J Mater Sci (2007) 42:2194–2197
DOI 10.1007/s10853-007-1543-8

LETTER

Preparation of a hydrotalcite-like compound using calcined dolomite and polyaluminum chloride

Tomohito Kameda · Toshiaki Yoshioka ·
Fumiko Yabuuchi · Miho Uchida · Akitsugu Okuwaki

Received: 17 December 2006 / Accepted: 22 January 2007 / Published online: 16 February 2007

A hydrotalcite-like compound (HT) is a layered double hydroxide that can perform anion exchange. A HT is represented by the general formula $[Mg^{2+}{}_{z}Al^{3+}(OH)_{2(z+1)}](A^{n-})_{1/n}\cdot mH_2O$, where A^{n-} represents an n-valent anion and $2.0 \leqq z \leqq 4.0$. A HT and its calcined material (Mg–Al oxide) have the potential to treat contaminants in wastewater. For example, a HT can uptake IO_3^-, TcO_4^-, anionic dyes, As(III), and Cr(VI) from aqueous solutions [1–7] due to the anion exchange property. The Mg–Al oxide can remove colored organics, dicamba, and terephthalate from an aqueous solution [8–10] and can treat hydrochloric acid and chloride solutions [11–16]. However, to date, HTs and Mg–Al oxide have not been used for wastewater treatment, although CO_3^{2-}-intercalated HT (CO_3^{2-}–HT) has been applied as an antacid and a flame retardant [17]. Current production methods are likely not suitable for preparing the large amounts of HTs required for commercial-scale applications to preserve water quality. In industry, CO_3^{2-}–HT has been produced using general reagents at temperatures above 80 °C and then further purified [18]. To apply HTs to water preservation and purification efforts, a simple and convenient method for preparing them must be developed.

Some researchers investigated $Mg(OH)_2$, $MgCO_3$, MgO, $NaAlO_2$, and $Al(OH)_3$ as new magnesium and aluminum sources for the production of HTs [19–21]. However, these preparation methods require very long reaction times at 95–100 °C in order to obtain pure HT crystals without by-products. In contrast, our research group has been successful in preparing pure HT crystals using calcined dolomite as new magnesium and alkali sources at 25 °C for a short time period [22]. In our new method, we used $AlCl_3$ as the aluminum source. However, a more convenient source is needed, because the $AlCl_3$ is purified reagent. In this study, to produce HTs, we investigated a polyaluminum chloride (PAC) solution, which has been used in the coagulation sedimentation process during water treatment. PAC is often-used in industrial-scale, and it is more inexpensive than other aluminum salts such as $AlCl_3$.

The PAC solution was manufactured by the Sumitomo Chemical Co. Inc. The concentrations of elements contained in the PAC solution were as follows: [Al] = 2.45 mol/L, [Mg] = 0.06 mol/L, [Ca] = 0.13 mol/L, [Cl] = 2.99 mol/L, [SO$_4$] = 0.33 mol/L. The composition of the PAC is represented as $AlMg_{0.02}Ca_{0.05}(OH)_{1.64}Cl_{1.22}(SO_4)_{0.14}$. Dolomite [$CaMg(CO_3)_2$] was supplied by Ube Material Industries, Ltd. Dolomite calcination was carried out in an electric furnace at 1,000 °C for 1 h. The contents of CaO and MgO in the calcined dolomite were 55.2% and 41.8% by weight, respectively, indicating that the composition of calcined dolomite is CaO·MgO. All general reagents were purchased from Kanto Chemical Co. Inc.

First, we attempted a mixed solution of $MgCl_2$ and PAC with initial Mg/Al molar ratios of 2.0–4.0 to produce the HTs, as expressed in Eq. (1):

T. Kameda · T. Yoshioka · F. Yabuuchi ·
M. Uchida · A. Okuwaki
Department of Applied Chemistry, Graduate School
of Engineering, Tohoku University, Aoba 07, Aoba-ku,
Sendai 980-8579, Japan

T. Kameda (✉)
Graduate School of Environmental Studies, Tohoku
University, 6-6-07 Aoba, Aramaki, Aoba-ku,
Sendai 980-8579, Japan
e-mail: kameda@env.che.tohoku.ac.jp

$$\begin{aligned}(z-0.02)Mg^{2+} + {} & (Al^{3+} + 0.02Mg^{2+} + 0.05Ca^{2+}) \\ & + 2(z+1)OH^{-} + 1/nA^{n-} \\ & \rightarrow Mg_zAl(OH)_{2(z+1)}(A)_{1/n} + 0.05Ca^{2+} \\ & \quad z = 2.0, 3.0, 4.0\end{aligned} \tag{1}$$

