

Thermal Characterization of the Intercalation Compound of *p*-Toluenesulfonate into a Layered Double Hydroxide

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Abstract. On intercalation of *p*-toluenesulfonate (PTS) into Mg/Al (0.73/0.27) layered double hydroxide (LDH), the layer expanded from 4.77 Å to 17.7 Å, indicating that the plane of PTS was perpendicular to the plane of the LDH layers. Thermal treatment of the PTS intercalate resulted in 82% of the included PTS being evolved as decomposition products. This value was higher than the value of 32.5% obtained with sodium PTS and 43.8% with a mixed sample of PTS and Mg/Al (0.73/0.27) LDH. It was considered that the intercalated PTS in Mg/Al (0.73/0.27) LDH was easy to decompose because interaction between intercalated PTS and Mg/Al (0.73/0.27) LDH was smaller than that between sodium and PTS in sodium PTS.

Key words: Intercalation, layered double hydroxide, mass spectrometry, thermogravimetric analysis, *p*-toluenesulfonate.

1. Introduction

Layered double hydroxides (LDHs) constitute an interesting class of layered compounds having compositions of $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/n}^{n-} \cdot mH_2O]^{x-}$ where A^{n-} is an exchangeable anion [1–5]. Interest in such materials lies in their potentially catalytic applications, although they have also found use as adsorbents and anion exchangers. A variety of inorganic anions may be exchanged into the LDH [6]. Incorporation of organic acids such as dodecylsulfate, naphthalenesulfonate and *p*-toluenesulfonate between the layers has also been reported [7–12].

We are interested in the preparation of organic intercalates because they are candidates for electronic devices and heterogeneous catalysts [13–15]. We have previously reported that sulfonated indolinespirobenzopyran (SP) and *p*-toluenesulfonate (PTS) were co-intercalated into Mg/Al (0.73/0.27) LDH, and that the intercalate exhibited reversible photochromic properties [16].

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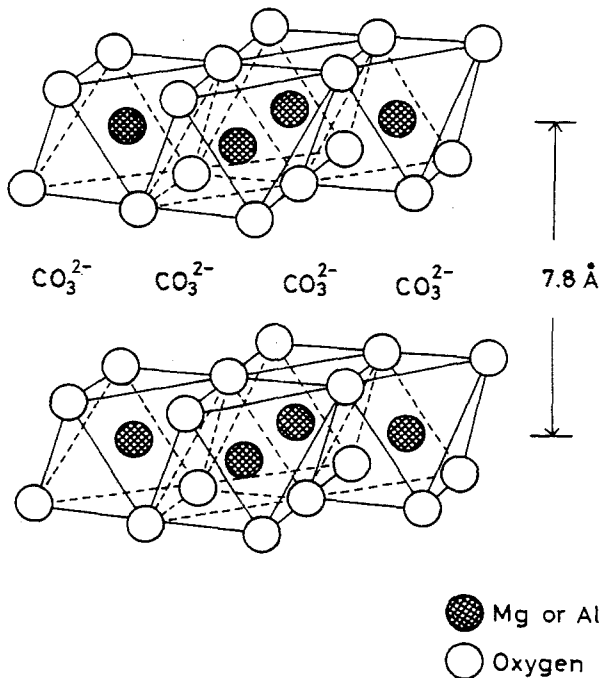


Fig. 1. Structure of carbonate Mg/Al LDH.

Recently, thermal analyses of various carbonate LDHs were undertaken and the weight losses at 200 ~ 300°C and > 400°C were attributed to the loss of adsorbed water and the sum of structural water and CO₂, respectively [6,17,18]. Thermogravimetric analyses of dodecylsulfate intercalates were also reported, the decomposition products from dodecylsulfate at more than 480°C were, however, not analyzed [17]. In the application of organic-inorganic intercalation compounds to electronic devices etc., thermal characteristics are very important. In this study, in order to understand further the properties of the organic intercalate, a detailed study of the thermal characteristics of intercalates is reported in which simultaneous TG/MS was carried out to analyze the decomposition products from the PTS intercalate of Mg/Al (0.73/0.27) LDH.

2. Experimental

All materials used were from commercial suppliers and used as received.

