

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

**Quarterly Report
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Abstract

In this quarter, we have made progress in the three approaches selected for preparing CO₂-affinity membrane. A defect free nanoporous membrane was prepared via slip casting. This membrane will then be used for post treatment to seal the micropores to become a non-porous membrane with CO₂ affinity. This post treatment study will be our focus in the next several quarters. Polymeric gel as a precursor was successfully prepared, which will be used for subsequent thin film deposition. Preparation of a defect-free thin film from this precursor will be our future focus using the sol-gel approach. Finally, the third approach, in-situ impregnation approach, was modified. Although we were able to deposit the precursor within the porous of the membrane, we have not been able to enhance the pH in-situ. Designing an unconventional approach to alternate the pH in-situ will be our focus of the next quarter.

Executive Summary

In this quarter, we have made progress in the three membrane preparation approaches selected: impregnation, sol-gel and slip casting. The slip casting approach delivers a defect free hydrotalcite membrane calcined at 80 and 200°C. The membrane after calcination to 300 and 400°C shows defects, which may be resulted from the characterization method applied. An alternative characterization method will be attempted next quarter. We have conducted a comprehensive literature search on the sol-gel technique for the preparation of the hydrotalcite powder. Further we have successfully generated powder with the characteristic XRD peaks of hydrotalcite. We will attempt to increase the yield of hydrotalcite through full equilibration of the solution at pH=10. The impregnation approach was modified in this quarter. A gas phase CO₂ delivery system was tried. Unfortunately the pH of the precursor solution increase from 0.3 to 0.5 after 24 hours, which is far from the target pH=10. In the next quarters, we will try alternative delivery systems.

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1. Introduction

In this quarter, we have been continuing the improvement of the hydrotalcite membrane preparation via slip casting and impregnation. Our focus has been placed on the improvement of the layer deposition via slip casting in order to minimize defect formation. As far as the impregnation is concerned, we tested the concept of pH enhancement via gas phase. In addition, we have conducted a comprehensive literature review on the sol-gel technique to prepare hydrotalcite, which will be the third approach for our membrane preparation.

2. Hydrotalcite Membrane Synthesis via Slip Casting

Experimental

In the previous quarterly report, we presented the feasibility of forming a hydrotalcite membrane on top of the $0.2\mu\text{ Al}_2\text{O}_3$ membrane. Further we characterized the pore size of the hydrotalcite thus formed is $<100\text{\AA}$. However, some defects exist and the big particles or agglomerates were found on the surface of the membranes. In this quarter we have been continuing the effort in this area with the focus below:

- Ball milling the hydrotalcite particles thoroughly to eliminate the big particles or its agglomerates.
- Improving layer deposition formula and technique; thus, minimizing the defect of the green layer.
- Thermal calcinations of the green layer to improve its adhesion to the base substrate.

The successful completion of the above tasks will offer us a defect free hydrotalcite membrane ready for the post treatment with CVD. Our progress made in this quarter are discussed below:

Results/Discussion

- Elimination of the big particles/agglomerate

In this quarter, we extend the ball milling time to achieve a thorough grinding. The layers result from this improved formula is shown in Figure 1 (SEM: 94-7-1/2, 1K) and Figure 2 (SEM: 94-7-1, 1K). Both show a uniform, defect-free coverage of the base substrate without big particles or agglomerates. Figure 1 represents the half of the particle density used in Figure 2. Evidently the $\frac{1}{2}$ density shown in Figure 1 is adequate to provide a complete surface coverage. The starting material after ball milled and dried at 80°C is characterized by XRD shown in Figure 3 (XRD: HT-094 Ball Milled & Dried). As expected a typical hydrotalcite pattern along with unconverted Al and Mg is present, typical of hydrotalcite prepared at $\text{pH}=6$. The unconverted Al and Mg supposedly act as a binder. In summary the improved recipe corrects the previous problems and

delivers a satisfactory green layer.

