

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

Quarterly Report for the Period April 2002- June 2002

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ABSTRACT

As part of our optimization effort, we have conducted a comprehensive study to investigate the morphology and crystal growth kinetics of hydrotalcite powder formation. Based upon the information obtained from this study, we resumed the membrane optimization activities. Although the selectivity of the membrane remains in the Knudsen regime, the permeance decreases along with the number of impregnation. Thus, the permeance could be reduced to a minimum through repeated impregnation. Then, the membrane can be sealed with chemical vapor deposition technique. More characterization results on the membranes prepared will be available in the next quarterly report.

1. Preparation of Hydrotalcite (HT) Crystals

To optimize the hydrotalcite membrane, a comprehensive knowledge in the area of the morphology and crystal growth kinetics is prerequisite. Unfortunately very scarce information is available in the literature in this area. As part of the optimization of the membrane synthesis, we have invested some effort to establish the database about the hydrotalcite crystal growth kinetics and its morphology. This quarterly report summarizes our progress made in this quarter.

1.1 HT Formation via Precipitation

Our previous experience has established that the $MgCl_2/AlCl_3$ mixture forms hydrotalcite precipitate once it is added into the Na_2CO_3 solution at an appropriate pH (e.g., 10). According to one of the literatures [1], aging did not affect the crystallinity of the HT formed. Puttadswamy and Kamath [2] further indicate that the crystallinity of the hydrotalcite formed via this type of precipitation is generally poor.

The literature findings are somewhat consistent with our XRD results obtained thus far using this synthesis method. Figures 1 to 6 show the XRD patterns of the samples prepared by precipitation, and then aging at $\sim 100^\circ C$ for 20 minutes to 2 hours. Compared with the XRD from well-crystallized material (see Figure 7), the crystallinity of the HT precipitate formed via this approach is considered poor. Further, we observe that the gel formed immediately once the solution is combined together via this precipitation approach. According to the analysis, this gel apparently shows a correct Al/Mg ratio. Thus, it is possible that HT formed immediately after precipitation (or at least that the gel formed) most likely contains the correct ratio of Al/Mg and could be hydrotalcite (or to a minimum can serve as a precursor). As far as the crystal size is concerned, we did not have the SEM observation. More study is under way to determine the crystal size based upon the SEM measurement.

Our conclusion from this part of the study is that HT forms via precipitation; however, its crystal structure is rather poor based upon the XRD analysis.

1.2 HT Formation via Co-precipitation

pH could be a major parameter to determine the morphology of the HT crystal. The above approach does not control the pH of the solution throughout the period of the addition of the Al/Mg mixture into the $Na_2CO_3/NaCl$ mixture. According to our experience, the initial pH could be as high as ~ 13 , while at the end of the addition remains to be >10 . The formation of hydrotalcite at pH= 8 and above is recommended [6,1]. At a lower pH, the chance for the precipitation of Brucite, $(Mg(OH)_2)$, is less likely; while the precipitation of $Al(OH)_3$ is more likely. Since, Al is the minor component (up to $\sim 1/3$) in the starting material, it is possible to form a small nucleus of hydrotalcite crystal at this lower pH range. On the other

hand, according to a US patent [6], the starting material and condition for preparing hydrotalcite is very flexible, using suspended Al and Mg chemicals as reagents are possible. However, the required crystal formation condition may be much harsher in order to form hydrotalcite. For comparison, this patent indicates that HT forms immediately if the reagents used are dissolved chemicals.

Under this part of the study, the pH is controlled by adding the two individual mixtures, i.e., Mg and Al, into a 3rd container with a pH control at 10, 8 and 6. In this report we refer this approach as “co-precipitation”, while the approach described in the above section as “precipitation”.