LDH, $[\text{Mg}_{0.73}\text{Al}_{0.27}(\text{OH})_2]^{0.27+}[(\text{CO}_3)_{0.135}]^{0.27-}$, as shown in Figure 1, was prepared in a similar manner to that reported previously [11]. The mixture of Mg(NO₃)₂ and Al(NO₃)₃ in Na₂CO₃ solution, whose pH was adjusted to *ca.* 10 with NaOH solution, was allowed to react at room temperature for 2 h. The products

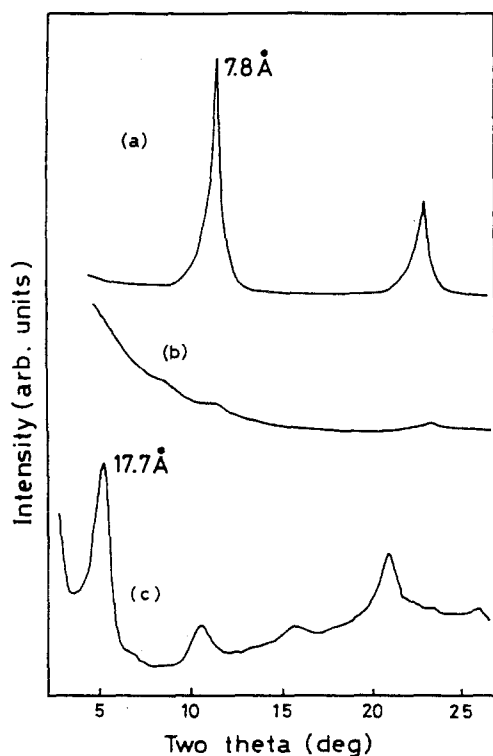


Fig. 2. XRD patterns of (a) Mg/Al (0.73/0.27) LDH, (b) calcined Mg/Al (0.73/0.27) LDH and (c) PTS intercalate.

were dried for 48 h at 80° giving carbonate Mg/Al (0.73/0.27) LDH. The LDH was treated at 500°C for 3 h to prepare calcined Mg–Al (0.73/0.27) LDH.

The composition of carbonate and calcined LDH was determined by ICP emission spectroscopy.

The PTS intercalate, was prepared by reacting the powdered, calcined LDH with PTS ions (40 mM) in distilled, degassed water for 30 min.

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku powder diffractometer unit using $\text{CuK}\alpha$ (filtered) radiation ($\lambda = 0.154$ nm) at 40 mA and 50 kV. Scan rates were 1 – 10 degrees min^{-1} , depending on the samples.

A Shimadzu combined TG/MS spectroscopic apparatus was used for the analysis of any evolved materials from the Mg/Al (0.73/0.27) LDH intercalates, sodium PTS and a mixed sample of PTS and the Mg/Al (0.73/0.27) LDH. The heating rate was $10^\circ\text{C min}^{-1}$.

TABLE I. Formulas of carbonate, calcined LDH and its intercalate.

carbonate LDH	$\text{Mg}_{0.73}\text{Al}_{0.27}(\text{OH})_2(\text{CO}_3^{2-})_{0.135}(\text{H}_2\text{O})_{0.71}$
calcined LDH	$\text{Mg}_{0.73}\text{Al}_{0.27}\text{O}_{1.07}(\text{CO}_3^{2-})_{0.07}(\text{H}_2\text{O})_{0.43}$
PTS intercalate	$\text{Mg}_{0.71}\text{Al}_{0.29}(\text{OH})_{2.1}(\text{PTS})_{0.09}(\text{CO}_3^{2-})_{0.04}(\text{H}_2\text{O})_{0.35}$
PTS/LDH mixture	$\text{Mg}_{0.73}\text{Al}_{0.27}(\text{OH})_2(\text{PTS})_{0.08}(\text{CO}_3^{2-})_{0.135}(\text{H}_2\text{O})_{0.79}$

TABLE II. Weight losses (%) of carbonate, calcined Mg/Al (0.73/0.27) LDH and its intercalate in thermal analysis.

carbonate LDH	~ 220°C: 15.9	220 ~ 500°C: 25.3		
PTS intercalate	~ 220°C: 7.4	220 ~ 480°C: 17.1	480 ~ °C: 14.9	
PTS/LDH mix.	~ 228°C: 13.0	228 ~ 510°C: 22.8	510 ~ °C: 6.4	
PTS H ₂ O	~ 120°C: 7.0	120 ~ 280°C: 77.9	280 ~ °C: 7.8	
sodium PTS		~ 477°C: 15.4	477 ~ °C: 17.1	