- Characterization of the green layer

As indicated above, the green layer formed with the improved formula appears defect free according to SEM examination. We also conduct initial flow analysis using helium flow saturated with water at room temperature. According to our previous experience, no initial flow can be detected for an Al_2O_3 membrane with 100Å commercially available from us. The initial flow measurements from the two samples are presented below:

Sample ID	Calcination Temperature °C	Initial Flow (%)	Selectivity (He/N ₂)
94-7-1/2-1	80	3.6	1.98
94-7-1/2-2	80	1.6	1.76
	200	6.4	1.83
94-7-1-1	80	1.5	1.89
	200	0.97	1.82
	300	87 ¹	1.91
94-7-1-2	80	2.0	1.78

It is believed that the green layer after drying at 80°C is nearly defect free as indicated by the very low initial flow for both 94-7-1/2 and 94-7-1. These low initial flows are consistent with the SEM observations as shown in Figure 1 and 2. Drying at 200°C increases the initial flow slightly, i.e., from 1.6 to 6.4%; however, this increased level of initial flow is considered within the tolerance of the micro porous membrane. Calcination at 300°C apparently significantly increases the initial flow, i.e., ~87%, indicative of the layer collapse. Hydroxide begins to release its interlayer water approaching 200°C according to TGA. Thus, the layer shrink during the calcinations; however, when the layer exposed to the initial flow testing, the layer re-expands, causing major defects throughout the layer. SEM examination is under way to verify this explanation.

Conclusion

To verify the role of water and the structure expansion, we plan to conduct the following tasks in the next quarter:

- Perform pore size distribution analysis of the samples calcined at 300°C and 400°C. Since no moisture is used for the pore size distribution analysis, we will be able to verify the quality of the layer before and after exposure to water.

¹ The initial flow went through a minimum, i.e., <1%, and then increased to this level throughout the measurement.

- Submit for SEM examination. Hopefully under the high magnification, i.e., 40K, we can detect the morphology change as a result of the exposure to water.

We may be able to overcome this problem during the initial phase of the project by avoiding the exposure to water at a low temperature. At a high temperature the uptake of water is considered much reduced and is nothing to do with the interlayer water. Since no permanent binder is added to the formula, calcinations at 400°C of the green layer is desirable to form the oxide bonding with the substrate.

3. Hydrotalcite membrane synthesis via sol-gel technique

A literature study has been conducted in this quarter to review the literature involving the preparation of hydrotalcite powder via sol-gel technique. Significant findings are summarized below:

- Essentially there are two approaches to prepare hydrotalcite via polymeric gels: Double Alkoxide (DA) and Single Alkoxide (SA). For DA, the magnesium and aluminum alkoxide are mixed together as a starting material for controlled hydrolysis to form polymeric gel. Since the hydrolysis rate could be different for each metal, the resultant mixed alkoxide may not be consistent with the stoichiometric ratio of the precursors. Under SA, magnesium alkoxide will be dissolved in alcohol and then mixed with aluminum chemicals, such as aluminum nitrate, which is also soluble in alcohol.
- For SA, once alkoxide is dissolved, hydrolysis in the presence of acid catalyst will take place. Then two approaches can be taken to convert the mixed alkoxide polymeric sol into hydrotalcite: (i) calcination in the presence of air after drying. According to the literature, about 10 to 20% HT will form along with unconverted brucite; (ii) raised the pH of the polymeric sol to 10 with NH_4OH to form HT. Again, according to the literature, the Al/Mg ratio of the HT formed is less than the stoichiometric ratio of the precursors.
- The under-stoichiometric ratio discussed above is believed due to the incomplete mixing of the precursor chemicals according to the literature. The reason may be the viscosity of the gel is too high. Thus, the pH change may cause local precipitation of magnesium molecules to form brucite. Or during calcination, conversion of mixed oxide to hydrotalcite takes place in the solid phase, which is considered more difficult.
- Based upon the above observations of the literature studies, many questions remain to be answered:
 - Even though some brucite forms along with hydrotalcite in the formed thin film, is it a problem with regard to the enhanced transport of CO_2 ? It may not be a problem. However, if brucite is present in a high

surface area, what is its hydrothermal stability? Can brucite morphology change during the performance test, which will cause the defect of the thin film?

- What is the particle size of the polymeric gel after raising the pH to 10? I suppose that the HT is formed at this pH. Can we coat this gel on the substrate?
- Can we convert the thin film prepared by the polymeric mixed oxide gel to HT as completely as possible using the gas phase CO_2 under the hydrothermal synthesis condition? Also under this conversion, does the thin film structure collapse?
- Since most literatures indicate that the CO_2 and dehydroxylation take place at 300 to 450°C, we should review the USC data on the high temperature range instead of 200°C data. According to the literature, the surface area change significantly as a result of CO_2 release. Thus, from the membrane synthesis standpoint, we should focus on:
 - Reversibility of CO_2 affinity at this temperature range in the presence and the absence of water.
 - Can we use SEM examination to the unsupported thin film before and after calcinations at 300°C to visibly examine the structure change or not?
 - Can we use surface area index for the reversibility of CO_2 ?
- To avoid the time investment on the thin film coating, can we design an experiment using the unsupported film to answer the above questions? Specifically
 - Prepare a thin film from mixed polymeric gel before pH adjustment. Take SEM and XRD. Then thermally calcine at 200°C in the presence of CO_2 under pressure. Then check the morphology change with SEM and verify the structure with XRD.
 - Follow the above using the polymeric gel after pH adjustment.