Thus far we have produced the HT crystals at pH=10, 8, and 6 via this method. All samples were subsequently aged at the same condition, i.e., 150°C for 4 hrs. In addition, these crystals have been well characterized. Table 1 presents the summary of this study. The HT formed at pH=10 exhibits an extremely sharp XRD pattern and shows the particles size in the range of ~5 microns (see Figures 7 and 8). This XRD pattern is consistent with the typical characteristics of hydrotalcite published in the literature (e.g., Ref. 3). It should be noted that this particle size could be the agglomerate of numerous crystals. SEM under a higher magnification may be required to determine the actual crystal size. The crystal formed at pH=8 and 6 are much smaller in the range of ~0.5 and <0.5 microns as shown in Figures 9 and 10, respectively. Their XRD patterns are vague; however, the characteristic peaks of HT are present as shown in Figure 11 and 12. In conclusion, the pH plays a role in the formation of the hydrotalcite crystal. As predicted, the lower the pH is, the smaller the crystal is formed. However, it is believed that all the three crystals formed contain hydrotalcite. The work remained includes:

- Determine the actual individual crystal size for the sample generated from pH=10.
- Determine the ratio of Mg/Al for the hydrotalcites generated from the three-pH levels.
- Evaluate the effect of the aging condition, i.e., time and temperature, on the crystal size, XRD pattern and Al/Mg ratio.

Although many loose ends need to be completed before we establish a comprehensive picture about the crystal formation and growth of hydrotalcite, some guidance for the preparation of the hydrotalcite membrane can be derived from the above studies. HT or its precursor should form within the porous membrane substrate under the conditions including:

- the Na_2CO_3 is impregnated within the porous structure of the membrane,
- $\text{MgCl}_2/\text{AlCl}_3$ is in contact with the Na_2CO_3 solution via dipping of the membrane into the $\text{MgCl}_2/\text{AlCl}_3$ swiftly, and

- The pH of the solution and the aging condition should be controlled at the target pH.

We have synthesized membranes according to the above conditions before; however, the results are mixed and unsuccessfully. Under this optimization phase of the project, we resume this activity with a rigorous control of each step. The preliminary results are presented in the next section.

2. Preparation of Hydrotalcite Membrane via Interphase Contact.

As mentioned previously, we have performed a very rigorous study for the preparation of the hydrotalcite membrane under this approach. They are discussed in this section.

2.1 Membranes impregnated with Na₂CO₃/NaOH

According to the previous experience, we believe that (i) the Na₂CO₃/NaOH solution should be impregnated in the porous substrate first, (ii) the Al/Mg mixture should then be in contact with one side of the membrane as briefly as possible to minimize the thickness of the HT crystal formation, and (iii) the pH of the Na₂CO₃/NaOH solution could determine the particle size of the crystal. To insure the crystal formed within the porous structure, instead of depositing on top of the membrane surface, it is advisable that the pH of the impregnant should not be too high, such as >12. The crystal may form immediately during the contact and deposit on the outside of the substrate if (i) the pH is too high, and/or (ii) the crystal is too big.

In this subsection, we summarize the result using the impregnant as received, i.e., the NaOH/Na₂CO₃ used in the preparation of the HT, whose pH is believed to be >12. The membrane after initial contact was then aged at 150°C for 4 hrs. Then the membrane is rinsed in tap water until its pH is less than 7 to eliminate impurities. Finally the membrane is dried at 120°C before the gas permeation measurement. The gas permeance of the membranes thus prepared is presented in Table 2. The results are somewhat unexpected. However, if one takes into consideration the solubility of Al or its impurities is most likely inversely proportional to the temperature. In addition, the dissolution of the substrate is most likely resulted in the permeance decrease. At a given temperature, the sample contacted with Al/Mg is most likely impregnated with the solution at a lower pH; thus, its permeance is expected to be higher due to the less likelihood of the dissolution.

2.2 Membrane Impregnated with Na₂CO₃

Since we suspect that the pH of the impregnant in Sec. 2.1 may be too high, we use the Na₂CO₃ without NaOH in this section. The pH of the impregnant is

believed to be ~xxx. The procedure remains similar to that used in Sec. 2.1 The gas permeation results are presented in Table 3. Comparison between the control and the sample, it is believe that solid deposition takes place in the sample with Al/Mg. However, the control also shows reduction in permeance although its degree of reduction is much less. Presently we (i) are continuing the number of deposition cycles, (ii) introduce the 2nd control membrane, which will be the control of the existing control, i.e., following the same procedure without using any chemicals, and (iii) submit the samples for SEM analysis to determine the location of the deposition.