3. Results and Discussion

The X-ray diffraction pattern of the carbonate Mg/Al (0.73/0.27) LDH is shown in Figure 2(a) which shows 003 and 006 reflections in which indexing was based on hexagonal symmetry. The lattice constant, a_0 , of the hexagonal cell was 3.10 Å. The XRD pattern indicates that the layer distance of the carbonate Mg/Al (0.73/0.27) LDH is about 7.8 Å. The composition of the carbonate Mg/Al (0.73/0.27) LDH determined by chemical analysis was given as $\text{Mg}_{0.73}\text{Al}_{0.27}(\text{OH})_2(\text{CO}_3^{2-})_{0.135}(\text{H}_2\text{O})_{0.71}$, as shown in Table I. Thermograms of the powdered carbonate Mg/Al (0.73/0.27) LDH are shown in Figure 3. Two weight loss regions were observed at ~ 220°C and ~ 420°C. Figure 3(c) indicates that the weight losses at ~ 220°C and ~ 420°C corresponded to the desorption of water and CO₂. Mg/Al (0.73/0.27) LDH film was easily prepared from the suspension of the Mg/Al (0.73/0.27) LDH. The thermal characteristics of the Mg/Al (0.73/0.27) LDH film were the same as that of powdered Mg/Al (0.73/0.27) LDH. The amounts of desorption were 15.9% at ~ 220°C and 25.3% at 220 ~ 500°C, as shown in Table II. We have already shown that complete desorption of CO₂ was attained by the treatment at 500°C for 3 h [5]. Therefore, 25.3% was the minimum value because of the possibility of incomplete desorption of CO₂ and structural water. The calculated value for weight loss corresponding to the sum of structural water and CO₂ is 30%, which is slightly higher than the observed value of 25.3%.

After treatment at 500°C for 3 h, diffraction peaks disappeared as shown in Figure 2(b). The chemical composition of the calcined Mg/Al (0.73/0.27) LDH was given as $\text{Mg}_{0.73}\text{Al}_{0.27}\text{O}_{1.07}(\text{CO}_3^{2-})_{0.07}(\text{H}_2\text{O})_{0.43}$. It suggested the presence of a small amount of CO₂. The presence of CO₂ indicates that CO₂ might be intercalated upon storage even though the value was small.

We have already reported that excellent reversible photochromism was observed by the co-intercalation of PTS and SP [16]. In the thermograms of PTS monohy-

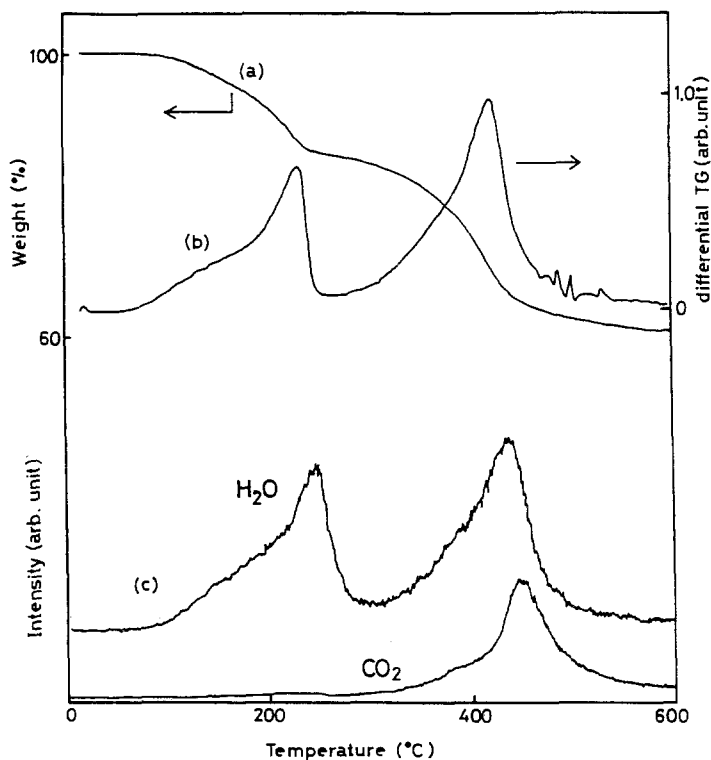


Fig. 3. Thermal analysis of Mg/Al (0.73/0.27) LDH. (a) Thermogravimetric analysis (TG), (b) differential thermogravimetric analysis and (c) MS spectra (H_2O and CO_2).

drate, weight losses occurred at $\sim 120^\circ\text{C}$ and at $120\text{--}280^\circ\text{C}$ as shown in Figure 4. The weight loss to 120°C was 7% as shown in Table II. MS spectra showed that the weight loss at $\sim 120^\circ\text{C}$ corresponded to desorption of water. More than 85% of the weight loss was observed at $120\text{--}400^\circ\text{C}$. The loss corresponded to evolution of PTS monohydrate decomposition products. More than 92% of PTS was evolved on heating to 400°C . The main peak at 246 and fragment peaks in the MS spectra indicate the presence of *p*-tolylsulfone.

