

**CO₂ SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS SHIFT REACTION WITH
CONCOMITANT RECOVERY OF CO₂**

Quarterly Report for the Period April 2001- June 2001

**Paul K. T. Liu
Project Director**

MEDIA AND PROCESS TECHNOLOGY, INC.

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ABSTRACT

Presently we have focused on the membrane synthesis, hydrotalcite surface and transport mechanism characterization, and quantitative measurement on CO₂ reversibility. This quarterly report presents the results from the surface characterization study. FTIR, DRIFTS and TGA/MS have been used to quantitatively characterize the thermal behavior of hydrotalcite materials. Based upon these characterization results, a thermal evolution pattern accounting for the loss of interlayer water, hydroxyl group, and CO₂ is proposed for the hydrotalcite we studied. According to the DRIFTS results, a small amount of CO₂ release (~2wt%) was observed at ~220°C, while the remaining releases at ~450°. TGA/MS result is consistent with the amount and the temperature region estimated from DRIFTS. Both regions are possible candidates for transport of CO₂ in a membrane configuration. In the next quarter, we will conduct adsorption/desorption study to verify the reversibility of the CO₂ released from these two regions.

1. Introduction

In this quarter we have pursued multiple tasks in parallel. They include:

- (i) preparation of the hydrotalcite membrane via in-situ crystallization,
- (ii) study of the CVD technique to backpatch the membrane, and
- (iii) performing surface study via FT-IR, TGA/MS and XRD to verify the CO₂ transport mechanism.

In the previous quarterly reports, we have reported the results on (i) and (ii). In this report, we focus on (iii), summarizing the results we have obtained thus far. A thermal evolution pattern is proposed to guide our next experimental study. The surface analysis offers us information of the degree of CO₂ release at a given temperature and the effect of water. Once the result from HTXRD is available, we will be able to design an efficient CO₂ selective membrane with excellent hydrothermal stability based upon these surface analysis results..

2. Proposed Mechanism for Thermal Evolution Pattern of Hydrotalcite

Based upon the results of in-situ DRIFTS coupled with TG/DTA/MS studies, we are proposing the following model for thermal evolution of hydrotalcite under an inert atmosphere. Five stages are identified as follows:

Stage A - the original hydrotalcite sample at room temperature;

Stage B - developed by the removal of loosely held interlayer water in the Stage A at the temperature range of 70 to 190EC;

Stage C - evolved from the Stage B by the removal of (i) OH⁻ groups bonded with Al³⁺ at the temperature range of 190 to 280EC and (ii) OH⁻ groups bonded with Mg²⁺ at the temperature range of 280 to 405EC;

Stage D - achieved by decarbonation of Stage C at the temperature range of 410 to 580EC;

Stage E - obtained when the temperature exceeds 580EC.

We have quantitatively determined the changes of the functional groups of the hydrotalcite sample along with the temperature increase (see Sec. 3 to 7), and proposed a model to describe these changes. In order to verify the model we proposed and determine how these changes influence the LDH structure, further study with an in-situ HTXRD is planned.

3. FT-IR Study of Hydrotalcite at Room Temperature

Figure 1 showed the comparison with DRIFTS and FT-IR results of hydrotalcite at room temperature. It shows that all the signals of the DRIFTS for the hydrotalcite coincide with those from FT-IR. The intensities of DRIFTS signals are strong enough to clearly identify all the species in the hydrotalcite. Based on the literatures for FT-IR on the hydrotalcite, we assigned all the DRIFTS signals to the corresponding species as below:

- (1) DRIFTS signal at ~3470 cm⁻¹ was assigned to OH⁻ group vibration in the hydrotalcite sample;
- (2) DRIFTS signal at ~3070 cm⁻¹ was assigned to hydrogen bonding between water and carbonate in the interlayer of the hydrotalcite;
- (3) DRIFTS signal at ~1620 cm⁻¹ was assigned to H₂O bending vibration of interlayer water in the hydrotalcite sample;
- (4) DRIFTS signals at $\nu_3=1370$ cm⁻¹, and $\nu_4=680$ cm⁻¹ at room temperature were assigned to CO₃⁻² group vibration bands in the hydrotalcite sample, which behave like in the water solution, i.e., $\nu_3=1415$ cm⁻¹, $\nu_2=880$ cm⁻¹, and $\nu_4=680$ cm⁻¹. In this case, no splitting of ν_3 band and ν_1 mode vibration at ~1080 cm⁻¹ were observed, which usually were generated from the symmetry degradation and the interaction between CO₃⁻² and Mg²⁺. This means that CO₃⁻² in the hydrotalcite sample has no or very weak direct interaction with positive ions, such as Mg²⁺ and Al³⁺ at room temperature.

