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Thermal decomposition of SO_4^{2-}-intercalated Mg–Al layered double hydroxide

Elimination behavior of sulfur oxides

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Abstract The thermal properties of SO_4^{2-}-intercalated Mg–Al layered double hydroxide (SO_4·Mg–Al LDH) were investigated using simultaneous thermogravimetry–mass spectrometry (TG–MS), and the elimination behavior of sulfur oxides from this double hydroxide was examined. The TG–MS results showed that SO_4·Mg–Al LDH decomposed in five stages. The first stage involved evaporation of surface-adsorbed water and interlayer water in SO_4·Mg–Al LDH. In the second, third, and fourth stages, dehydroxylation of the brucite-like octahedral layers in SO_4·Mg–Al LDH occurred. The fifth stage corresponded to the elimination of SO_4^{2-} intercalated in the interlayer of Mg–Al LDH, producing SO_2 and SO_3. The thermal decomposition of SO_4·Mg–Al LDH resulted in the formation of SO_2 and SO_3 at 900–1000 °C, which then reacted with H_2O to form H_2SO_3 and H_2SO_4. The elimination of sulfur oxides increased with the decomposition time and temperature. Almost all of the intercalated SO_4^{2-} was desulfurized from SO_4·Mg–Al LDH at 1000 °C; however, Mg–Al oxide was not formed due to the production of MgO and $MgAl_2O_4$.

Keywords Elimination · Sulfur oxides · Mg–Al layered double hydroxide · Thermal decomposition · TG–MS

Introduction

Mg–Al layered double hydroxide (Mg–Al LDH) is represented by the formula $[Mg_{1-x}^{2+}Al_x^{3+}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where A^{n-} is an anion, such as CO_3^{2-} or SO_4^{2-}, and x is the Al/(Mg + Al) molar ratio ($0.20 \leqq x \leqq 0.33$) [1, 2]. Mg–Al LDH consists of brucite-like octahedral layers that are positively charged due to the replacement of some Mg^{2+} units by Al^{3+}, while the interlayer anions help to maintain the charge balance. Water (H_2O) molecules occupy the remaining spaces in the interlayer. CO_3^{2-}-intercalated Mg–Al LDH (CO_3·Mg–Al LDH) can be converted to Mg–Al oxide by calcination at 450–800 °C. The formation of Mg–Al oxide is represented by the following reaction:

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + x/2CO_2 + H_2O \quad (1)$$

The resulting Mg–Al oxide undergoes rehydration and combines with anions to afford the original LDH structure, as shown in the following equation:

$$Mg_{1-x}Al_xO_{1+x/2} + x/nA^{n-} + (1 + x/2)H_2O \rightarrow Mg_{1-x}Al_x(OH)_2A_{x/n} + xOH^- \quad (2)$$

Frost's review presents that the thermal decomposition of CO_3·Mg–Al LDH, which is the representative LDH, occurs in three steps: (i) removal of adsorbed water, (ii) elimination of the interlayer structural water, and (iii) simultaneous dehydroxylation and decarbonation of the hydrotalcite framework [3]. Mg–Al LDH and Mg–Al oxide can be used as an adsorbent for the removal of anionic pollutants in aqueous solution [4–9]. The abovementioned rehydration and subsequent combination of Mg–Al oxide with anions in solution are accompanied by the release of OH^-. Previously, we have found that Mg–Al oxide is excellent for the treatment of mineral acids, such as H_3PO_4, H_2SO_4, HCl, and HNO_3 [10]. That is, Mg–Al oxide can neutralize and fix PO_4^{3-}, SO_4^{2-}, Cl^-, and NO_3^- in the interlayer of reconstructed Mg–Al LDH.

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Treatment of HCl with Mg–Al oxide results in the reconstruction of Cl^--intercalated Mg–Al LDH (Cl·Mg–Al LDH). We also found that the thermal decomposition of Cl·Mg–Al LDH produced HCl with the reformation of Mg–Al oxide [11, 12]. The treatment of HNO_3 with Mg–Al oxide results in the reconstruction of NO_3^--intercalated Mg–Al LDH (NO_3·Mg–Al LDH). The NO_3·Mg–Al LDH produces NO_2 during its thermal decomposition, which reacts with H_2O and O_2, forming HNO_3 and HNO_2 [13]. The treatment of H_2SO_4 with Mg–Al oxide results in the reconstruction of SO_4^{2-}-intercalated Mg–Al LDH (SO_4·Mg–Al LDH). In practical waste H_2SO_4 treatment, the produced SO_4·Mg–Al LDH must be further treated in order to reduce the solid waste. One of the treatment is the calcination of SO_4·Mg–Al LDH. Therefore, it is necessary to examine in detail the thermal decomposition behavior of SO_4·Mg–Al LDH and the elimination of sulfur oxides.

