Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Research Bulletin 40 (2005) 347–359
Materials Research Bulletin
www.elsevier.com/locate/matresbu

# Hydrothermal synthesis of Mg–Al hydrotalcites by urea hydrolysis

M. Mohan Rao*, B. Ramachandra Reddy, M. Jayalakshmi, V. Swarna Jaya, B. Sridhar

*Indian Institute of Chemical Technology, Inorganic Chemistry Division, Uppal Road, Hyderabad 500007, India*

Received 18 August 2003; received in revised form 18 October 2004; accepted 19 October 2004

**Abstract**

We report a simple method to prepare hydrotalcites involving both urea hydrolysis and hydrothermal synthetic conditions. Out of a series of Mg/Al ratios tried, pure hydrotalcite like phase was obtained for Mg/Al ratios of 1:1 and 2:1. Unlike in conventional co-precipitation method we succeeded in preparing Mg/Al ratio of 1:1 by this route. The high temperature (180 °C) applied and pressure developed in the autoclave during the synthesis might have altered the topochemical transformation. The materials were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared, thermo gravimetric and differential thermal analysis and transmission electron microscopy.


*Keywords:* A. Layered compounds; B. Chemical Synthesis; C. Infrared spectroscopy

## 1. Introduction

Hydrotalcites represented by the formula $[Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O]$ occur as a natural mineral. The applications of hydrotalcites are numerous. When synthetically prepared, these materials are called layered double hydroxides (LDHs) or hydrotalcite like compounds (HTlcs) and represented by the formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]A_{x/n}^{n}{\cdot}mH_2O$. Observed $M^{2+}$ and $M^{3+}$ cations include $Mg^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Zn^{2+}$ or $Cd^{2+}$ and $Al^{3+}$, $Cr^{3+}$, $Ga^{3+}$or $Fe^{3+}$, respectively. The value of $x$ is normally between 0.17 and 0.33 but there is no limitation. However, pure phases only exist for $0.2 \leq x \leq 0.33$. For $x$ values not in this

* Corresponding author. Tel.: +91 40 27193510; fax: +91 40 27160921.
*E-mail address:* mandapati@iict.res.in (M.M. Rao).

0025-5408/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2004.10.007

range compounds with different structures are obtained [1]. The structure of LDH can best be explained by considering structure of brucite $Mg(OH)_2$, which consists of $Mg^{2+}$ ions co-ordinated octahedrally by hydroxyl groups. In an LDH, isomorphous replacement of a fraction of the $Mg^{2+}$ ions with a trivalent cation such as $Al^{3+}$ results a positive charge on the layers, which necessitates the presence of interlayer charge balancing anions. These $M^{2+}/M^{3+}(OH)_6$ octahedra form two-dimensional sheets via edge sharing and may stack together by hydrogen bonding between the hydroxyl groups of adjacent sheets. The stacking of the repeat units constituted by an octahedral layer and an interlayer can be arranged in two ways, rhombohedral and hexagonal, and the difference being confined to the long-distance layer–layer interactions [2]. Usually synthetic hydrotalcites are reported to have hexagonal structure.

Co-precipitation is the most widely used method to prepare HTlcs. Often co-precipitated samples are subsequently subjected to hydrothermal treatment to obtain well-crystallized samples. Hydrothermal synthesis is a well-known and established method to prepare transition metal oxides, ternary systems and inorganic–organic hybrid materials [3]. A few researchers have employed hydrothermal synthesis recently to prepare HTlcs. A series of Ni–Al–Cr and Ni–Al–Fe HTlcs were prepared by co-precipitation at 60 °C, followed by hydrothermal treatment at 150 °C [4]. Direct hydrothermal synthesis of MgAl–LDH and MgCr–LDH compounds has been reported [5–7]. Costantino et al. innovated a new synthetic route to hydrotalcite (2:1) synthesis via thermally induced urea hydrolysis [8]. In this method, solid urea was added to aqueous solutions of magnesium chloride and aluminum chloride and the clear homogeneous solutions were heated under stirring at temperatures between 60 and 100 °C. The slow decomposition of urea produces an alkaline pH, which is a prerequisite for HTlc precipitation. The same author successfully used this urea method to prepare ZnAl–LDH and NiAl–LDH [9,10]. Urea hydrolysis of cobalt nitrate melts at 80 °C yielded a HTlc like Co(II,III) hydroxide and further increase in temperature produced a compound with a new phase [11]. In a recent work by Oh et al., hydrotalcite particles were prepared by two methods, urea hydrolysis and hydrothermal synthesis and the particle sizes were compared [6]. Hexagonal plates of monodispersed hydrotalcite (4:1) particles were obtained by urea hydrolysis at 120 °C. At lower temperatures particle sizes are larger while at high temperatures, particle sizes are smaller and uniform [12]. When the concentrations of metal chlorides and urea were increased, a deviation from 4:1 ratio of Mg/Al was observed.

Urea hydrolysis is basically a modification of hydrothermal method where the precipitating agent remains to be urea. The advantage of using urea against NaOH is that the urea hydrolysis progresses slowly, which leads to a low degree of super saturation during precipitation. Urea is a very weak Bronsted base. It is highly soluble in water and its controlled hydrolysis in aqueous solutions can yield ammonium cyanate or its ionic form ($NH_4^+$, $NCO^-$). Prolonged hydrolysis results in either $CO_2$ in acidic medium or to $CO_3^{2-}$ in basic medium as shown below [13].

$$H_2N - CO - NH_2 \rightarrow NH_4^+ + NCO^-$$

$$NCO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-}$$

$$NCO^- + 2H^+ + 2H_2O \rightarrow NH_4^+ + H_2CO_3$$

A homogeneous solution containing urea, Mg and Al nitrates during hydrothermal reaction may tend to undergo the following reactions resulting in the formation of hydrotalcite compounds. A hypothetical reaction scheme may be proposed as:

$$Mg(H_2O)_n^{2+} + H_2O \rightarrow Mg(OH)(H_2O)_{n-1}^+ + H_3O^+$$