3. Alternative Membrane Synthesis Methods

In this period, we also updated our literature search with the focus on the potential membrane synthesis methods. They are documented as follows:

3.1 In-site Formation of Hydrotalcite Membranes

Formation of hydrotalcite on the interface of the porous γ -Al₂O₃ catalyst with Ni has been reported [4]. The protocol involves the preparation of the Ni-solution using ammonium nitrate. Further to avoid the precipitation, additional ammonium nitrate is added to complex with the metal present. The solution was kept at pH=8 via ammonia bubbling. After aging of 5 to 6 hours, hydrotalcite formation on the interphase was observed. Can we take this approach to form hydrotalcite on a 40A membrane? The challenge we believe is that (i) the crystal size thus formed is sufficient to plug the 40A pore opening completely, or (ii) the residual opening may be small enough for CVD.

3.2 Use of Ammonia Salts

The 2nd approach possibly useful to us is to prepare the metal solutions which are complexes with ammonium ions. Thus, the precipitation of single hydroxide would not take place during depositing into the porous structure of the membrane. Then the crystallization of HT relies on the aging condition/or alternating pH. This method may be a good approach for us. However, we did not know the yield of the hydrotalcite and the potential of the formation of the single oxide. We may try this approach in a free solution to determine the yield under this proposed condition.

3.3 Sol-Gel Approach

The last method mentioned in the literature [5] is the sol-gel scheme. It is possible to form a HT with the gel particles, which are small enough to penetrate into the porous structure of the substrate. We will investigate the chemistry end

of the sol-gel scheme to assess its feasibility. This is an alternative to chemical precipitation, which, according to our experience, tends to produce a large particle, and thus causing the problem from the membrane formation standpoint.

4. Reduction of Unreacted Al and Mg

Although most literature indicates the formation of hydrotalcite follows the stoichiometric ratio of the reagents, no literature explicitly discusses the amount of unreacted Al and Mg (except the one via sol-gel scheme, which produces significant single oxides). Several approaches can be taken to minimize the impurities. They are discussed as follows:

- The higher temperature and higher-pressure condition can facilitate the growth and it is possible to utilize the Al and Mg as completely as possible. Thus, the amount of residual Al and Mg is minimum.
- Since $\text{Al}(\text{OH})_3$ is soluble at $\text{pH} > 10$ (or 11) and the hydrotalcite is expected to be stable at this alkali environment, it is possible to leach the unreacted $\text{Al}(\text{OH})_3$ via alkali rinse.
- MgCO_3 is soluble in acid, it is possible to rinse the hydrotalcite briefly at this low pH to leach MgCO_3 without dissolve hydrotalcite.
- Finally MgCO_3 is soluble in CO_2 , thus, it is possible using the supercritical CO_2 to leach MgCO_3 as much as possible.
- According to Brindley and Kikkawa, the maximum substitution is $\text{Mg}:\text{Al}=2:1$. Any larger substitution places Al ions in adjacent octahedral groups and may thereby lead to nucleation of $\text{Al}(\text{OH})_3$.

The above guidelines will be taken into consideration for our future optimization study of the membrane synthesis.

References:

1. Vaccari, Angelo, "Preparation and Catalytic Properties of Cationic and Anionic Clays", *Catalysis Today*, 41, 53(1998)
2. Puttaswamy, N. S., and P. Visbnu Kamath, "Reversible Thermal Behaviour of Layered Double Hydroxides: A Thermogravimetric Study", *J. Mater. Chem.*, 7, 1941(1997)
3. Olsbye, U., D. Akporiaye, e. Rytter, M. Ronnekleiv, and E. Tangstad, "On the Stability of Mixed $\text{M}+2/\text{M}+3$ Oxides", *Applied Catalysis A: General*, 224, 39(2001)
4. E. Merlen, P. Gueroult, J-B Caillerie, B. Rebours, C. Bobin, and O. Clause, "Hydrotalcite Formation at the Alumina/Water Interface during Impregnation with Ni(II) Aqueous solutions at Neutral pH", *Applied Clay Science*, 10, 45(1995)
5. T. Lopez, P. Bosch, E. Ramos, R. Gomez, O. Novaro, D. Acosta, and F. Figueras, "Synthesis and Characterization of Sol-Gel Hydrotalcites. Structure and Texture", *Langmuir*, 12, 189(1996)