In this study, we investigated the thermal properties of SO_4·Mg–Al LDH by simultaneous thermogravimetry–mass spectrometry (TG–MS). Additionally, we investigated the thermal decomposition of SO_4·Mg–Al LDH in air to determine the effect of temperature on the elimination behavior of sulfur oxides.

Experimental

Preparation

SO_4·Mg–Al LDH was prepared by the co-precipitation method, as expressed in Eq. 3.

$$0.71Mg^{2+} + 0.29Al^{3+} + 0.14\ SO_4^{2-} + 2\ OH^- \rightarrow Mg_{0.71}Al_{0.29}(OH)_2(SO_4)_{0.14} \quad (3)$$

The Mg–Al solution (0.36 M $MgSO_4$ + 0.14 M $Al_2(SO_4)_3$) was prepared by dissolving $MgSO_4$ (0.089 mol) and $Al_2(SO_4)_3$ (0.018 mol) in 250 mL of deionized water. The Mg–Al solution was added dropwise to 250 mL of 0.14 M Na_2SO_4 solution at 30 °C with mild agitation. The solution pH was adjusted to 10.5 by adding 0.5 M NaOH solution. The mixture was then stirred continuously at 30 °C for 1 h. The SO_4·Mg–Al LDH formed was isolated by filtration and the resulting suspension was washed thoroughly with deionized water and dried under reduced pressure (133 Pa) at 40 °C for 40 h. The SO_4·Mg–Al LDH crystals were ground into a powder using a mortar and pestle, and then characterized by X-ray diffraction (XRD) using a Rigaku RINT-2200VHF diffractometer (Rigaku Corp., Tokyo, Japan) with Cu Kα radiation at 40 kV and 20 mA (scan rate: 2° min^{-1}). The SO_4·Mg–Al LDH was dissolved in 1 M HNO_3, and analyzed for Mg^{2+} and Al^{3+} using inductively coupled plasma–atomic emission spectrometry (ICP–AES). The SO_4·Mg–Al LDH was also dissolved in 0.1 M HCl, and analyzed for SO_4^{2-} using a Dionex DX-120 ion chromatograph equipped with an AS-12A column (eluent: 2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$; flow rate: 1.3 mL min^{-1}).

Thermal properties of SO_4·Mg–Al LDH

A 10-mg sample of SO_4·Mg–Al LDH was analyzed by simultaneous TG (Seiko Instruments TG/DTA 6200) and MS (Hewlett Packard 5973) at a heating rate of 5 °C min^{-1} in a He flow rate of 100 mL min^{-1}. The decomposition products were introduced to the MS ion source through an inactivated stainless steel capillary tube heated at 300 °C to prevent condensation of the evolved products.

Elimination behavior of sulfur oxides from SO_4·Mg–Al LDH

The experimental apparatus used to study the thermal decomposition of SO_4·Mg–Al LDH is illustrated in Fig. 1. An aluminum boat containing 0.5 g of SO_4·Mg–Al LDH was inserted in a quartz reaction tube, which was placed in an electric furnace. SO_4·Mg–Al LDH decomposed at 800–1000 °C at an air flow rate of 50 mL min^{-1}. The