Experimental

During this quarter, we have prepared one sol based upon the polymeric sol formula with single alkoxide (SA) using AlNO_3 as the alumina source. The sol after drying was submitted for XRD analysis.

Results/Discussion

Figure 3 & 4 (HT-SG-03 80°C and 80°C +2 hrs) shows the XRD for the sol after drying at 80°C and drying at 80°C with 2 hrs. Both show typical characteristics of

hydrotalcite with the unconverted bohemite. These XRD profiles are similar to the literature study targeting the preparation of the mixed oxide. In that study, the gel after formed does not undergo the pH increase to 10 to form hydrotalcite. In our case, although we have adjust the pH to 10, however, we did not check the pH after the adjustment to make sure the solution reached the equilibrium of pH=10. Therefore, we plan to repeat this experiment with the hope that the yield to hydrotalcite from this gel can be increased after the correction of the pH. The gel thus prepared was calcined at 250 and 400°C; their XRD profiles were presented in Figure 5 and 6 (HT-SG-03 250°C and HT-SG-03 400°C).

Conclusion

It is believe that some CO₂ release took place as a result the typical hydrotalcite characteristic disappears. Since the XRD pattern changed at such a low temperature, i.e., 250°C, we plan to repeat this experiment with the next batch of the powder we prepare to confirm this temperature.

4. Hydrotalcite Membrane Synthesis via Impregnation

Experimental

Our previous report indicates that the impregnation approach did not produce a defect free membrane. In this quarter we attempt to correct the defect by modifying the impregnation approach. Our modification includes the (i) impregnation with the liquid solution, and then (ii) condition the layer with a high pressure CO₂ (~100 psi) at 150°C in autoclave.

Results/Discussion

To prove this concept is experimentally feasibly, we prepare a solution and then exposed it under the above condition. The pH of the solution increases from 0.3 to 0.5 after 24 hour exposure, far from the target pH=10.

Conclusion

Evidently the gas phase diffusion is not very efficient to acheive the pH desired. In the next quarter, we will explore other alternatives.

Figure 1 SEM photomicrograph of hydrotalcite membrane prepared via slip casting (HT-094-7-1/2)

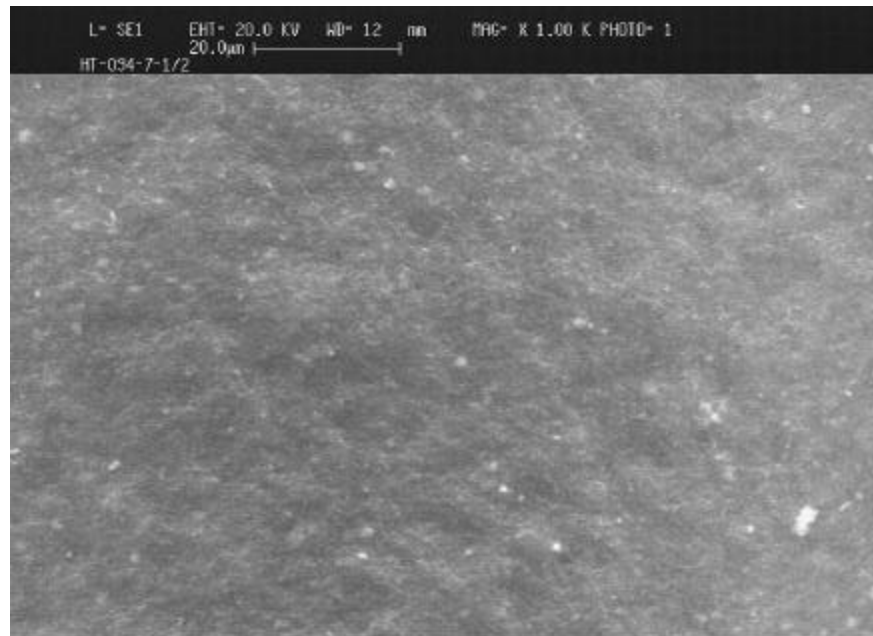


Figure 2 SEM photomicrograph of hydrotalcite membrane prepared via slip casting using the half of the particle density used for Figure 1 (HT-094-7-1)