6. Kumura, T. etc., "Novel Synthetic Hydrotalcite And Antacid Comprising Said Synthetic Hydrotalcite", US Patent 3,650,704, March 21, 1972.

Table 1 Summary of SEM and XRD Analysis of Hydrotalcites

Sample ID	pH	Aging	Special Condition	SEM	XRD	Al/(Mg + Al)
HT-062		?? for 6 hrs	Precipitation	Uniform hexagonal disk, about 0.5 μ	NA	NA
HT-069-0.5hr		95°C for 0.5 hr	Precipitation	(too dilute)	Good (some Mg(OH) ₂)	NA
HT-069-1.5 hr		95°C for 1.5 hr	Precipitation	(too dilute)	Good (Some Mg(OH) ₂)	NA
HT-070		95°C for 4hr	Precipitation and then transfer to NaOH/Na ₂ CO ₃ solution	(too dilute)	OK (Some Mg(OH) ₂)	0.151
HT-077	10	150°C for 4hr	Co-precipitation	~5 μ	Excellent	0.155
HT-078	8	150 °C for 4hr	Co-precipitation	~0.5 μ	Typical HT contaminated with extraneous peaks (unknown)	0.155
Ht-081	6	150 °C for 4hr	Co-precipitation	< ~0.5 μ , no resolution under 1000X	Typical HT with a lot of noise and not sure the presence of Impurity peaks	0.498
HT-084-1	10	150C for 0 hr (control)	Co-precipitation	NA	NA	NA

Table 2 Permeance of Membranes Prepared via Interphase using NaOH/Na₂CO₃ as Impregnant

Sample #	Impregnant	Solution	Aging Temperature °C	Permeance (m ³ /m ² /hr/bar)	
				N ₂	He
HT-079-1	NaOH/Na ₂ CO ₃	AlCl ₃ /MgCl ₂	95	11.35	20.82
HT-079-2	NaOH/Na ₂ CO ₃	-	95	2.30	4.42
HT-079-3	NaOH/Na ₂ CO ₃	AlCl ₃ /MgCl ₂	150	21.54	37.03
HT-079-4	NaOH/Na ₂ CO ₃	-	150	22.11	-

Table 3 Permeance of Membranes Prepared via Interphase using Na₂CO₃ as Impregnant

Sample #	Impregnant	Solution	Aging Temp °C	Permeance (m ³ /m ² /hr/bar)		Notes
				N ₂	He	
HT-080-1	Na ₂ CO ₃	AlCl ₃ /MgCl ₂	95	9.53	18.56	
HT-080-2	Na ₂ CO ₃	-	95	26.54	46.32	
HT-080-3	Na ₂ CO ₃	AlCl ₃ /MgCl ₂	150	5.60	9.88	
HT-080-4	Na ₂ CO ₃	-	150	42.31	80.00	
HT-080-5	Na ₂ CO ₃		150	48.73	92.88	Repeate of HT-080-3
HT-080-6	Na ₂ CO ₃	AlCl ₃ /MgCl ₂	150	18.40	28.76	Repeate of HT-080-4
HT-080-5	Na ₂ CO ₃		150	24.11	44.06	2 nd deposition
HT-080-6	Na ₂ CO ₃	AlCl ₃ /MgCl ₂	150	13.40	22.79	2 nd deposition