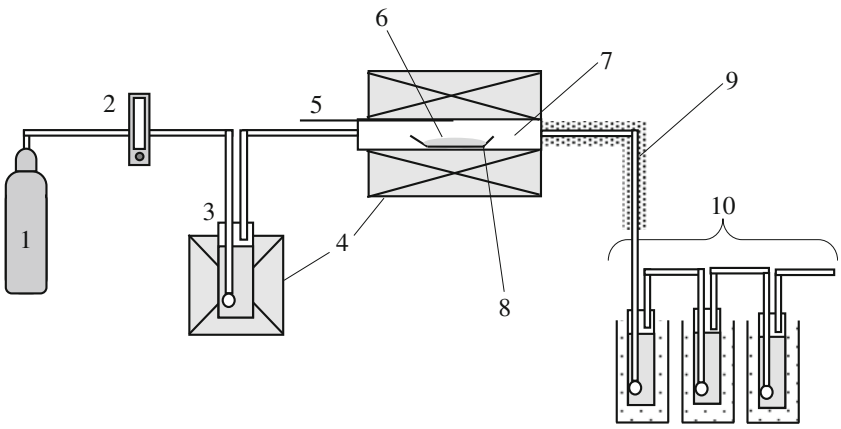

Fig. 1 Experimental apparatus used for thermal decomposition of SO_4·Mg–Al LDH. *1* Air cylinder, *2* flow meter, *3* water vapor generator, *4* electric furnace, *5* thermocouple, *6* sample, *7* quartz reaction tube, *8* aluminum boat, *9* flexible heater, *10* water trap (0 °C)

evolved gas was collected in three water traps (0 °C) containing 30 mL of deionized water. To prevent condensation of the evolved gas, the line from the quartz reaction tube to the trap was heated to 110–140 °C using a flexible heater. Anions in the traps were quantified using an ion chromatograph. The products obtained from the thermal decomposition of SO_4·Mg–Al LDH were identified by XRD analysis. For the experiment under steam using a water vapor generator, the SO_4·Mg–Al LDH was decomposed for 2 h under air flow containing water vapor (partial pressure: 30%) at 50 mL min^{-1}.

Results and discussion

Preparation

The XRD patterns obtained for SO_4·Mg–Al LDH (Fig. 2) were ascribed to hydrotalcite (JCPDS card 22-700), a naturally occurring hydroxycarbonate of magnesium and aluminum ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$), and revealed that SO_4·Mg–Al LDH has an LDH structure. The basal spacing (d_{003}) of 8.7 Å was similar to that of SO_4·Mg–Al LDH (8.6 Å) reported by Sato et al. [14], suggesting the intercalation of SO_4^{2-} in the interlayer of prepared Mg–Al LDH. Table 1 lists the chemical composition of SO_4·Mg–Al LDH. The molar ratios of Mg/Al and SO_4/Al were 2.6 and 0.60, respectively. The Mg/Al molar ratio was similar to the expected value for the preparation procedure in this study. The SO_4/Al molar ratio was 120% of the expected value, which was calculated from the neutralization of the positive charge of the Al-bearing brucite-like octahedral layers. This suggests that the SO_4^{2-} content in SO_4·Mg–Al LDH is governed by the charge balance in Mg–Al LDH, and some SO_4^{2-} is adsorbed on the surface of Mg–Al LDH. As a result, SO_4^{2-}-intercalated Mg–Al LDH was confirmed to be prepared by the co-precipitation method.