In the case of sodium PTS, a sharp weight loss started at 477°C ; however, only 15.4% was lost below 477°C as shown in Figure 5 and Table II. The weight loss continued to above 700°C . From the MS spectra above 477°C , it was confirmed that the evolved compound was only carbon dioxide. The total weight loss from 450 to 800°C was only 32.5%. This indicated that not much PTS was evolved, probably because of its polymerization reaction. Certainly, the color of the measured sample after TG analysis was black. The MS spectra of evolved products at 480°C indicate that *p*-tolylsulfone was the main decomposition product from sodium PTS.

Intercalation via ion exchange of organic anions such as SP with carbonate anion was not easy [5, 11], although calcined LDH gave intercalation compounds

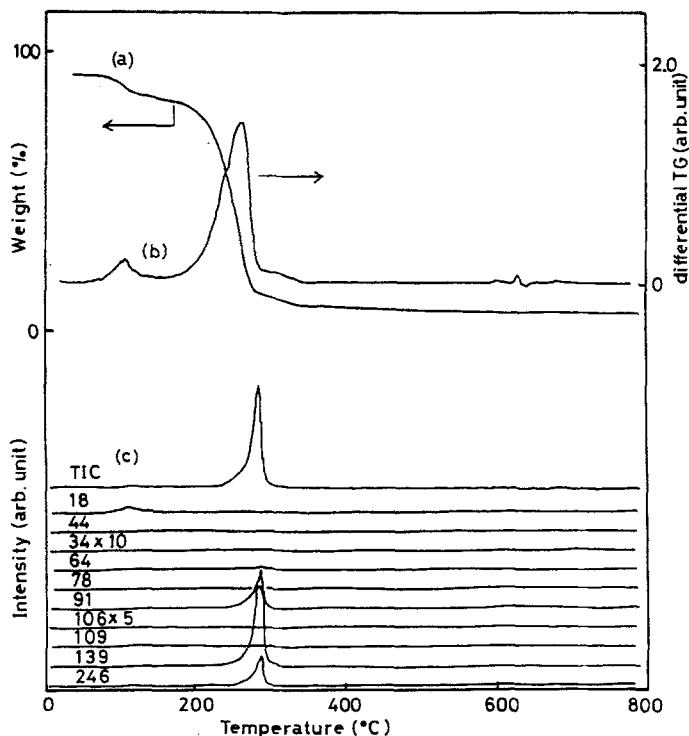


Fig. 4. Thermal analysis of PTS monohydrate. (a) Thermogravimetric analysis (TG), (b) differential thermogravimetric analysis and (c) MS spectra.

by reaction with organic anions. In this study PTS reacted with calcined Mg/Al (0.73/0.27) LDH.

Upon reaction of calcined Mg/Al (0.73/0.27) LDH with PTS, the interlayer distance expanded to 17.7 Å as shown in Figure 2(c). The length of PTS was about 8.5 Å, and the thickness of the brucite layer of the Mg/Al LDH is 4.77 Å [19]. Therefore, layer expansion was about 12.9 Å. This indicated that the plane of PTS was perpendicular to the plane of the host layers. The chemical composition of PTS intercalated into Mg/Al (0.73/0.27) LDH was given as $\text{Mg}_{0.71}\text{Al}_{0.29}(\text{OH})_{2.1}(\text{PTS})_{0.09}(\text{CO}_3^{2-})_{0.04}(\text{H}_2\text{O})_{0.35}$.