Figure 3 XRD of the starting materials used to prepare HT-094-7-1/2 and HT-094-7-1)

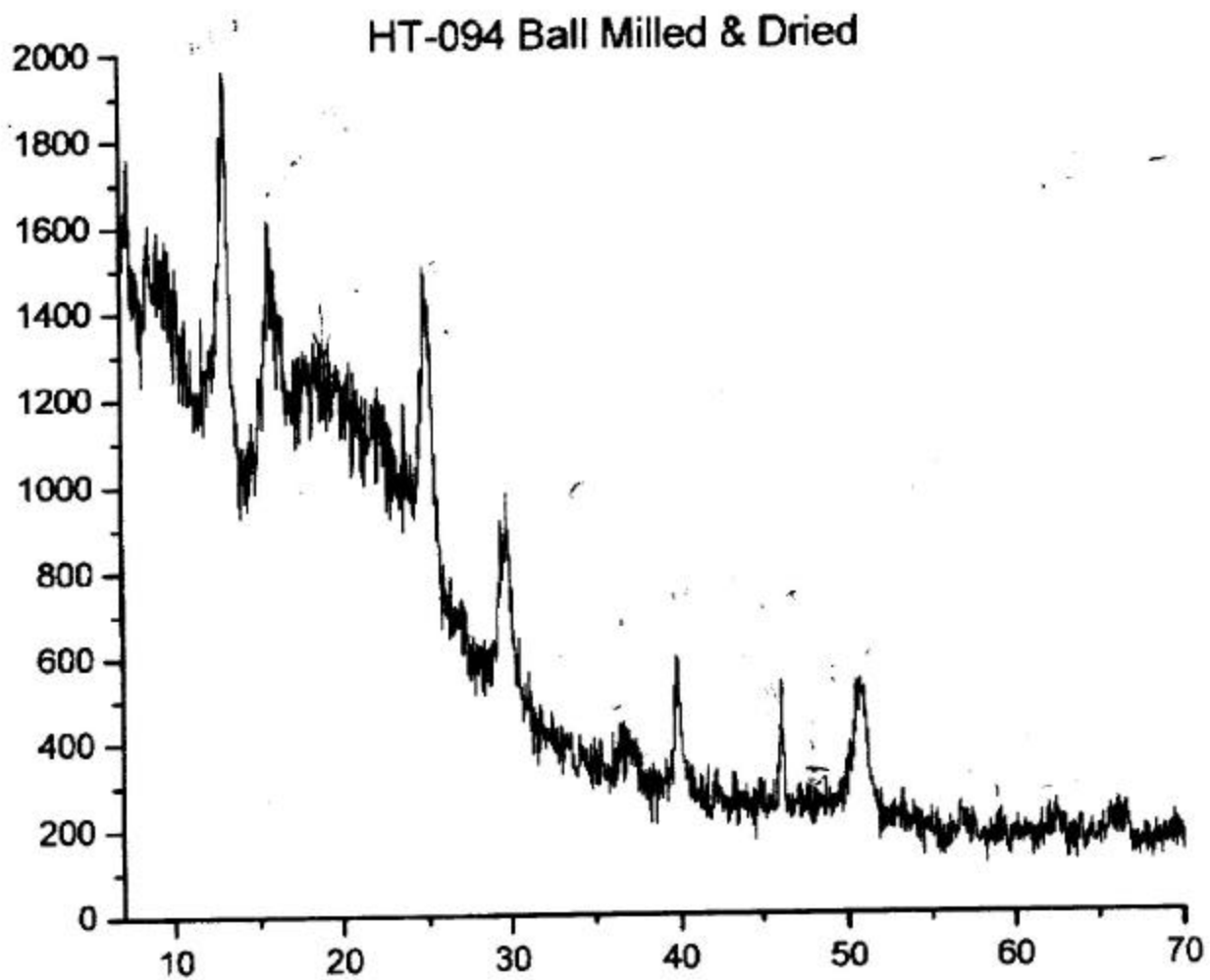


Figure 4 XRD of hydrotalcite powder prepared via sol-gel technique. HT-SG-03 dried at 80°C