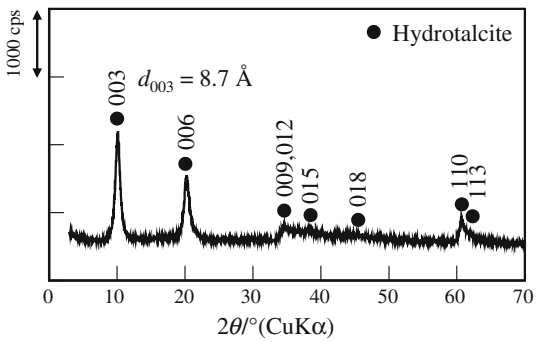

Fig. 2 XRD patterns for SO_4·Mg–Al LDH

Table 1 Chemical composition of SO_4·Mg–Al LDH

Mass%			Molar ratio	
Mg	Al	SO_4	Mg/Al	SO_4/Al
15.6	6.7	14.2	2.6	0.60

Thermal properties of SO_4·Mg–Al LDH

Figure 3 shows the TG and derivative thermogravimetry (DTG) curves for SO_4·Mg–Al LDH. The decomposition of SO_4·Mg–Al LDH occurred in the following five stages: (1) mass loss of 0–14% until 210 °C, (2) mass loss of 14–24% at 210–430 °C, (3) mass loss of 24–33% at 430–490 °C, (4) mass loss of 33–38% at 490–800 °C, and (5) mass loss of 38–42% above 800 °C. The first stage corresponded to the evaporation of surface-adsorbed water and interlayer water in SO_4·Mg–Al LDH. The second, third, and fourth stages were attributable to the dehydroxylation of the brucite-like octahedral layers in SO_4·Mg–Al LDH. The fifth stage was most probably due to the elimination of SO_4^{2-} intercalated in the Mg–Al LDH interlayers. Figure 4 shows the selected-ion mass spectra of major products formed from the thermal decomposition of SO_4·Mg–Al LDH. The mass spectrum exhibited signals at m/z 18, 32, and 64, corresponding to the molecular ion peaks of H_2O^+, O_2^+, and SO_2^+, respectively. The H_2O^+ peak in the spectrum indicated that H_2O was produced during the elimination of surface-adsorbed water and interlayer water at stage 1, the dehydroxylation of SO_4·Mg–Al LDH components whose properties were similar to those of $Al(OH)_3$ at stage 2, the dehydroxylation of SO_4·Mg–Al LDH components whose properties were similar to those of $Mg(OH)_2$ at stage 3, and the dehydroxylation of SO_4·Mg–Al LDH components whose properties were similar to those of $Al(OH)_3$ at stage 4. We have already

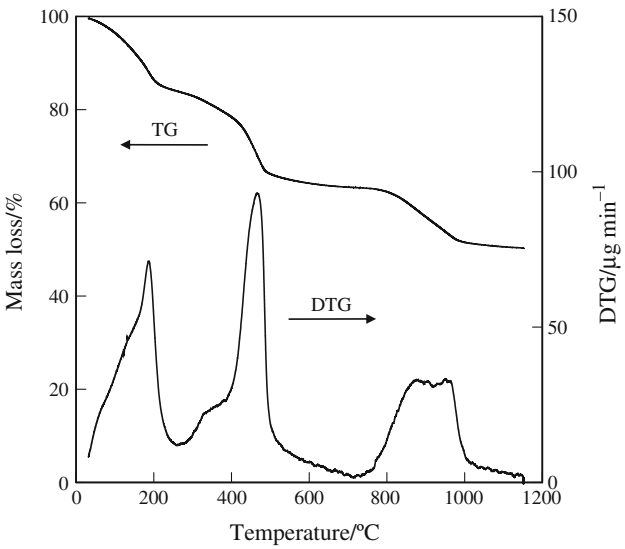

Fig. 3 TG and DTG curves for SO_4·Mg–Al LDH

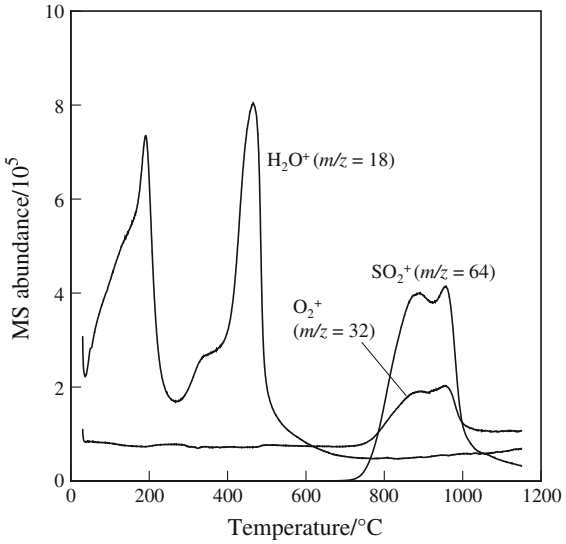

Fig. 4 Selected-ion mass spectra of major products formed in the thermal decomposition of SO_4·Mg–Al LDH

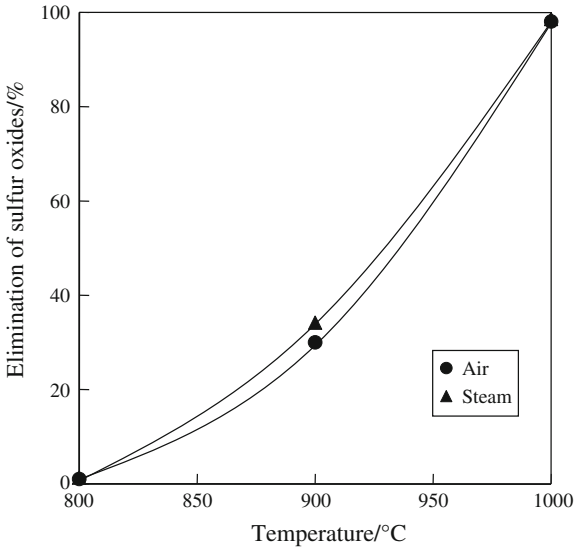

Fig. 5 Effect of temperature and atmosphere on the elimination of sulfur oxides in the thermal decomposition of SO_4·Mg–Al LDH for 2 h