In this case, “$Al^{3+} + 0.02Mg^{2+} + 0.05Ca^{2+}$” was derived from the PAC. $MgCl_2$ was added to 100 mL of PAC solution containing 0.167, 0.125, or 0.1 mol/L of Al^{3+} in Mg/Al molar ratios of 2.0, 3.0, or 4.0, respectively. The total concentrations of Mg^{2+} and Al^{3+} in each solution were 0.5 mol/L. A 2 mol/L NaOH solution and deionized water were then added to the solution while stirring until the pH and total volume of the solution approached 10.5 and 150 mL, respectively. The mixture was stirred continuously at 25 °C for 1 h and then was left at 25 °C for 12 h. The resulting suspension was washed with deionized water and centrifuged repeatedly; the precipitate was dried at 105 °C for 24 h.

Second, we attempted the PAC and calcined dolomite to produce the HTs, as expressed in Eq. (2):

$$\begin{aligned}(0.5z + 0.1175)(CaO \cdot MgO) + (0.5z - 0.1375)Mg^{2+} + (Al^{3+} + 0.02Mg^{2+} + 0.05Ca^{2+}) + (z + 0.235)H_2O \\ + 1.53OH^{-} + 1/nA^{n-} \rightarrow Mg_zAl(OH)_{2(z+1)}(A)_{1/n} + (0.5z + 0.1675)Ca^{2+} \qquad z = 2.0, 3.0, 4.0\end{aligned} \tag{2}$$

In this case, “CaO·MgO” was derived from the calcined dolomite. $MgCl_2$ crystals and calcined dolomite were added to 100 mL of PAC solution containing 0.167, 0.125, or 0.1 mol/L of Al^{3+} in Mg/Al molar ratios of 2.0, 3.0, or 4.0, respectively, according to Eq. (2).

The precipitates were identified using X-ray diffraction (XRD) by CuKα radiation. The Mg^{2+} and Al^{3+} concentrations in the precipitates were ascertained using ICP-AES after dissolving the sample in 1 M HNO_3. The concentrations of Cl^- and SO_4^{2-} were determined using ion chromatography (DIONEX QIC).

Figure 1 and Table 1 show the XRD patterns and molar ratios of Mg/Al, Cl/Al, and SO_4/Al for precipitates prepared from a mixed solution of $MgCl_2$ and PAC at various Mg/Al molar ratios, respectively. Based on Fig. 1, the XRD peaks at all Mg/Al molar ratios were ascribed to hydrotalcite (JCPDS card 22-700), a hydroxycarbonate of magnesium and aluminum formulated as $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ that occurs in nature. This indicated that the prepared precipitates had the structure of a HT. As shown in Table 1, the precipitates contained Cl^- and SO_4^{2-}, which were derived from $MgCl_2$ and PAC. Accordingly, the precipitates were definitely HTs intercalated with Cl^- and SO_4^{2-}. For all initial Mg/Al molar ratios, Cl/Al molar ratios were larger than SO_4/Al molar ratios; that is, the content of Cl^- was larger than that of SO_4^{2-}. Therefore, the basal spacing, d(003), values of the precipitates shown in Fig. 1 were very close to the spacing values of the Cl^--intercalated HT (Cl^-–HT) reported in our previous work and by Sato et al. [13, 23, 24]. This confirmed that the precipitates consisted mainly of Cl^-–HT. Consequently, PAC was found to be a potentially useful aluminum source for preparing HTs.

Table 1 shows that the Mg/Al molar ratios of the precipitates did not correspond to the initial values of the starting solutions. For initial Mg/Al molar ratios of 2.0 and 3.0, the ratios in the precipitates were larger than the initial values, suggesting that Al^{3+} remained in solution. In contrast, Mg^{2+} definitely remained in solution at the initial Mg/Al molar ratio of 4.0 because the ratio in the precipitate was lower than the initial value. These results indicate that the reaction leading to HT formation probably did not reach equilibrium. Furthermore, the Mg/Al molar ratios in the precipitates tended to be close to 3.0 [25], suggesting that the stable Mg/Al molar ratio in HT is 3.0. This may have resulted because the Mg/Al molar ratio in natural hydrotalcite is 3.0. As shown in Fig. 1, the crystallinity of the precipitate decreased as the initial Mg/Al molar ratio decreased [22, 25], which can be attributed to the disordered brucite-like octahedral layer distances of the HT accompanied by the increased Al^{3+}content incorporated into that layer.