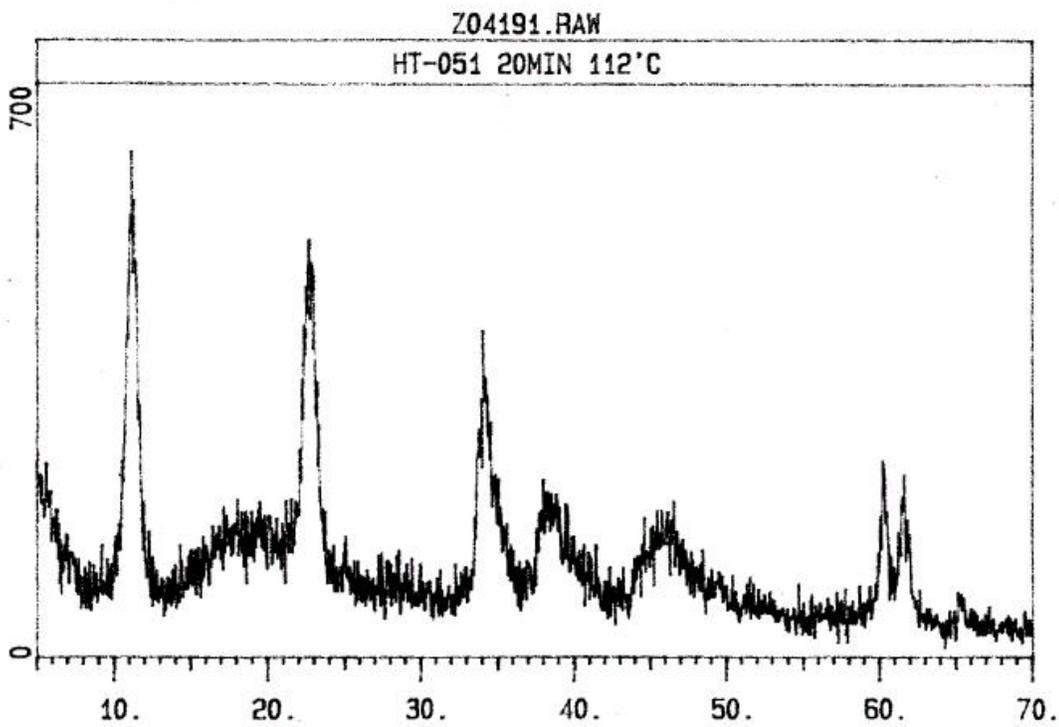


Figure 1: XRD of hydrotalcite prepared via precipitation and then aged at 112°C for 20 minutes.

