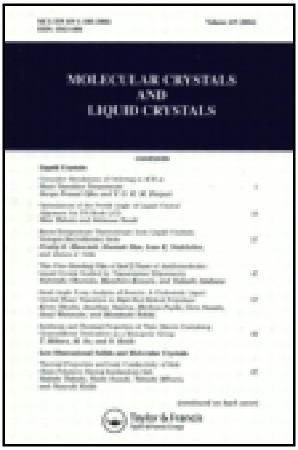

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of Hydrotalcite using Magnesium from Seawater and Dolomite

Tomohito Kameda [a] , Toshiaki Yoshioka [a] , Miho Uchida [a] & Akitsugu Okuwaki [a]

[a] Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba 07, Aoba-ku, Sendai, 980-8579, Japan

Version of record first published: 27 Oct 2006

To cite this article: Tomohito Kameda, Toshiaki Yoshioka, Miho Uchida & Akitsugu Okuwaki (2000): Synthesis of Hydrotalcite using Magnesium from Seawater and Dolomite, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 407-412

To link to this article: http://dx.doi.org/10.1080/10587250008026173

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 407-412
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Synthesis of Hydrotalcite using Magnesium from Seawater and Dolomite

TOMOHITO KAMEDA, TOSHIAKI YOSHIOKA, MIHO UCHIDA
and AKITSUGU OKUWAKI

Department of Applied Chemistry, Graduate School of Engineering,
Tohoku University, Aoba 07, Aoba-ku, Sendai, 980–8579, Japan

(In final form June 29, 1999)

Three methods of synthesizing hydrotalcite(HT) have been developed using magnesium from seawater and dolomite($MgCa(CO_3)_2$). In the first process, 1.0M Na_2CO_3solution was added to calcium ion free artificial seawater containing $AlCl_3$with an initial Mg/Al molar ratio of 2.0~3.7 until a pH of 10 was obtained. The solution was then continuously stirred for lh at 60°C. CO_3^{2-}-HT was precipitated as a single phase, and the initial Mg/Al molar ratio, which each recovery of $Mg^{2+}$and Al^{3+} from the solution was above 98%, was 2.0–2.3. In the second process, a $Ca(OH)_2$ slurry was added to artificial seawater containing $AlCl_3$ with an initial Mg/Al molar ratio of 1.0~5.0 until a pH of 10.5 was obtained, and then was stirred for 1h at 60°C. HT was also precipitated as a single phase with initial Mg/Al molar ratio 2.0~4.0. The initial Mg/Al molar ratio, which each recovery of Mg^{2+} and Al^{3+} from the solution was above 98%, was 2.2~3.3, but SO_4^{2-} and Cl^- were contained in the precipitated HT. When HT was produced using initial Mg/Al molar ratio of 3.0 at 25°C, SO_4^{2-} and Cl^-in the HT were ion-exchanged with CO_3^{2-} in a 0.05M Na_2CO_3solution for 24h at 25°C, and SO_4^{2-} and Cl^- content of the HT were decreased to 0.5 and 0.05wt%, respectively. In the third process, dolomite calcined at 1000°C was added to an $AlCl_3$ solution with an initial Mg/Al molar ratio of 1.0~2.0, and the solution was stirred for 1~4h at 25~90°C. HT was precipitated with the smallest amount of MgO and $Mg(OH)_2$ when the initial Mg/Al molar ratio was 1.5 and the solution was stirred for 4h at 90°C.

Keywords: hydrotalcite; seawater; dolomite; $Ca(OH)_2$; Na_2CO_3

INTRODUCTION

Hydrotalcite(HT)($[Mg^{2+}{}_{1-x}Al^{3+}{}_{x}(OH)_2](A^{n-})_{x/n} \cdot mH_2O$) is a layered double hydroxide with anion exchange property. HT and its calcined product (Mg-Al oxide) are often used as an anionic exchanger, catalyst, photocatalyst or precursor for the preparation of inorganic materials. Therefore, there have been numerous studies on the anion exchange or adsorption capacity and the catalytic activity of HT and its calcined product, and several studies on their use for the preservation of water environment. HT is usually produced by adding Na_2CO_3 solution or NaOH and Na_2CO_3 solutions to a mixed solution of $MgCl_2$ and $AlCl_3$1), but the production cost is quite high. There are few studies on the production of HT on a commercial scale production2)3)4)5). The aim of the present study is to examine the feasibility of a new inexpensive method to prepare HT using seawater and dolomite.

EXPERIMENTAL

Starting solution (i)Artificial seawater contained 0.41M NaCl, 0.028M Na_2SO_4, 0.053M $MgCl_2$ and 0.010M $CaCl_2$. (ii)Filtrate was obtained by adding a mixed 0.1MNa_2CO_3-0.2M$NaHCO_3$ solution to (i) until the 1.2 equivalent of calcium ion in (i) and stirring for 1h at 95℃6).