Thermograms of the PTS intercalate are shown in Figure 6. Weight losses to 220°C and 220–480°C were 7.4% and 17.1%, respectively. The calculated value for the weight loss corresponding to the sum of structural water and CO_2 is 23.8%. This value is larger than the observed value, 17.1%, probably because of incomplete desorption of CO_2 and water in the case of thermal treatment to 480°C. Clear MS peaks of evolved products were observed at 488°C. The temperature was slightly higher than that of sodium PTS. The weight of included PTS in Mg/Al (0.73/0.27) LDH was 18.1%, and the weight loss from 480 ~ 800°C was 14.9%. Therefore,

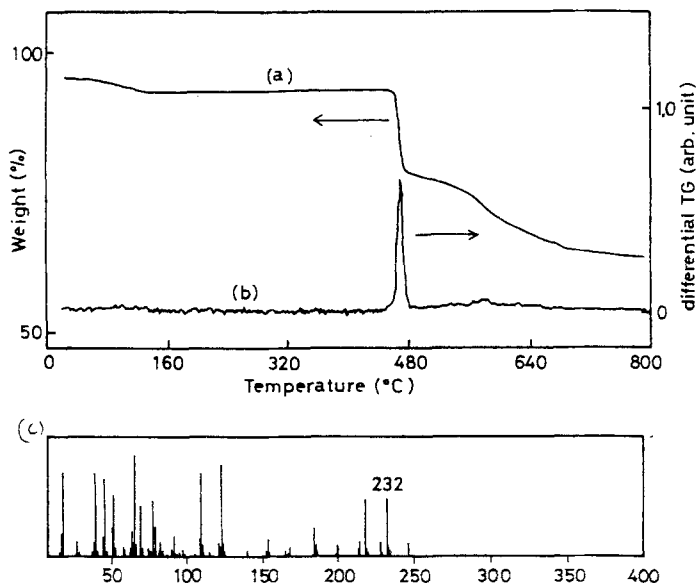


Fig. 5. Thermal analysis of sodium PTS and MS spectrum of the evolved compounds at 477°C. (a) Thermogravimetric analysis (TG), (b) differential thermogravimetric analysis and (c) MS of evolved products at 480°C.

TABLE III. TG/MS analysis for PTS monohydrate, sodium PTS, PTS intercalated into LDH and a mixed sample of PTS and LDH.

m/z	assignment	PTS	sodium	mixed	PTS	
		H ₂ O 286°C	PTS 482°C	PTS+LDH 550°C	intercalate 540°C	560°C
18	H ₂ O		○	○	○	○
44	CO ₂			○	○	○
64	SO ₂			○	⊙	⊙
78	C ₆ H ₆			○		○
91	CH ₃ C ₆ H ₄ -	△		⊙	○	○
109	C ₆ H ₅ S-		○	△		○
123	CH ₃ C ₆ H ₄ S-		○			○
139	CH ₃ C ₆ H ₄ SO-	⊙				
185	C ₆ H ₅ SC ₆ H ₄					△
218	C ₆ H ₅ SSC ₆ H ₅		△			△

⊙: relatively high intensity. ○: medium intensity. △: low intensity.

the observed weight loss was 82% of the included PTS. We have already mentioned above that only 32.5% of sodium PTS was lost by thermal treatment to 800°C. It is probable that evolution of guests from layer compounds is not easy. However, the

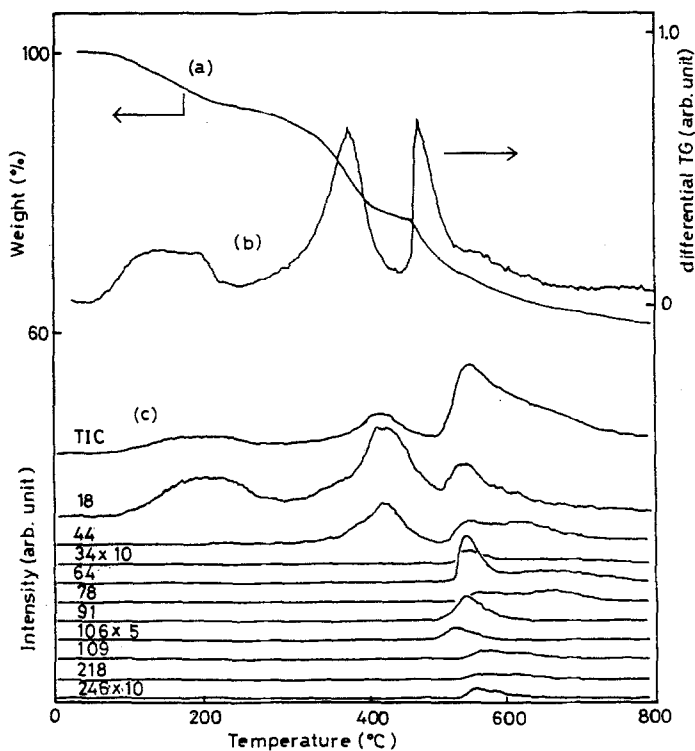


Fig. 6. Thermal analysis of PTS intercalated into Mg/Al (0.73/0.27) LDH. (a) Thermogravimetric analysis (TG), (b) differential thermogravimetric analysis and (c) MS spectra.

results indicate that evolution of PTS between the host layers is easy, compared to sodium PTS.