In the case involving $MgCl_2$, PAC, and NaOH, the HT was most likely formed by the reaction of Mg^{2+} and $Al(OH)_4^-$. For the Al species, $Al(OH)_3$ may be produced due to the dropwise addition of NaOH solution to a mixed solution of $MgCl_2$ and PAC to a pH of 10.5 because PAC can create polymers of aluminum hydroxides. $Al(OH)_4^-$ is certainly formed by the dissolution of $Al(OH)_3$ due to the high local pH caused by

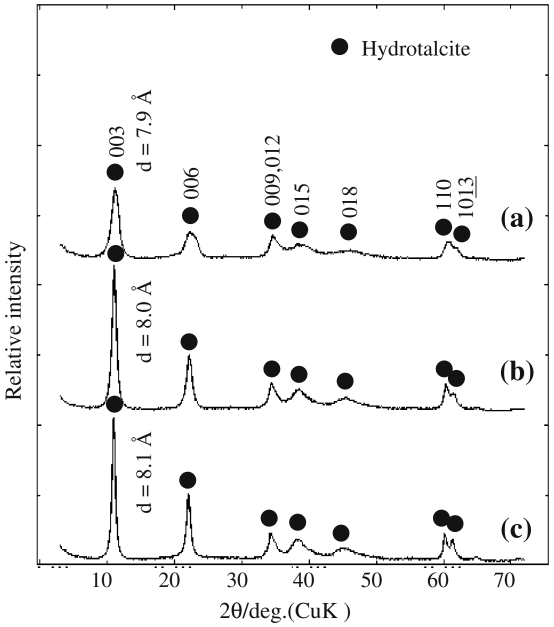

Fig. 1 XRD patterns of precipitates prepared from a mixed solution of $MgCl_2$ and PAC. Initial Mg/Al molar ratios: (**a**) 2.0, (**b**) 3.0, and (**c**) 4.0

Table 1 Molar ratios of Mg/Al, Cl/Al, and SO_4/Al for precipitates prepared from a mixed solution of $MgCl_2$ and PAC with initial Mg/Al molar ratios of 2.0, 3.0, and 4.0

Initial	Precipitate		
Mg/Al	Mg/Al	Cl/Al	SO_4/Al
2.0	2.71	0.40	0.08
3.0	3.29	0.64	0.08
4.0	3.70	0.66	0.07

adding the NaOH solution. This $Al(OH)_4^-$ was reacted with Mg^{2+}, leading to the HT formation.

Figure 2 shows the XRD patterns of precipitates prepared from calcined dolomite and a mixed solution of $MgCl_2$ and PAC. For all Mg/Al molar ratios, the XRD patterns indicated the formation of a HT. In particular, $Al(OH)_3$ also formed at the Mg/Al molar ratios of 3.0 and 4.0. The HT was produced without by-products only for the Mg/Al molar ratio of 2.0, and the molar ratios of Mg/Al, Cl/Al, and SO_4/Al were 2.16, 0.24, and 0.13, respectively.

The calcined dolomite (CaO·MgO) is immediately hydrated after its addition to the mixed solution of $MgCl_2$ and PAC. A HT would be formed by the reaction of $MgOH^+$ and $Al(OH)_4^-$. The $MgOH^+$ is an intermediate produced in the hydration process of the MgO component of CaO·MgO. The CaO component is converted into $Ca(OH)_2$ due to the hydration, which leads to the increase in the pH of the solution. This results in the production of $Al(OH)_4^-$ through the formation of $Al(OH)_3$ derived from Al^{3+} in PAC.

The production of $Al(OH)_3$ was observed for initial Mg/Al molar ratios of 3.0 and 4.0, which may be interpreted as follows. With an increasing initial Mg/Al molar ratio, the amount of added CaO·MgO increased as expressed in Eq. (2), which caused the prompt hydration of MgO. Therefore, the $Al(OH)_4^-$ was not sufficiently reacted with the $MgOH^+$. Because of the consumption of OH^- in the formation of a HT, the pH of the solution decreases. Accordingly, the remaining $Al(OH)_4^-$ converts into $Al(OH)_3$. As seen in Fig. 2, the intensity ratio of $Al(OH)_3$ to HT was observed to decrease with increases in the initial Mg/Al molar ratio, indicating that the precipitate for the initial Mg/Al molar ratio of 4.0 scarcely contained $Al(OH)_3$. This suggests that the pH of the solution did not decrease substantially until the stable region of $Al(OH)_3$ formation [26] due to the large amount of OH^- derived from the CaO·MgO.

