Materials Research Bulletin 47 (2012) 3568–3572

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Mechanochemical synthesis of layered hydroxy salts

Nygil Thomas *

Materials Research Group, Department of Chemistry, St. Joseph's College, 36 Langford Road, Bangalore 560027, India

ARTICLE INFO

Article history:
Received 3 January 2012
Received in revised form 11 May 2012
Accepted 15 June 2012
Available online 23 June 2012

Keywords:
A. Inorganic compounds
A. Layered compounds
B. Chemical synthesis
B. Intercalation reactions

ABSTRACT

A simple one minute synthesis method was adapted for the preparation of layered hydroxy salts of copper, zinc, nickel and cadmium by grinding the metal salts with sodium hydroxide in a mortar. This solvent free method is environment friendly and fast. This method could be extended to the preparation of Ni/Zn hydroxy double salts. The Ni/Zn ratio could be varied from 1.2 to 1.9 by varying the metal contents of the precursor salts without the formation of any impurities in the sample. The prepared compounds had similar characteristics as that of the samples prepared by precipitation route. No sign of carbonate contamination was observed in any of the prepared samples.

1. Introduction

LDHs (layered double hydroxides) are materials in which positively charged layers are stacked with anions intercalated in the interlayer region together with water molecules [1]. There are other layered solids like layered hydroxy salts (LHSs) also known as basic salts and alpha hydroxides which are structurally similar to LDHs [2]. LDHs and LHSs derive their structure from that of brucite, $Mg(OH)_2$. In brucite-like hydroxides, OH^- ions are hexagonally closely packed and the M^{2+} ions occupy alternate layers of octahedral sites. Thus the structure can be described as a stacking of charge neutral $M(OH)_2$ layers. In LDHs, the layer charge is developed by the partial substitution of divalent cations by trivalent ones and hydrated anions are intercalated between the layers to balance the charge [3]. In LHS, the cation composition of the layer consists of divalent metal ions. The existence of anion in such a structure can be explained by two common mechanisms. The excess layer charge can be created by the occurrence of octahedral sites which are unoccupied by cations, which are located tetrahedrally above and below the empty octahedron [4]. The uncompensated charge on the tetrahedral cations is balanced by intercalating anions in the interlayer. The second mechanism involves the substitution of a part of the hydroxide groups located above and below the layer by anions and water molecules [4]. The general formula of a layered hydroxy salt can be expressed as $M^{II}(OH)_{2-x}(A^{n-})_{x/n}\cdot nH_2O$ where M^{II} = Mg, Co, Ni, Cu; $A^{n-} = NO_3^-$, Cl^-, SO_4^{2-} etc. The interlayer spacing of these solids is determined by the size of the anion. The commonly observed values of x are 0.5, 0.67 and 1.0 [4]. LDHs and LHSs show interesting properties such as anion mobility, anion exchange and surface basicity. Due to these properties, these compounds find many applications in varied fields such as sorption, catalysis, flame-retardation, polymer stabilization, sensing, electrochemistry, photochemistry and medicine to cite a few [5–9].

There are many methods available for the synthesis of LHSs. The common method involves the hydrolysis of divalent metal salts in the presence of a metal oxide [10,11]. This method involves a long synthesis time typically from hours to days. Another method of preparation is by the controlled precipitation of metal salts by the addition of alkaline solutions [12]. A number of LHSs have been prepared by this method. This method is time consuming and generates considerable amount of waste. Many times quantitative precipitation was not observed [13]. Urea hydrolysis method is used for the preparation of LHSs of high crystalline nature [14]. The disadvantage of this method is that CO_2 produced in the decomposition of urea reacts with water and generates carbonate. This carbonate may appear as a contamination in the final sample. LHSs synthesized by polyol method were of low crystallinity and removal of polyol completely from the final product was difficult [15]. There are other methods which are not very common like heating the metal salt solution in a bomb reactor, melting reaction and hydrothermal preparation [16]. Each of the above method has its own advantages and disadvantages. One main drawback of all the above methods is the time taken to obtain the product. Since all the above methods take considerable amount of time, it will be of significance if one can develop methods with shorter preparation time.

---

* Tel.: +91 80 2221 1429; fax: +91 80 2224 5831.
E-mail address: nygill@gmail.com.

0025-5408/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2012.06.057

The mechanochemical method has been widely used to synthesize large variety of materials [17,18]. This solvent free method is rapid as well as environment friendly. There are different forms of mechanochemical activation used for the synthesis of novel materials. This synthesis method induces solid state reactions between the hydrated and hydroxide samples by grinding or milling. Li–Al LDH was prepared by a reaction between solid lithium and aluminium hydroxide in a mortar and then exposing the mixture with water vapour [19]. Recently, there are reports on the preparation of nitrate intercalated Mg–Al LDH by two step milling process [19]. Mg–Al nitrate LDHs were prepared by the mixing of metal salts and NaOH in a mortar [20,21]. In this paper, we describe the preparation of LHSs by simple grinding of a mixture which consists of metal salts and sodium hydroxide. The grinding time was kept as one minute for LHS and three minutes for HDS.

2. Experimental

2.1. Preparation of layered hydroxy salts

All the chemicals used were of pure analytical grade. The chemical formula of the salts are as follows, $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ and NaOH. 2.18 g of copper nitrate was mixed with 0.18 g of NaOH in a mortar. The mixture was ground well for 1 min using a pestle. The resultant paste was washed with water and dried at room temperature. No precautions were taken to avoid carbonate contamination during synthesis. This procedure was repeated with zinc, cadmium and nickel nitrates using same amount of nitrate salts and NaOH.