In order to obtain further information, thermal analysis of a mixed sample of PTS and carbonated Mg/Al (0.73/0.27) LDH (PTS/LDH = 0.2) was carried out as shown in Figure 7. Weight losses to 228°C, 228–510°C and 510–800°C were 13%, 22.8% and 6.4%, respectively. The MS spectra indicate that the weight loss at ~ 510°C corresponded to the desorption of water and CO₂ and there were no decomposition products from PTS. PTS monohydrate alone decomposed at 120–400°C as already mentioned. Therefore, the thermal analysis of PTS/Mg/Al (0.73/0.27) LDH mixed sample indicated that almost all of the PTS might interact with Mg/Al (0.73/0.27) LDH resulting in a formation of salts. The calculated value for weight loss corresponding to structural water and CO₂ was 24.2% and almost the same as the observed value of 22.8%. The weight of included PTS was 14.6% and the weight loss measured by TG was 6.4%, indicating that 43.8% of PTS was evolved. The value was higher than that for sodium PTS, 32.5%, but considerably lower than that for the PTS intercalate, 82%. It is suggested that an interaction between PTS and Mg/Al (0.73/0.27) LDH was relatively weak

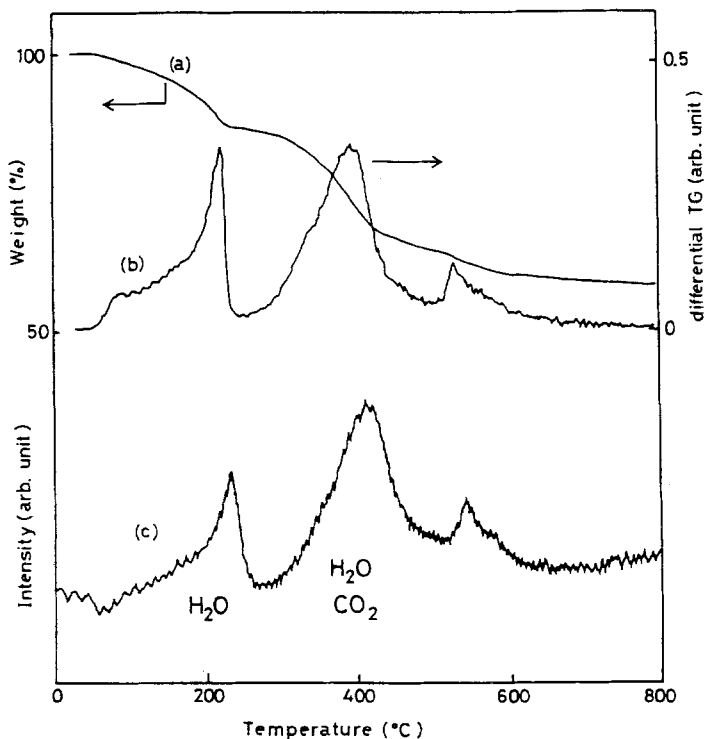


Fig. 7. Thermal analysis of PTS/Mg/Al (0.73/0.27) LDH mixed sample. (a) Thermogravimetric analysis (TG), (b) differential thermogravimetric analysis and (c) MS spectra (H_2O and CO_2).

compared to the interaction of PTS with sodium or the Mg/Al (0.73/0.27) LDH surface. Decomposition products from PTS intercalates were analyzed by mass spectrometry and GC/MS. They indicated the presence of SO_2 , benzene and toluene as shown in Figure 6 and Table III.

The results indicate that decomposition products from sodium PTS and a mixed sample of PTS and Mg/Al (0.73/0.27) LDH were similar. The decomposition products of the PTS intercalate at high temperature (560°C) were also similar. It was considered that PTS in Mg/Al (0.73/0.27) LDH did not form a salt and that PTS did not polymerize to give unevolved products similar to those observed on thermal treatment of sodium PTS.

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