Based upon the above assignments, we can characterize the surface functional group change along with the temperature increase. The results obtained in this quarter are summarized in the rest of this report.

4. DRIFTS Study of Hydrotalcite at High Temperature

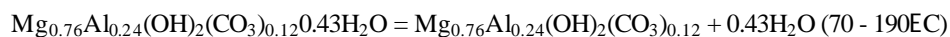
According to the above assignments, we can use in-situ DRIFTS technique to characterize the evolution process of hydrotalcite, i.e., the changes of the functional groups as a function of temperatures. The in-situ DRIFTS results are shown in Figure 2. The hydrotalcite sample was treated in Ar with continuously increasing temperature to 560EC, and the in-situ DRIFTS was recorded at each temperature under an isothermal condition for a period of ~2 minutes with an 20EC interval. From Figure 3, several conclusions can be drawn as follows:

- (1) The intensities of DRIFTS bands for interlayer water at 3070 cm⁻¹ and 1620 cm⁻¹ gradually decrease with the increase of temperature, and disappear at 220EC. This means that more and more interlayer water in the hydrotalcite is removed with the increase of temperature, and completely removed at 220EC.
- (1) The intensity of OH⁻ vibration signal at 3470cm⁻¹ begins to decrease at temperature of 190EC and disappears at 440EC, which suggests that the partial dehydroxylation of the hydrotalcite occurs at 190EC, and completed at 440EC.
- (1) (i) The splitting of signal at 1370 cm⁻¹ for <₃ vibration of CO₃⁻² to two signals, i.e., 1530cm⁻¹ and 1350cm⁻¹, at temperatures higher than 170EC and (ii) appearance of <₁ at 1090cm⁻¹ which is infrared inactive in the free CO₃⁻² at temperatures higher than 340EC, indicate that symmetry of the hydrotalcite sample becomes worse after thermal treatment. It is interesting to observe that the intensity of the signal at a lower wavenumber (~1350cm⁻¹) decreases and the intensity of the signal at a higher wavenumber (-1530cm⁻¹) increases with the increase of temperature. Furthermore, the position of these two split signals becomes closer with the increase of temperature, which behaves more like CO₃⁻² in MgCO₃ as shown in Figure 3. The <₃ vibration of CO₃⁻² in MgCO₃ was split to two signals, i.e., 1499 cm⁻¹ and 1425cm⁻¹, and the <₁ vibration band of CO₃⁻² in MgCO₃ was observed at 1100 cm⁻¹ due to the symmetry degradation of CO₃⁻² in MgCO₃. These results indicate that after removal of the interlayer water and OH⁻ groups at high temperatures (170 to 400EC), CO₃⁻² is directly bonded with Mg²⁺ to form MgCO₃-like species. This conclusion is also confirmed by the fact that the decarbonation temperature range of 410 to 560EC for the hydrotalcite shown in Figure 2 is quite similar to the decomposition temperature range of 400EC to 560EC for MgCO₃, shown in Figure 3.

Figure 4 is a semi-quantitative interpretation of the insitu DRIFTS (shown in Figure 2), indicating the fraction of each particular species that is removed at a given temperature. The calculations are based on the peak area of the corresponding species, i.e., 3470cm⁻¹ represent OH⁻ group, 3070cm⁻¹ and 1620cm⁻¹ represent interlayer water, and 1370cm⁻¹ at lower temperatures or 1530 cm⁻¹ and 1350cm⁻¹ at higher temperatures represent CO₃⁻². For the interlayer water, it begins to release at 70EC and is completely lost at 220EC. For OH⁻ groups, the big difference in slope between the temperature range of 190 -250EC and that of 250 - 430EC suggests that there are two different kinds of OH⁻ groups in the hydrotalcite sample. One kind of OH⁻ group is removed at the temperature range of 190 - 250EC, and another kind of OH⁻ group is removed at the temperature range of 250 - 430EC. A small amount of CO₃⁻² is removed at the temperature range of 180 - 240EC (~2wt%), and most of CO₃⁻² is removed at the temperature range of 390 - 560EC (~98%), which is also confirmed by in-situ MS, as shown in Figure 5. A small amount of CO₂ from the hydrotalcite was detected at the temperature range of 190 - 280EC, and most of the CO₂ was detected at the temperature range of 370 - 600EC.