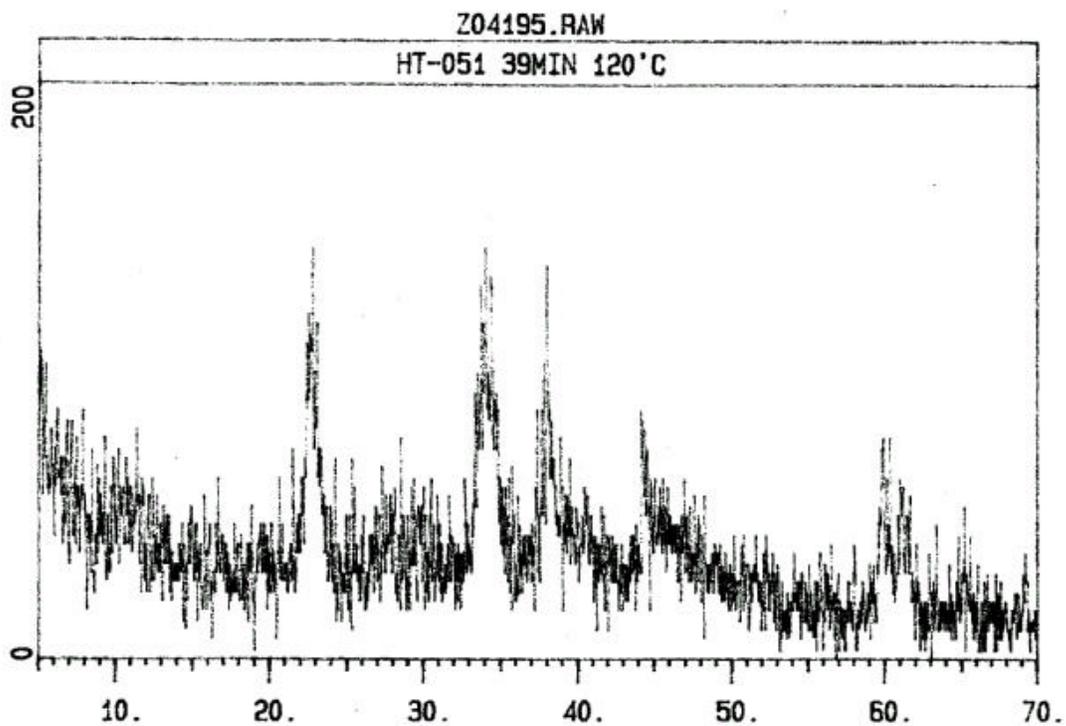


Figure 2: XRD of hydrotalcite prepared via precipitation and then aged at 120°C for 39 minutes.

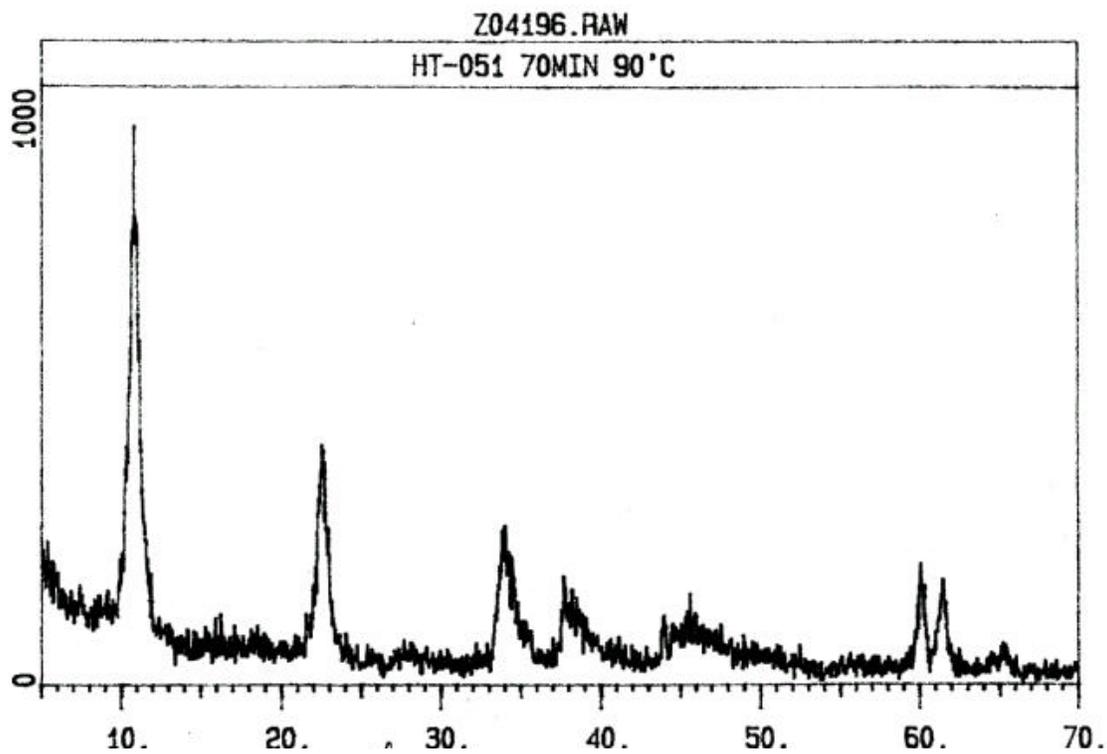


Figure 3: XRD of hydrotalcite prepared via precipitation and then aged at 90°C for 70 minutes.