In summary, a HT was prepared with PAC as a new aluminum source at ambient temperature, and also with PAC and calcined dolomite as magnesium and alkali sources. This method mainly produced Cl^-–HT, which can be used for anion exchange with, for example, phosphate ions [27, 28]. Furthermore, Cl^-–HT can be transformed by calcination at 400–600 °C

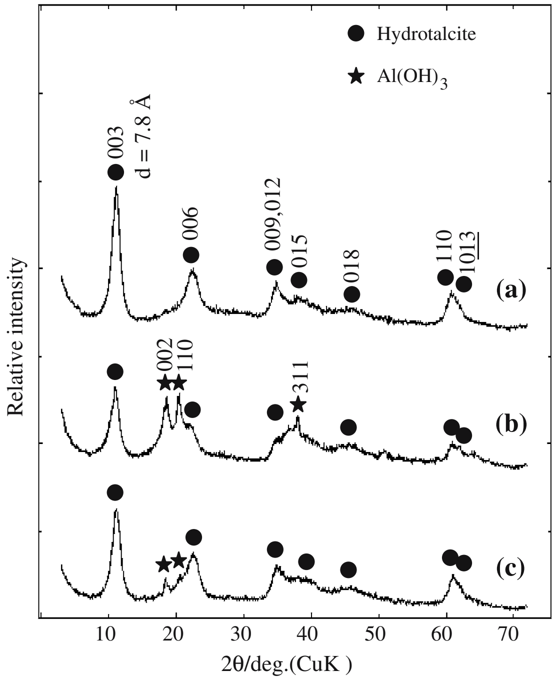

Fig. 2 XRD patterns of precipitates prepared from calcined dolomite and a mixed solution of $MgCl_2$ and PAC. Initial Mg/Al molar ratios: (**a**) 2.0, (**b**) 3.0, and (**c**) 4.0

[24] into Mg–Al oxide, which can be applied for wastewater treatment.

References

1. Manju GN, Gigi MC, Anirudhan TS (1999) Indian J Chem Technol 6:134
2. Houri B, Legrouri A, Barroug A, Forano C, Besse JP (1999) J Chim Phys 96:455
3. Manju GN, Anirudhan TS (2000) Indian J Environ Health 42:1
4. Toraishi T, Nagasaki S, Tanaka S (2002) Appl Clay Sci 22:17
5. Lazaridis NK, Karapantsios TD, Georgantas D (2003) Water Res 37:3023
6. Zhu MX, Li YP, Xie M, Xin HZ (2005) J Haz Mater B120:163
7. Wang Y, Gao H (2006) J Colloid Interf Sci 301:19
8. Crepaldi EL, Tronto J, Cardoso LP, Valim JB (2002) Colloids Surf A: Physicochem Eng Aspects 211:103
9. You YW, Zhao HT, Vance GF (2002) Appl Clay Sci 21:217
10. Orthman J, Zhu HY, Lu GQ (2003) Sep Purif Technol 31:53
11. Kameda T, Miyano Y, Yoshioka T, Uchida M, Okuwaki A (2000) Chem Lett 29:1136
12. Kameda T, Yoshioka T, Uchida M, Miyano Y, Okuwaki A (2002) Bull Chem Soc Jpn 75:595
13. Kameda T, Yabuuchi F, Yoshioka T, Uchida M, Okuwaki A (2003) Water Res 37:1545
14. Kameda T, Yoshioka T, Mitsuhashi T, Uchida M, Okuwaki A (2003) Water Res 37:4045
15. Kameda T, Yoshioka T, Hoshi T, Uchida M, Okuwaki A (2005) Sep Purif Technol 42:25
16. Kameda T, Yoshioka T, Hoshi T, Uchida M, Okuwaki A (2006) Sep Purif Technol 51:272
17. Cavani F, Trifiro F, Vaccari A (1991) Catal Today 11:173
18. Kumura T, Imataki N, Hasui K, Inoue T, Yasutomi K (1971) Jpn. Patent 46/2280
19. Mirsa C U.S. (1990) Patent 4 904 457
20. Tsuboi T, Midera T, Kabeya R (1994) Jpn. Patent 6/329410
21. Kasai T, Mizota T (1996) Shigen Sozai 112:131
22. Kameda T, Yoshioka T, Uchida M, Okuwaki A (2002) J Mater Sci Lett 21:1747
23. Sato T, Wakabayashi T, Shimada M (1986) Ind Eng Chem Prod Res Dev 25:89
24. Kameda T, Yoshioka T, Watanabe K, Uchida M, Okuwaki A (in press) Appl Clay Sci
25. Kameda T, Yoshioka T, Uchida M, Okuwaki A (2000) Mol Cryst Liq Cryst 341:407
26. Pourbaix M (1974) Atlas of electrochemical equilibria in aqueous solutions. National Association of Corrosion Engineers, Houston 171 pp
27. Shin H, Kim M, Nam S (1996) Water Sci Technol 34:61
28. Kawamoto A, Ookubo A, Sato T, Suzuki T (1999) Mizu Kankyou Gakkaishi 22:75