5. TGA Study on 1st Weight Loss Peak

In-situ DRIFTS is a powerful technique to monitor the changes of the functional groups in the hydrotalcite sample during the thermal treatment. However, for precise quantitative purpose, TG/DTA is one of the best choices. Figure 6 shows the weight change and the heat flow of the hydrotalcite sample as a function of temperature under inert gas atmosphere. Combined with the results of in situ DRIFTS in Figure 2, we know that the first weight loss, ~14wt% by weight, at the temperature range of 70 - 190EC should be from the interlayer water in the hydrotalcite plus a small amount of CO₂ and H₂O from OH⁻ group. The theoretical percentage by weight of the interlayer water in the hydrotalcite can be calculated based up the following reaction,



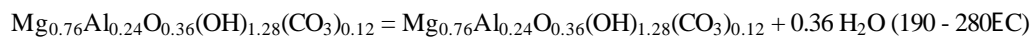
The total molecular weight of $\text{Mg}_{0.16}\text{Al}_{0.24}(\text{OH})_2(\text{CO}_3)_{0.12} \cdot 0.43\text{H}_2\text{O}$ is 73.89, and the total weight of the interlayer water in the hydrotalcite is 7.74 ($0.43 \times 18 = 7.74$). So, the theoretical percentage of interlayer water in the hydrotalcite is 10.48% by weight ($7.74/73.89 = 10.48$). The difference (3.52% by weight) should be attributed to the contribution of CO_2 and H_2O from OH^- group because there indeed is a small amount of CO_2 and H_2O from OH^- group which were removed at the temperature range of 70 - 190EC, as shown in Figure 3. At the same time, DTA result shows that only a small amount of heat (no heat flow peak was observed at the temperature range of 70 - 190EC) is needed for the first weight loss, which indicates that the interlayer water physically adsorbed in the nanoslits between the layers of the hydrotalcite.

6. TGA Study on 2nd and 3rd Weight Loss Peaks

The second weight loss peak (~6.7% by weight) occurs at 190 - 280EC, which is accompanied by two heat flows (endothermic) with their peaks at 205 (small shoulder peak) and 255EC. The third weight loss (~15.4% by weight) peak occurs at 280 - 405EC, which is accompanied by a heat flow (endothermic) with its peak at 340EC. According to the above DRIFTS results in Figure 2, there are two kinds of OH^- groups, which are removed at the temperature range of 190 - 430EC, i.e., one at 190 - 250EC, and another at 250 - 430EC. Therefore, the second weight loss at 190 - 280EC, and the 3rd weight loss at 280 - 405EC are attributed to the removal of two different kinds of OH^- group, which may be associated with Al^{3+} and Mg^{2+} respectively. In order to clarify the properties of these two kinds of OH^- groups, we performed TG/DTA experiments on pure $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ samples. The results are shown in Figure 7 and 8. Figure 7 shows that the OH^- group associated with Al^{3+} was lost at the temperature range of 190 - 315EC, and two heat flows (endothermic) were observed associated with this loss. Figure 8 showed that the OH^- group associated with Mg^{2+} was removed at the temperature range of 290 - 405EC, and only one heat flow (endothermic) was observed in this case. Compared Figure 6 with Figures 7 and 8, one can conclude that the weight loss and the thermal behavior of the hydrotalcite in Figure 6 at the temperature range of 190 - 200EC are nearly identical to those of $\text{Al}(\text{OH})_3$ (Figure 7). By the same token, the weight loss and the thermal behavior of the hydrotalcite in Figure 6 at the temperature range of 280 - 405EC are similar to those of $\text{Mg}(\text{OH})_2$ shown in Figure 8. These results mean that the second weight loss (~6.7% by weight) in Figure 6 at the temperature range of 190 - 280EC is likely resulted from the removal of water from the OH^- group bonded with Al^{3+} and the third weight loss (~15.4wt%) in Figure 6 at temperature range of 280 - 405EC is the removal of H_2O from the OH^- group bonded with Mg^{2+} . These assignments were further supported with the theoretical calculation presented in Sec. 7.