clarified this division of the dehydroxylation process of Mg–Al LDH into three stages by applying MS spectra of H_2O during the thermal decomposition of $Mg(OH)_2$ and $Al(OH)_3$ [11, 13]. The SO_2^+ and O_2^+ peaks were observed over 750 °C in the mass spectra, corresponding to the fifth (decomposition) stage in the TG curve. The SO_2^+ peak corresponds to the occurrence of SO_2 and SO_3. This indicates that the mass loss of SO_4·Mg–Al LDH in the fifth stage was due to the formation of SO_2 and SO_3 by the elimination of intercalated SO_4^{2-}. The O_2^+ peak corresponds to the production of O_2, derived from the decomposition of SO_4^{2-} in SO_4·Mg–Al LDH in the fifth stage. The relationships among SO_2, SO_3, and O_2 are expressed as follows:

$$SO_3 = SO_2 + 1/2\ O_2 \quad (4)$$

In summary, the decomposition of SO_4·Mg–Al LDH proceeded in five stages. Stage 1: evaporation of surface-adsorbed water and interlayer water in SO_4·Mg–Al LDH. Stages 2, 3, and 4: dehydroxylation of the brucite-like octahedral layers in SO_4·Mg–Al LDH. Stage 5: elimination of SO_4^{2-} intercalated in the interlayer of Mg–Al LDH to produce SO_2 and SO_3.

Elimination behavior of sulfur oxides from SO_4·Mg–Al LDH

We examined the elimination behavior of sulfur oxides from SO_4·Mg–Al LDH using the experimental apparatus depicted in Figure 1 and the production of Mg–Al oxide. The temperature range examined was 800–1000 °C, corresponding to the fifth stage of the TG curve (Fig. 3). Figure 5 shows the effect of temperature and atmosphere on the elimination of sulfur oxides in the thermal decomposition of SO_4·Mg–Al LDH for 2 h. Because SO_4^{2-} and SO_3^{2-} were detected in the water traps, the unstable SO_3^{2-} was oxidized by 0.15% H_2O_2 to SO_4^{2-}, followed by quantification using ion chromatography. The elimination of sulfur oxides is expressed as the ratio of the mole percent of SO_4^{2-} in the traps to that of SO_4^{2-} in SO_4·Mg–Al LDH. In both air and steam, the elimination of sulfur oxides increased with increasing temperature, and was >98% at 1000 °C. The solutions in the traps were acidic, suggesting the production of H_2SO_3 and H_2SO_4. The thermal decomposition of SO_4·Mg–Al LDH resulted in the formation of SO_2 and SO_3. SO_2 and SO_3 then react with H_2O to form H_2SO_3 and H_2SO_4, as described in Eqs. 5 and 6, respectively.

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad (5)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (6)$$

In both cases, the thermal decomposition of SO_4·Mg–Al LDH at 800 °C did not produce sulfur oxides. The elimination of sulfur oxides in steam was similar to that in air at all temperatures. The steam did not promote the desulfurization of SO_4·Mg–Al LDH, although it did promote the dehydrochlorination of Cl·Mg–Al LDH [11]. This is related to the fact that the desulfurization of SO_4·Mg–Al LDH does not require H_2O. The thermal properties of sulfates on SO_4·Mg–Al LDH are assumed to resemble those of $MgSO_4$ and $Al_2(SO_4)_3$. The desulfurization of $MgSO_4$ and $Al_2(SO_4)_3$ is expressed as follows:

$$MgSO_4 \rightarrow MgO + SO_3 \quad (7)$$

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3 \quad (8)$$

These reactions do not require H_2O. Thus, steam did not play a role in the desulfurization of SO_4·Mg–Al LDH, in contrast to the case of the dehydrochlorination of Cl·Mg–Al LDH. Figure 6 shows the variation in the elimination of sulfur oxides with time in the thermal decomposition of SO_4·Mg–Al LDH at 1000 °C in air. The elimination of sulfur oxides increased gradually from 0 to 30 min, increased rapidly from 30 to 60 min, reaching about 95% at 60 min, and increased slightly from 60 to 180 min. Almost all of the intercalated SO_4^{2-} was lost from SO_4·Mg–Al LDH at 1000 °C, which explains why the SO_2^+ peak was detected primarily in the mass spectrum until 1000 °C (Fig. 4). Figure 7 shows the XRD patterns for the products obtained from the thermal decomposition of SO_4·Mg–Al LDH under different heating conditions. Although Mg–Al oxide was obtained at 800 °C after 120 min, XRD peaks ascribed to $MgSO_4$ and $MgSO_4·6H_2O$ were also observed. These observations are in good agreement with the results reported by Miyata and Okada [15]. The production of $MgSO_4$ and $MgSO_4·6H_2O$ supports that the elimination of sulfur oxides at 800 °C was around 1% (Fig. 5). The product at 900 °C after 120 min was a mixture of MgO, $MgAl_2O_4$, $MgSO_4$, and $MgSO_4·6H_2O$. The production of MgO and $MgAl_2O_4$ is attributed to the decomposition of Mg–Al oxide. At 1000 °C after 180 min, crystal growth of MgO and $MgAl_2O_4$ was observed, and the XRD peaks ascribed to $MgSO_4$ and $MgSO_4·6H_2O$ disappeared, confirming the desulfurization of SO_4·Mg–Al LDH. In contrast with the case of Cl·Mg–Al LDH and NO_3·Mg–Al LDH [12, 13], the thermal decomposition of SO_4·Mg–Al LDH did not result in the formation of Mg–Al oxide alone.

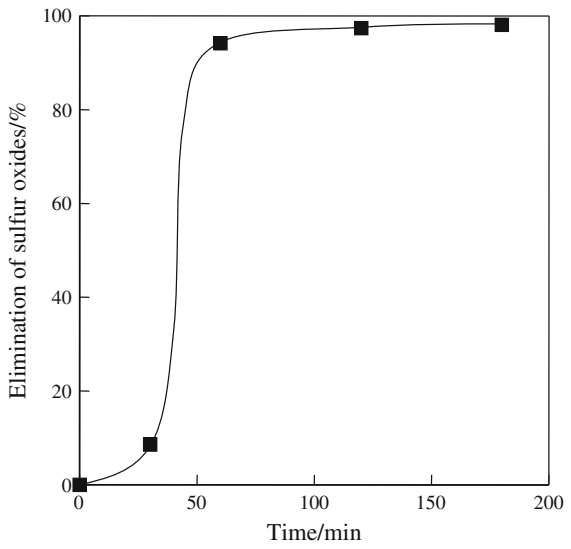

Fig. 6 Variation in the elimination of sulfur oxides over time from the thermal decomposition of SO_4·Mg–Al LDH at 1000 °C in air

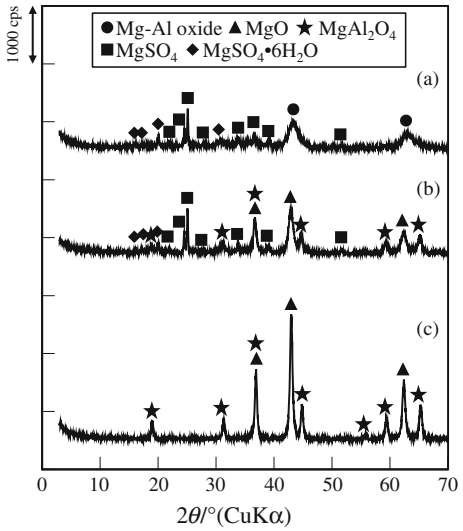

Fig. 7 XRD patterns for products obtained from the thermal decomposition of SO_4·Mg–Al LDH under different heating conditions: (*a*) 800 °C, 120 min; (*b*) 900 °C, 120 min; (*c*) 1000 °C, 180 min

Taken together, the thermal decomposition of SO_4·Mg–Al LDH at 800 °C could not produce sulfur oxides, although Mg–Al oxide was obtained with by-products. On the other hand, the thermal decomposition of SO_4·Mg–Al LDH at 1000 °C could not form Mg–Al oxide; however, almost all of the intercalated SO_4^{2-} was desulfurized from SO_4·Mg–Al LDH.