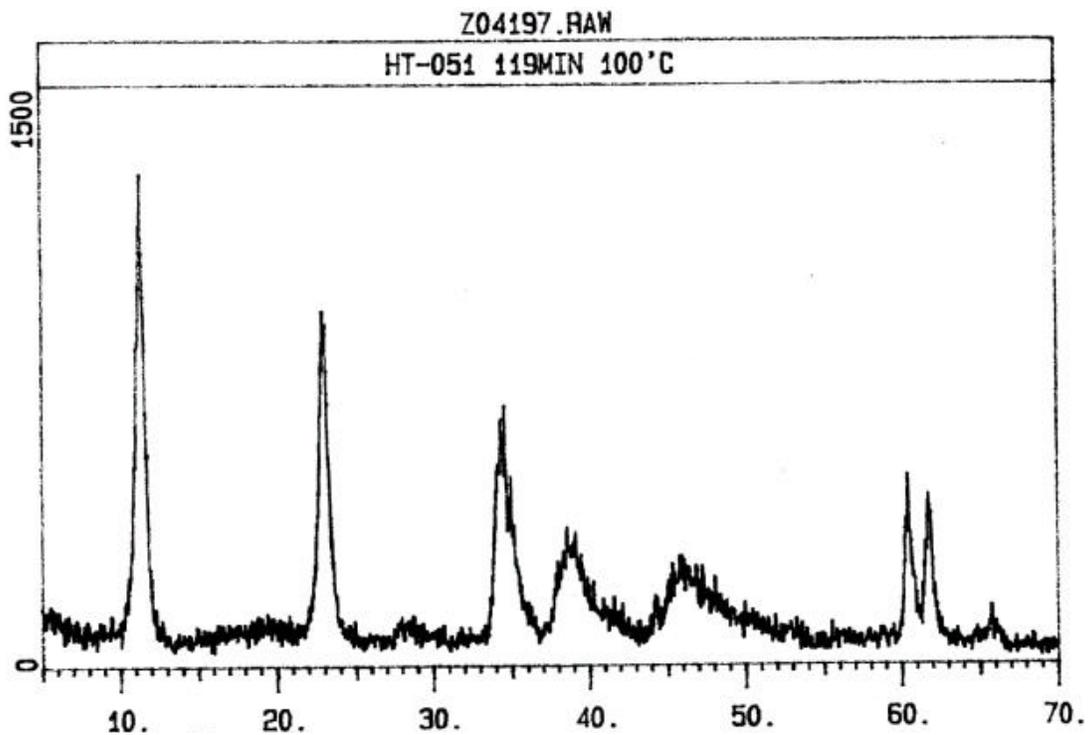


Figure 4: XRD of hydrotalcite prepared via precipitation and then aged at 100°C for 117 minutes.