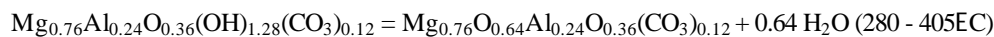
7. Theoretical Calculation on Weight Loss

Quantitative weight loss vs temperature can be estimated based upon the theoretical calculation with the chemical formula of hydrotalcite incorporated with the evolution behavior discussed in Sec. 3 to 4. The weight loss for the OH^- bonded with Al^{3+} in the hydrotalcite was calculated based on the following reactions:



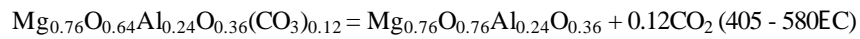
by assuming that Al^{3+} only bonded with OH^- because in-situ DRIFTS results in Figure 2 already show that CO_3^{2-} only bonded with Mg^{2+} , and there is almost no interactions between CO_3^{2-} and Al^{3+} . Thus, the percentage for the loss of the OH^- bonded with Al^{3+} in the hydrotalcite is 8.77% by weight ($0.36 \times 18 / 73.98 = 8.77\%$). The experimental value (6.7%) is slightly lower than the theoretical value (8.77%) due to the removal of a small amount of OH^- group bonded with Al^{3+} at the lower temperature range of 70 - 190EC, as shown in Figure 3. The large heat flow in this case also confirms that the OH^- group chemically bonded with the higher valence element, i.e., Al^{3+} .

The percentage for the loss of the OH^- group bonded with Mg^{2+} in the hydrotalcite was calculated based on the following reaction:



The result shows that the percentage for the loss of the OH^- bonded with Mg^{2+} in the hydrotalcite was 15.5% by weight ($0.64 \times 18 / 73.98 = 15.59\%$), which is almost same as the experimental value of ~15.4%.

The last weight loss (~5.9%) at the temperature of 405 - 580EC shown in Figure 6, was attributed to the removal of CO₂ from CO₃⁻². The theoretical percentage of the loss of CO₂ from CO₃⁻² in the hydrotalcite was calculated based on the following reaction:



The result shows that the theoretical percentage for the loss of CO₂ is 7.15% by weight (0.12x44/73.89=7.15%). The experimental value (~5.9%) is slightly lower than the theoretical value (7.15%) at the temperature range of 405 - 580EC due to a small amount of CO₂ already removed at a lower temperature range, i.e, 190 - 250EC (see Figure 4). Thus, the quantitative information obtained here is consistent with the thermal behavior inferred from the DRIFTS and TGA/DTA study.