Conclusions

In summary, the thermal decomposition of SO_4·Mg–Al LDH occurred in the following five stages: evaporation of surface-adsorbed water and interlayer water (stage 1), dehydroxylation of the brucite-like octahedral layers in SO_4·Mg–Al LDH (stages 2, 3, and 4), and elimination of SO_4^{2-} intercalated in the interlayer of Mg–Al LDH to produce SO_2 and SO_3 (stage 5). The thermal decomposition of SO_4·Mg–Al LDH resulted in the formation of SO_2 and SO_3 at 900–1000 °C, which then reacted with H_2O to form H_2SO_3 and H_2SO_4. The elimination of sulfur oxides increased with decomposition time and temperature. Almost all of the intercalated SO_4^{2-} was desulfurized from SO_4·Mg–Al LDH at 1000 °C; however, Mg–Al oxide was not formed, due to the production of MgO and $MgAl_2O_4$.

The treatment of H_2SO_4 with Mg–Al oxide results in the production of SO_4·Mg–Al LDH. The calcination of SO_4·Mg–Al LDH could yield H_2SO_4, making it available for practical use. The decomposition products, MgO and $MgAl_2O_4$, are considered to be useful as refractory materials, leading to the reduction of the solid waste.

References

1. Ingram L, Taylor HFW. The crystal structures of sjogrenite and pyroaurite. Mineral Mag. 1967;36:465–79.
2. Allmann R. The crystal structure of pyroaurite. Acta Cryst. 1968; B24:972–7.
3. Palmer SJ, Frost RL, Nguyen T. Hydrotalcites and their role in coordination of anions in Bayer liquors: anion binding in layered double hydroxides. Coord Chem Rev. 2009;253:250–67.
4. Auxilio AR, Andrews PC, Junk PC, Spiccia L, Neumann D, Raverty W, Vanderhoek N. Adsorption and intercalation of Acid Blue 9 on Mg–Al layered double hydroxides of variable metal composition. Polyhedron. 2007;26:3479–90.
5. Cornejo J, Celis R, Pavlovic I, Ulibarri MA. Interactions of pesticides with clays and layered double hydroxides: a review. Clay Miner. 2008;43:155–75.
6. Wang SL, Liu CH, Wang MK, Chuang YH, Chiang PN. Arsenate adsorption by Mg/Al–NO_3 layered double hydroxides with varying the Mg/Al ratio. Appl Clay Sci. 2009;43:79–85.
7. Wu Y, Chi Y, Bai H, Qian G, Cao Y, Zhou J, Xu Y, Liu Q, Xu ZP, Qiao S. Effective removal of selenate from aqueous solutions by the Friedel phase. J Hazard Mater. 2010;176:193–8.
8. Douglas GB, Wendling LA, Pleysier R, Trefry MG. Hydrotalcite formation for contaminant removal from ranger mine process water. Mine Water Environ. 2010;29:108–15.
9. Wajima T, Shimizu T, Yamato T, Ikegami Y. Removal of NaCl from seawater using natural zeolite. Toxicol Environ Chem. 2010;92:21–6.
10. Kameda T, Yabuuchi F, Yoshioka T, Uchida M, Okuwaki A. New method of treating dilute mineral acids using magnesium–aluminum oxide. Water Res. 2003;37:1545–50.
11. Kameda T, Yoshioka T, Watanabe K, Uchida M, Okuwaki A. Dehydrochlorination behavior of a chloride ion–intercalated hydrotalcite-like compound during thermal decomposition. Appl Clay Sci. 2007;35:173–9.
12. Kameda T, Yoshioka T, Watanabe K, Uchida M, Okuwaki A. Dehydrochlorination and recovery of hydrochloric acid by thermal treatment of a chloride ion-intercalated hydrotalcite-like compound. Appl Clay Sci. 2007;37:215–9.
13. Kameda T, Fubasami Y, Uchiyama N, Yoshioka T. Elimination behavior of nitrogen oxides from a NO_3^--intercalated Mg–Al layered double hydroxide during thermal decomposition. Thermochim Acta. 2010;499:106–10.
14. Sato T, Wakabayashi T, Shimada M. Adsorption of various anions by magnesium aluminum oxide ($Mg_{0.7}Al_{0.3}O_{1.15}$). Ind Eng Chem Prod Res Dev. 1986;25:89–92.
15. Miyata S, Okada A. Synthesis of hydrotalcite-like compounds and their physico-chemical properties-The systems Mg^{2+}–Al^{3+}–SO_4^{2-} and Mg^{2+}–Al^{3+}–CrO_4^{2-}. Clays Clay Miner. 1977;25:14–8.