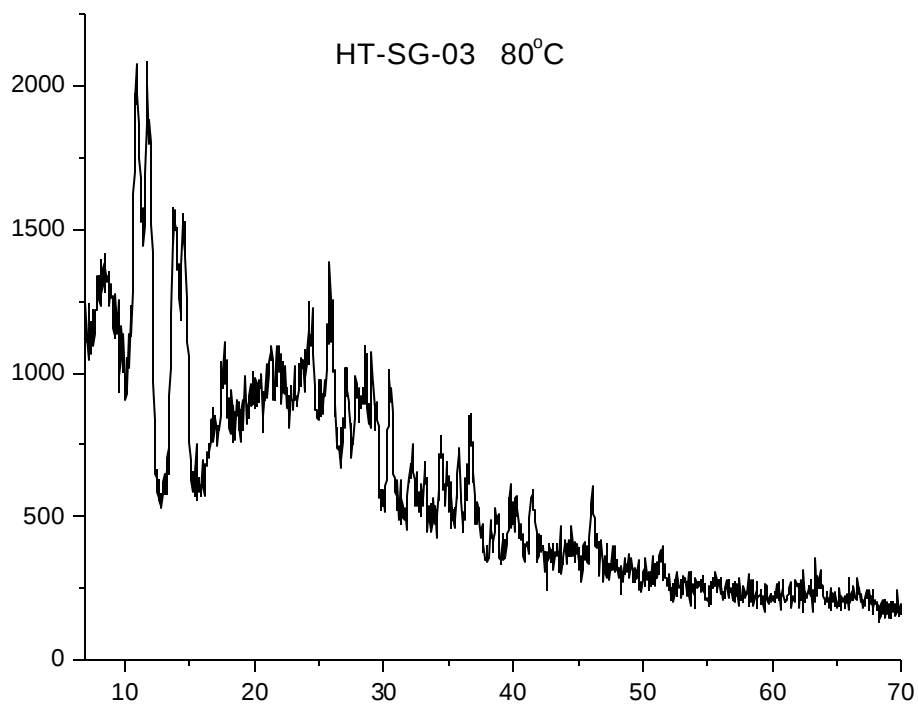


Figure 5 XRD of hydrotalcite powder prepared via sol-gel technique. HT-SG-03 dried at 80°C with an extended period (i.e., 2 hours)

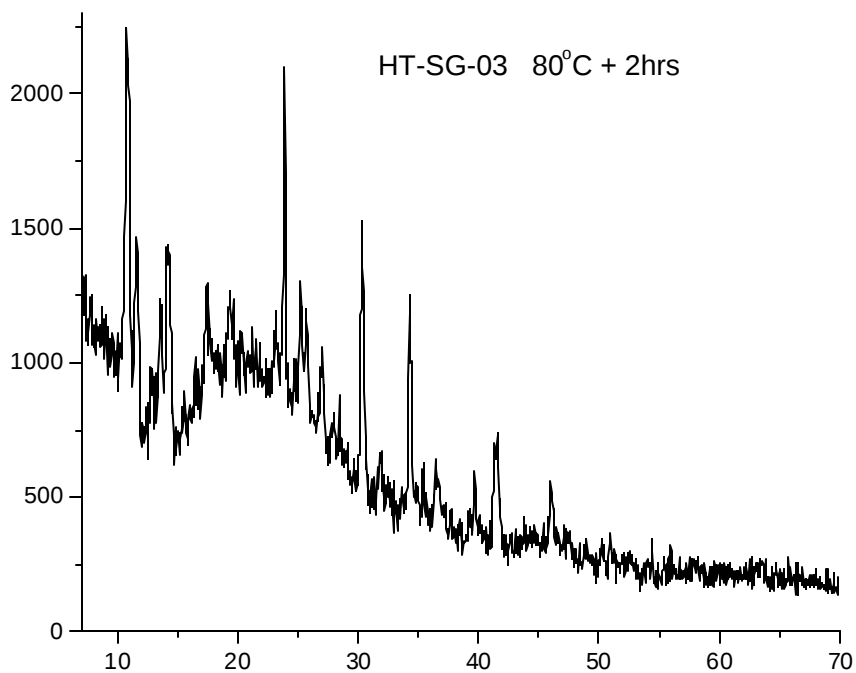


Figure 6 XRD of hydrotalcite powder prepared via sol-gel technique. HT-SG-03 dried at 250°C