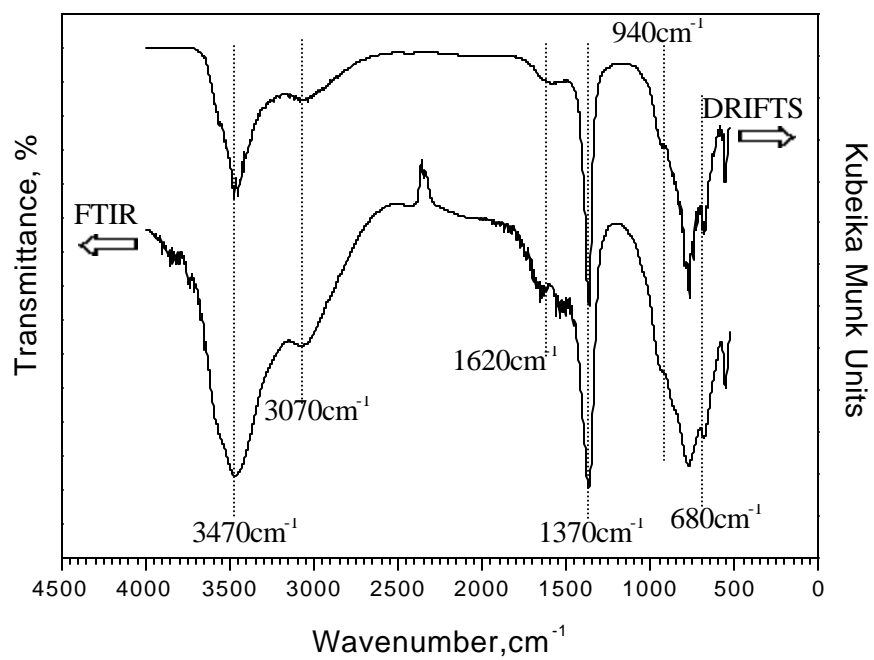


Figure 1 Comparison of FT-IR with DRIFTS Results on Hydrotalcite Material

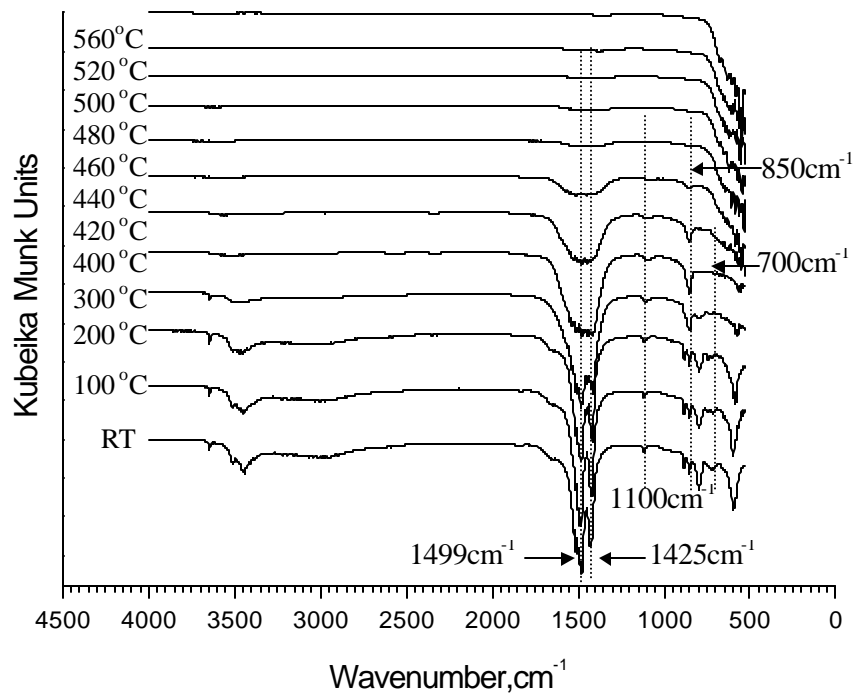


Figure 2 DRIFTS Results on Hydrotalcite Material at 25 to 560EC

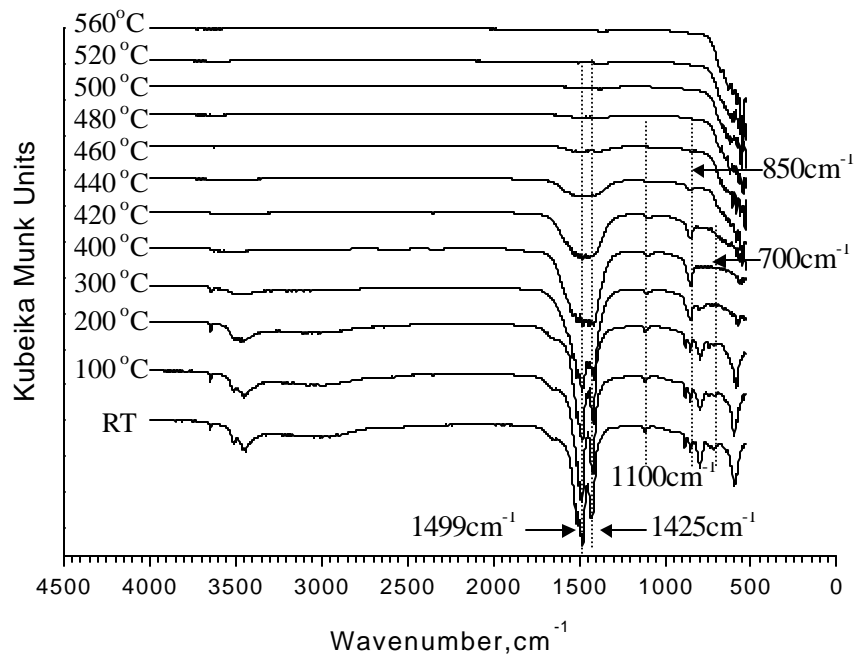


Figure 3 DRIFTS Results on MgCO₃ for Comparison with the Hydrotalcite Results Shown in Figure 2.