2.2. Preparation of copper hydroxy nitrate by co-precipitation

Copper hydroxy nitrate was synthesized by drop wise addition of 50 mL of sodium hydroxide (0.75 mol/L) to 20 mL boiling copper nitrate solution (3.5 mol/L) with vigorous stirring [22]. The resultant precipitate was washed and dried at room temperature.

2.3. Preparation of hydroxy double salts

Stochiometric quantities of nickel acetate, zinc acetate and NaOH (Nickel(II) acetate tetrahydrate, 99.8%, 0.59 g, Zinc(II) acetate dihydrate, 99.7%, 0.44 g and NaOH, 0.46 g) were mixed in a mortar to prepare a compound of the formula $Ni_3Zn_2(OH)_8(CH_3COO)_2{\cdot}nH_2O$. This mixture was ground well for 3 min. The paste was washed with water and dried at room temperature. Ni/Zn ratio was varied systematically to investigate if the resultant solid had the same metal ratio as that of the precursor.

2.4. Characterization

Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical Xpert Pro X-ray Diffractometer using CuKα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA, at a scanning rate of $2^\circ\,min^{-1}$. The infrared (IR) spectra of samples were collected using a Nicolet IR200 FT-IR spectrometer using KBr pellets, in the range 4000–400 cm^{-1} with 4 cm^{-1} resolution. The interlayer nitrate content was obtained by ion chromatography (IC) using a Metrohm 861 Advanced Compact ion chromatograph with Metrosep A Supp5 250 anion column and conductivity detector. The samples were dissolved in 1 mol/L acetic acid and diluted suitably for this purpose. The copper, zinc, cadmium and nickel contents of the samples were estimated by atomic absorption spectroscopy (Varion AA240). The OH content was obtained by dissolving a known weight of the sample in dilute HCl and back titrating the excess acid with standard NaOH using a pH meter.

3. Results and discussion

Fig. 1a and b shows the PXRD patterns of the product obtained on grinding copper nitrate and NaOH before and after washing with water. Both samples exhibit all the characteristic reflections of copper hydroxy nitrate and match well with the values reported in literature [23]. The sharp and symmetrical reflections at $2\theta = 12.7^\circ$ and its multiple at 25.9° were observed at same positions in both the samples. This proves without doubt that the formation of the layered compound happened during grinding itself. The PXRD patterns of the products match well with that of the control sample prepared by co-precipitation (Fig. 1c). In both the sample peaks after $2\theta = 30^\circ$ are considerably broadened due to the stacking faults. Biswick et al. indexed the PXRD pattern of the copper hydroxy nitrate based on a monoclinic lattice [23]. But the phase had a few peaks matching closely to orthorhombic phase. This well ordered sample was prepared by a hydrolysis method from hydrated copper nitrate. It is difficult to distinguish these peaks in our sample due to the peak broadening. The peaks positions are directly compared with reported powder data (ICSD CC 31353) and marked in Fig. 1. The sample obtained before washing shows three additional reflections which are due to sodium nitrate (PCPDF No. 850850) formed in the reaction medium. The washed sample was completely free from any such impurities. The basal spacing of the prepared sample was 7.0 Å and matches well with the values reported in the literature. There was

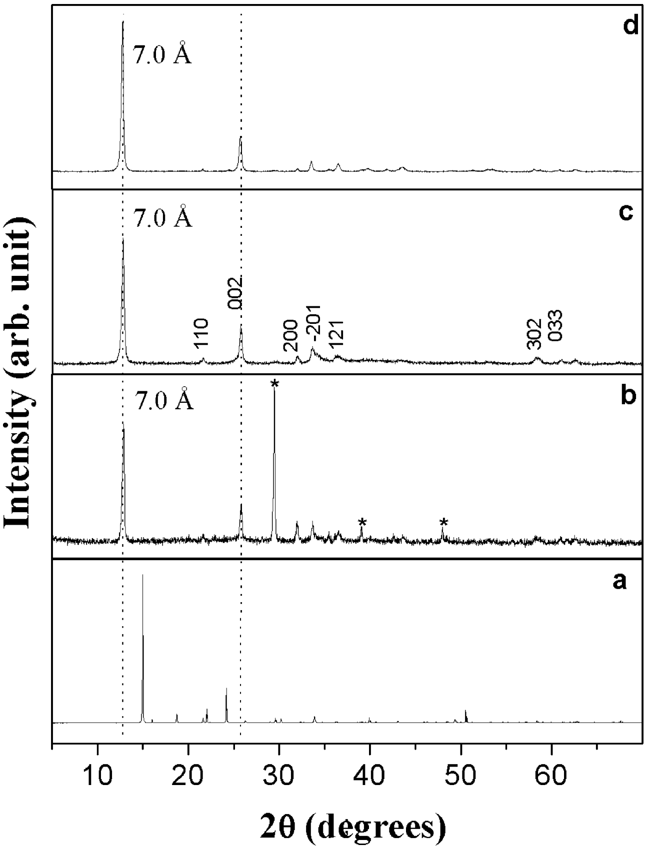

Fig. 1. PXRD patterns of the cupric nitrate (a), product obtained on grinding cupric nitrate and NaOH for 1 min before washing (b), after washing (c) and the product obtained on co-precipitation (d), reflections due to sodium nitrate impurity are marked with *.