition to a sample containing carbonate in the interlayer space, used as a reference. To synthesise the Cu–Al–carbonate sample (hereafter CAC), 200 ml of an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Cu/Al molar ratio 2) was dropwise added to 100 ml of a water solution containing the stoichiometric amount of sodium carbonate. Mixing was carried out under laboratory atmosphere and $\text{pH} = 8.3$. The pH was maintained constant by adding NaOH 1 M with a Dosimat 725 Metrohm, coupled to a Metrohm pH-meter. The suspension was stirred during 24 h in air, then centrifuged, washed with distilled water and dried at room temperature.

The anions intercalated were surfactants with different organic chains, i.e., octanesulphonic acid sodium salt, octylbenzenesulphonate acid sodium salt octyldodecylsulphonic acid sodium salt and dodecylbenzenesulphonic acid sodium salt.

To prepare the samples with the anionic surfactant (sulphonates) in the interlayer, 200 ml of a decarbonated water solution of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a Cu/Al molar ratio of 2 was prepared. This solution was dropwise added to 100 ml of a decarbonated water solution of the surfactant. The quantity of surfactant was always twice that corresponding to the exchange capacity of the layered double hydroxide to be formed (corresponding to the aluminium content). pH was maintained at 8.3 by adding NaOH 1 M during the synthesis as for the synthesis of the CAC sample above described. The suspension obtained was stirred for 24 h under an inert atmosphere (nitrogen) at room temperature, centrifuged, washed with decarbonated water

and dried under vacuum conditions, to avoid contamination by atmospheric carbon dioxide. Samples were labelled as CAOS, CAOBS, CADBS and CAC18 when the interlayer anionic surfactants were octylsulphonate ($\text{CH}_3(\text{CH}_2)_7\text{SO}_3$), octanebenzenesulphonate ($\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{SO}_3$), dodecylbenzenesulphonate ($\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3$) and octadecanesulphonate ($\text{CH}_3(\text{CH}_2)_{17}\text{SO}_3$), respectively.

3. Techniques

Element chemical analyses for Cu, Al, S and Na were carried out by atomic absorption in a Mark-2 ELL-240 apparatus at Servicio General de Análisis Químico Aplicado (University of Salamanca, Spain). The powder X-ray diffraction (PXRD) patterns were recorded using Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in a Siemens D-500 diffractometer with a DACO-MP microprocessor. Diffractograms were evaluated by means of Diffract-AT software. Differential thermal analyses (DTA) and thermogravimetric (TG) analyses for thermal stability were carried out in DTA-7 and TG-7 instruments from Perkin Elmer, respectively. The analyses were carried out under dynamic oxygen (from L'Air Liquide, Spain) atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The FT-IR spectra were recorded using the KBr pellet technique in a Perkin-Elmer FTIR-1730 spectrometer at a nominal resolution of 4 cm^{-1} and averaging 100 scans to improve the signal-to-noise ratio.

Magnetic susceptibilities of the samples were measured in a vibrating sample magnetometer (MLVSM9 MagLab 9 T, Oxford Instruments) in the temperature range between 5 and 300 K under an applied magnetic field of 0.01 T. For these measurements, the powders were packed into plastic tubes such that the axial ratio of the resulting sample was larger than 5 to avoid the correction of the data from shape demagnetising effects.

4. Results and discussion

4.1. Element chemical analyses

Table 1 summarises the Cu/Al and S/Al ratios calculated from the element chemical analysis of the samples and their corresponding formulae. These have been calculated from the element chemical analysis data and assuming that the sulphonate (or carbonate in sample CAC) is the only interlayer anion, as FT-IR spectroscopy data (vide infra) do not provide evidence of the presence of other anions (i.e., nitrate from the metal salts used to prepare the samples).

Sample CAC has a Cu/Al molar ratio of 2 and the LDHs with intercalated anionic surfactant have Cu/Al ratios just above 2, maximum deviation being ca. 15%; these values are within the range usually accepted to yield well-defined hydrotalcite-like structures [1]. The S/Al ratios found for these solids are fairly close to 1 for samples CAOS, CAOBS and CADBS. The ratio expected for this kind of

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