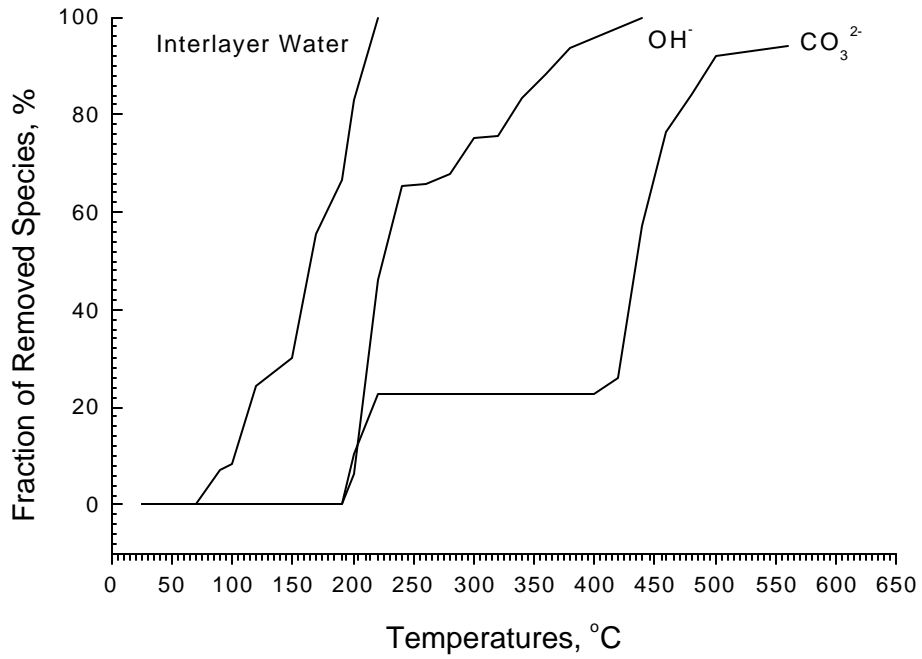


Figure 4 Weight Loss vs Temperature for Each Components Evolved from Hydrotalcite as a result of Thermal Treatment

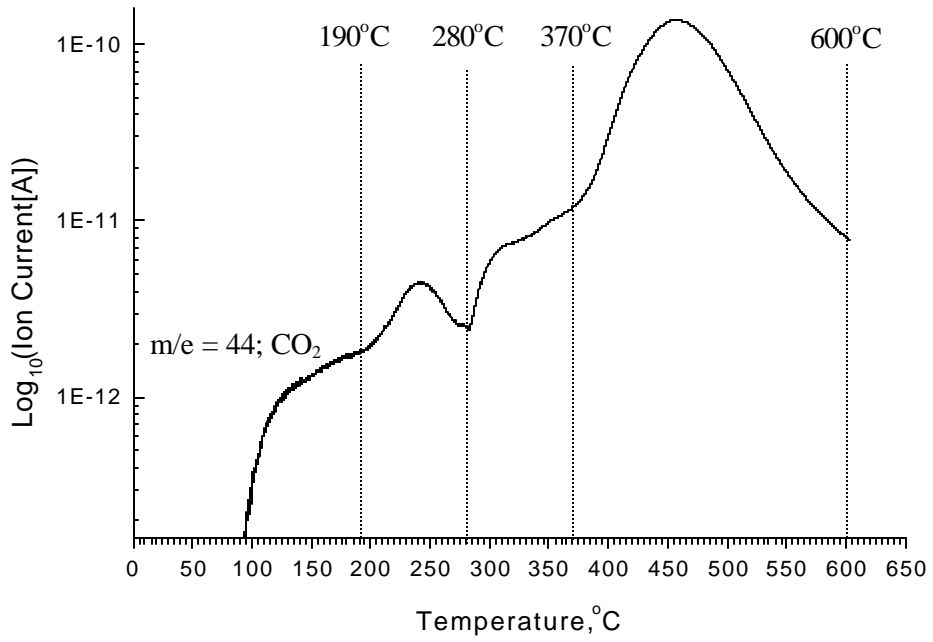


Figure 5 Mass Spectrum vs Temperature for Off-gas from Hydrotalcite at 25 to 600EC