Procedures

1. The seawater and soda ash process.

1.0M Na_2CO_3 solution was added to 500 ml of (ii) containing $AlCl_3$ with an initial Mg/Al molar ratio of 2.0~3.7 until a pH of 10 was obtained, and then the solution was stirred for 1h at 60℃.

2. The seawater and slaked lime process.

0.1M(0.74%) $Ca(OH)_2$ slurry was added to 500 ml of (i) containing $AlCl_3$ with an initial Mg/Al molar ratio of 1.0~5.0 until a pH of 10.5 was obtained, and stirred for 1h at 60℃. Also, 0.6g of product prepared at 25℃ with initial Mg/Al molar ratio of 3.0 was added to 30ml of 0.01~0.05M Na_2CO_3 in a 50ml polyethylene tube and shaken at 25℃ for 1~24 h.

3. The dolomite process.

Dolomite calcined at 1000℃ for 1h was added to an $AlCl_3$ solution with an initial Mg/Al molar ratio of 1.0~2.0, and stirred for 1~4h at 25~90℃.

Precipitates were filtered, washed with water, dried at 105℃ for 24h, then were identified by X-ray diffraction(XRD). Chemical composition of filtrates and precipitates was determined by ICP-AES and ion chromatography.

RESULTS AND DISCUSSION

1. The seawater and soda ash process.

Calcium ion must be removed from seawater as $CaCO_3$ since it is an impurity that coprecipitates with HT when Na_2CO_3 solution is added to seawater containing $AlCl_3$. When a mixed Na_2CO_3-$NaHCO_3$ solution was added to (i) to prepare (ii), 3% and 96% of Mg^{2+} and Ca^{2+} were precipitated, respectively. Thus, Ca^{2+} was selectively removed from (i). Figure 1 shows XRD pattern of product precipitated from (ii) containing $AlCl_3$ with an initial Mg/Al molar ratio of 2.1 at 60℃. HT was

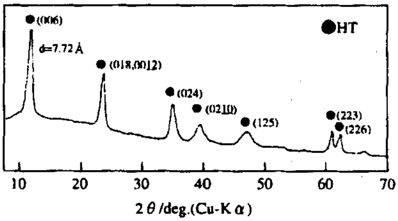

FIGURE 1 XRD pattern of product precipitated from (ii) containing $AlCl_3$ with an initial Mg/Al molar ratio of 2.1 at 60℃.

precipitated as a single phase, and Mg^{2+} and Al^{3+} were quantitatively precipitated. HT could also be precipitated as a single phase with initial Mg/Al molar ratio of 2.0~3.7, and the initial Mg/Al molar ratio, which each recovery of Mg^{2+} and Al^{3+} from the solution was above 98%, was 2.0~2.3. The unit layer distance calculated from (006) of HT shown in Figure 1 was 7.72Å. It was thought that CO_3^{2-} was intercalated into the precipitated HT since unit layer distance of HT intercalated CO_3^{2-} is 7.70Å.

2. The seawater and slaked lime process.

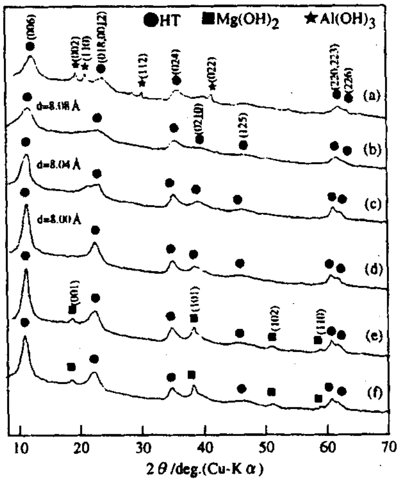

FIGURE 2 XRD patterns of products precipitated from (i) containing $AlCl_3$ with various initial Mg/Al molar ratios at 60℃.
Initial Mg/Al : (a) 1.0 (b) 2.0 (c) 3.0
molar ratio (d) 4.0 (e) 4.5 (f) 5.0

Figure 2 shows XRD patterns of products precipitated from (i) containing $AlCl_3$ with various initial Mg/Al molar ratios at 60℃. At initial Mg/Al molar ratio of 2.0~4.0 HT was precipitated as a single phase. A mixture of HT and $Al(OH)_3$ was precipitated with initial Mg/Al molar ratio of 1.0, and mixtures of HT and $Mg(OH)_2$ were precipitated with initial Mg/Al molar ratio of 4.5~5.0. Over 98% of Mg^{2+} and Al^{3+} were precipitated when the initial Mg/Al molar ratio was 2.2~3.3. Table 1 shows the contents of anions in precipitated HT. The Cl^- content of HT (b)~(d) was only 1~2wt%, but SO_4^{2-} content was 3.5~8.5wt%. Unit layer distances of HT(b)~(d) were over 8Å. It was