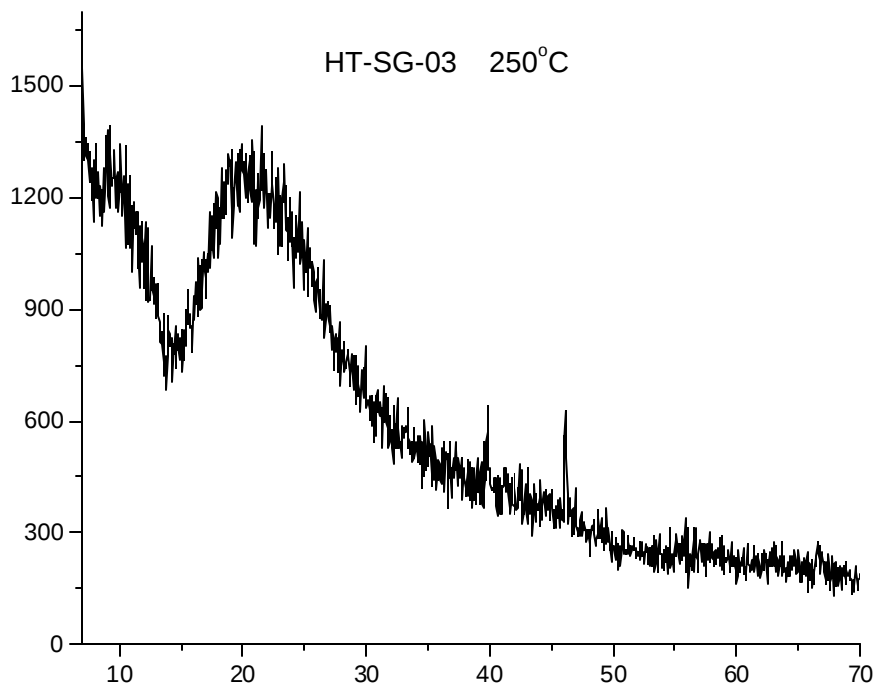
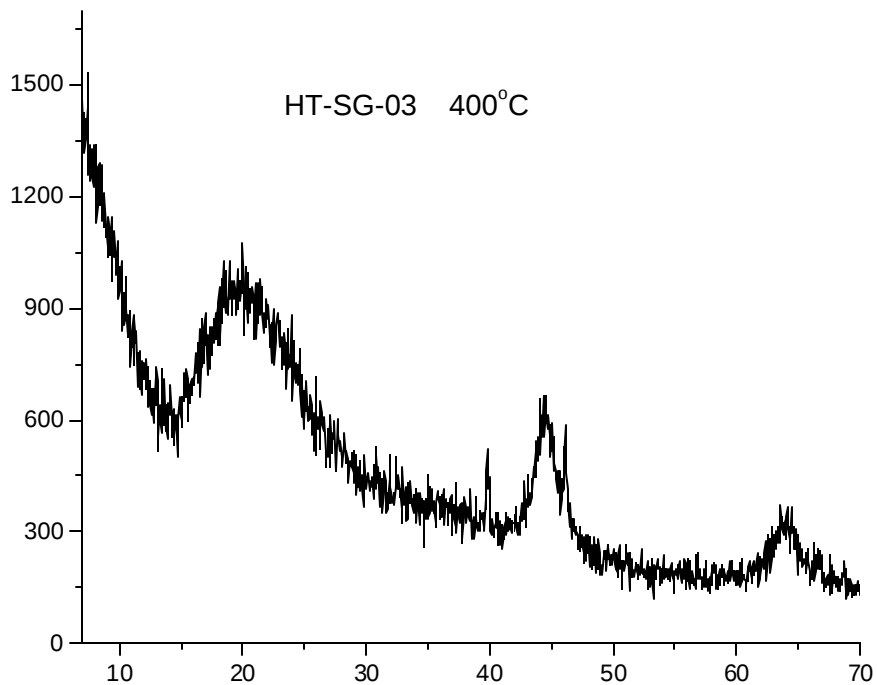


Figure 7 XRD of hydrotalcite powder prepared via sol-gel technique. HT-SG-03 dried at 400°C



List Of Acronyms and Abbreviations

CVD:	Chemical Vapor Deposition
DA:	Double Alkoxide
HT:	Hydrotalcite
SA:	Single Alkoxide
SEM:	Scanning Electro Microscopy
XRD:	X-ray Diffraction