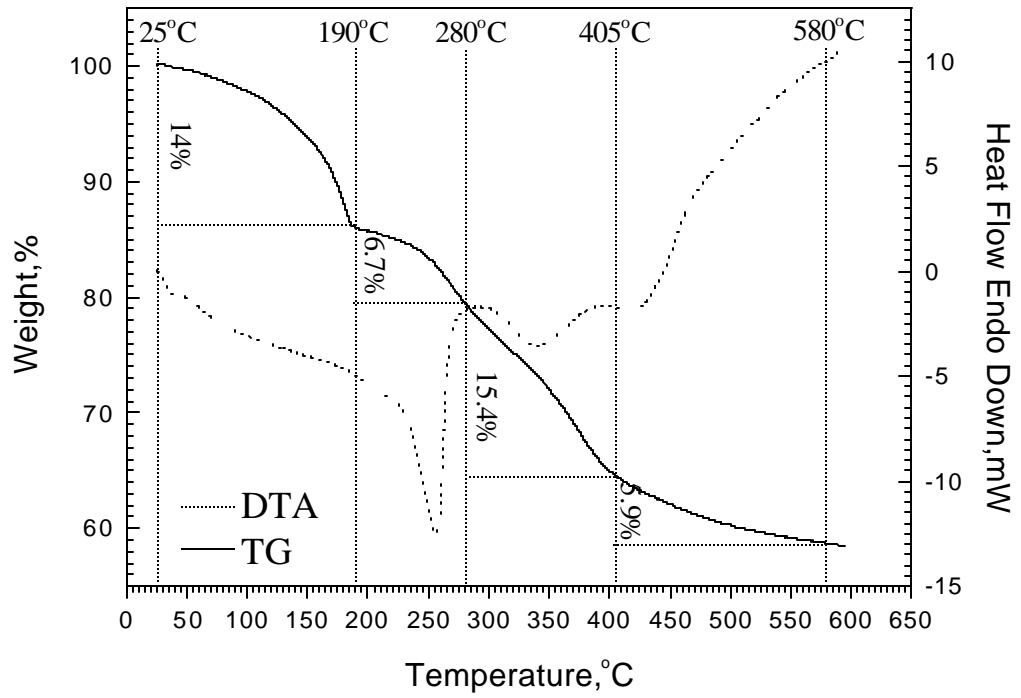


Figure 6 TG/DTA Results on Hydrotalcite

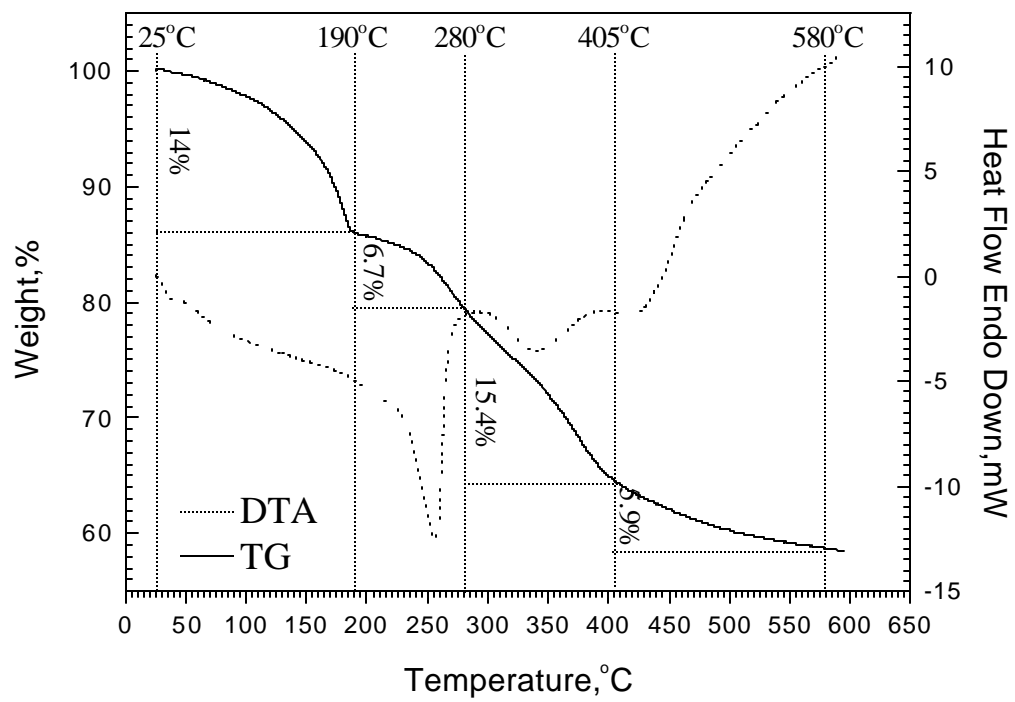


Figure 7 TG/DTA for Al(OH)_3 