TABLE 1 The contents of anions in precipitated HT.
(wt%)

Initial Mg/Al molar ratio	Cl^-	SO_4^{2-}
(b) 2.0	1.18	8.27
(c) 3.0	1.73	6.55
(d) 4.0	2.13	3.87

thought that SO_4^{2-} was intercalated into precipitated HT because unit layer distance of HT intercalated SO_4^{2-} is 8.60Å. Since intercalated SO_4^{2-} and Cl^- into HT remain in the resulting Mg-Al oxide after heating, they lower anion uptake. Therefore, it is necessary to transform HT produced into CO_3^{2-}-HT. Table 2 shows E and degree of CO_3^{2-} ion-exchanged for SO_4^{2-}(6.55wt%) and Cl^-(1.32wt%) in HT produced at initial Mg/Al molar ratio of 3.0 at 25℃. E is the ratio of the moles of CO_3^{2-} added as Na_2CO_3 to the moles of SO_4^{2-} and Cl^- in HT. The greatest percent of CO_3^{2-} ion-exchanged for SO_4^{2-} and Cl^- in HT was 93.1% at E=7.1 for 24h. The SO_4^{2-} and Cl^- content of HT were decreased to 0.5 and 0.05wt%, respectively.

TABLE 2 Degree of CO_3^{2-} ion-exchanged for SO_4^{2-} and Cl^- in HT.

Time(h)	$E = \frac{[CO_3^{2-}]}{m_{SO_4^{2-}} + 2m_{Cl^-}}$	Degree of ion-exchange(%)
1	2.3	18.2
	8.7	83.7
4	2.5	75.7
	10.5	90.8
24	2.4	87.4
	7.1	93.1

$m_{SO_4^{2-}}$: Number of moles of SO_4^{2-} in HT.
m_{Cl^-} : Number of moles of Cl^- in HT.

3. The dolomite process.

HT was precipitated at an initial Mg/Al molar ratio of 1.0~2.0 at 25℃, but a large amount of $Al(OH)_3$ remained with an initial Mg/Al molar ratio of 1.0 and a large amount of $Mg(OH)_2$ remained with an initial Mg/Al molar ratio of 2.0, so 1.5 was believed to be the optimum initial Mg/Al molar ratio. Figure 3 shows XRD patterns of products precipitated from an $AlCl_3$ solution containing calcined dolomite with an initial Mg/Al molar ratio of 1.5 stirred for (a)1h and (b)4h at

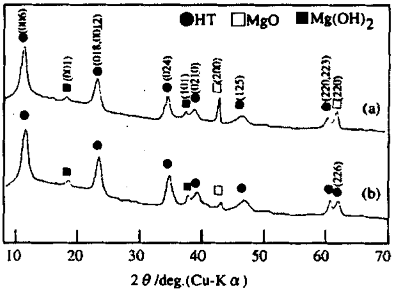

FIGURE 3 XRD patterns of products precipitated from an $AlCl_3$ solution containing calcined dolomite with an initial Mg/Al molar ratio of 1.5 stirred for (a)1h (b)4h at 90℃ .

90℃. A mixture of HT, $Mg(OH)_2$ and MgO was precipitated. The amount of MgO decreased remarkably after stirring for 4h.

These results indicate that a new method of HT preparation could be developed using magnesium from seawater and dolomite.

SUMMARY

1. In the seawater and soda ash process, Na_2CO_3 solution was added to calcium ion free artificial seawater containing $AlCl_3$ to give a final pH of 10, and stirred for 1h at 60℃. CO_3^{2-}-HT was quantitatively precipitated as a single phase with an initial Mg/Al molar ratio of 2.1.
2. In the seawater and slaked lime process, $Ca(OH)_2$ slurry was added to artificial seawater containing $AlCl_3$ to give a final pH of 10.5, and stirred for 1h at 60℃. HT was quantitatively precipitated as a single phase with an initial Mg/Al molar ratio of 3.0, and CO_3^{2-}-HT was produced by washing HT with Na_2CO_3 solution .
3. In the dolomite process, HT was precipitated by stirring an $AlCl_3$ solution containing calcined dolomite with an initial Mg/Al molar ratio of 1.5 for 4h at 90℃, but a small amount of MgO and $Mg(OH)_2$ remained.

References

[1] S. Miyata, Clays Clay Miner., **28,** 50(1980).
[2] T. Tsuboi, Jp.Patent 6/6329410,1994.
[3] C. Misra, U.S. Patent 4 904 457, 1990.
[4] W. Preston, U.S. Patent 5 250 279, 1993.
[5] K. Kosuge, A. Tsunashima and R. Otsuka, *Shigen-to-Sozai,* **10,** 108(1992).
[6] S. Ishizaka and M. Terada, *Tokyo Kogyo Shikensho Hokoku,* **52,** 201(1957).