for Comparison with Hydrotalcite Results

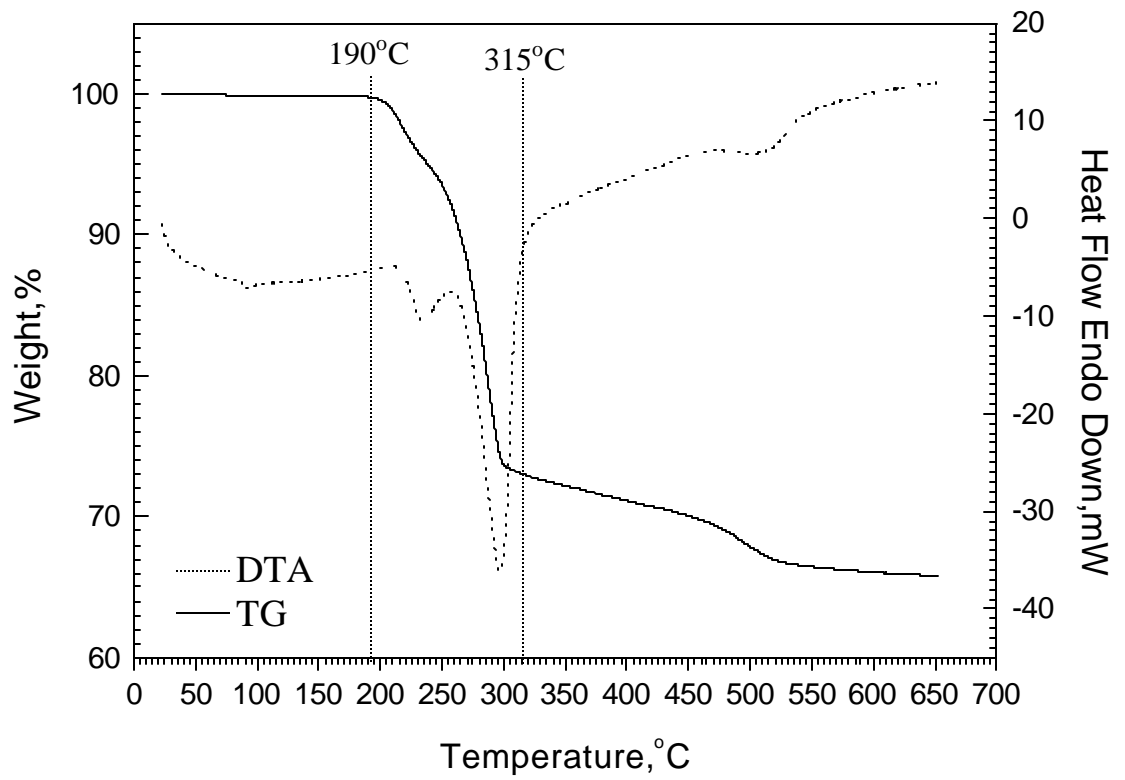


Figure 8 TG/DTA of Mg(OH)₂ for Comparison with Hydrotalcite Results