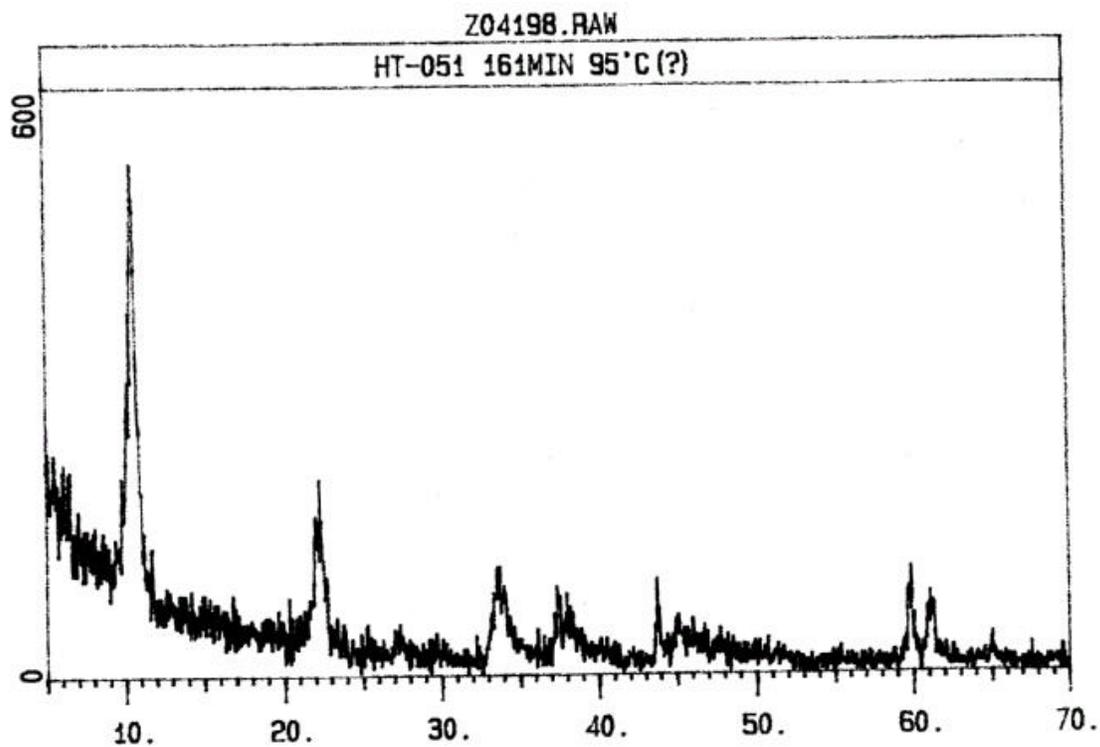


Figure 5: XRD of hydrotalcite prepared via precipitation and then aged at 95°C for 161 minutes.

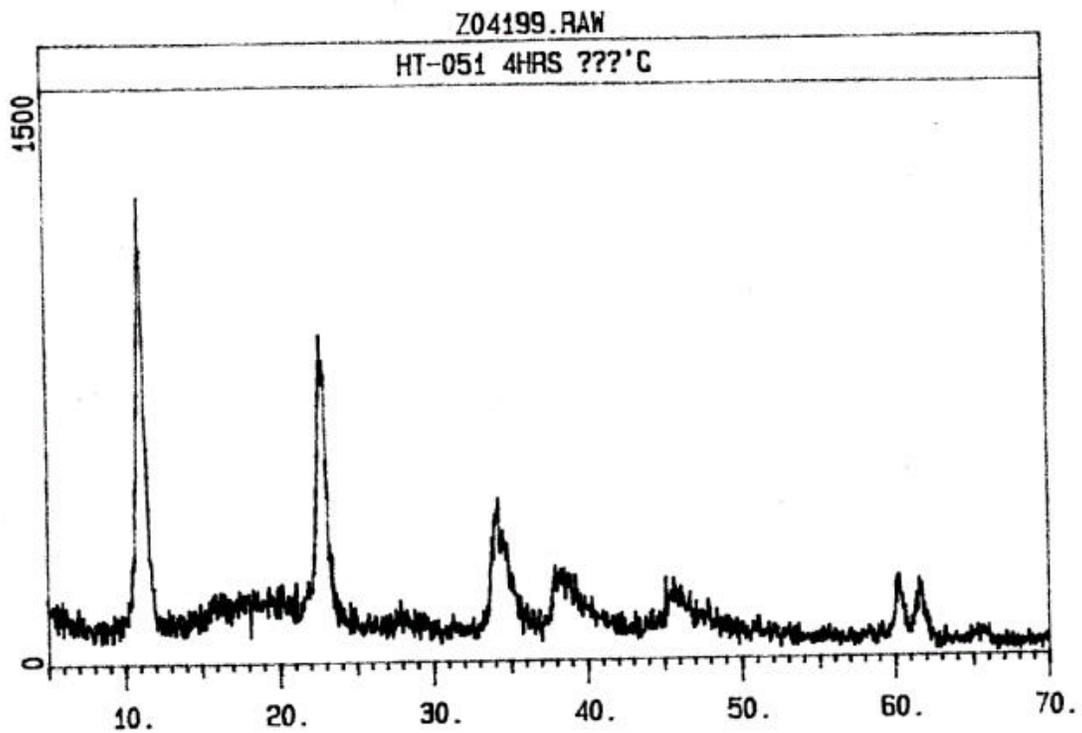


Figure 6: XRD of hydrotalcite prepared via precipitation and then aged at 100°C for 4 hours

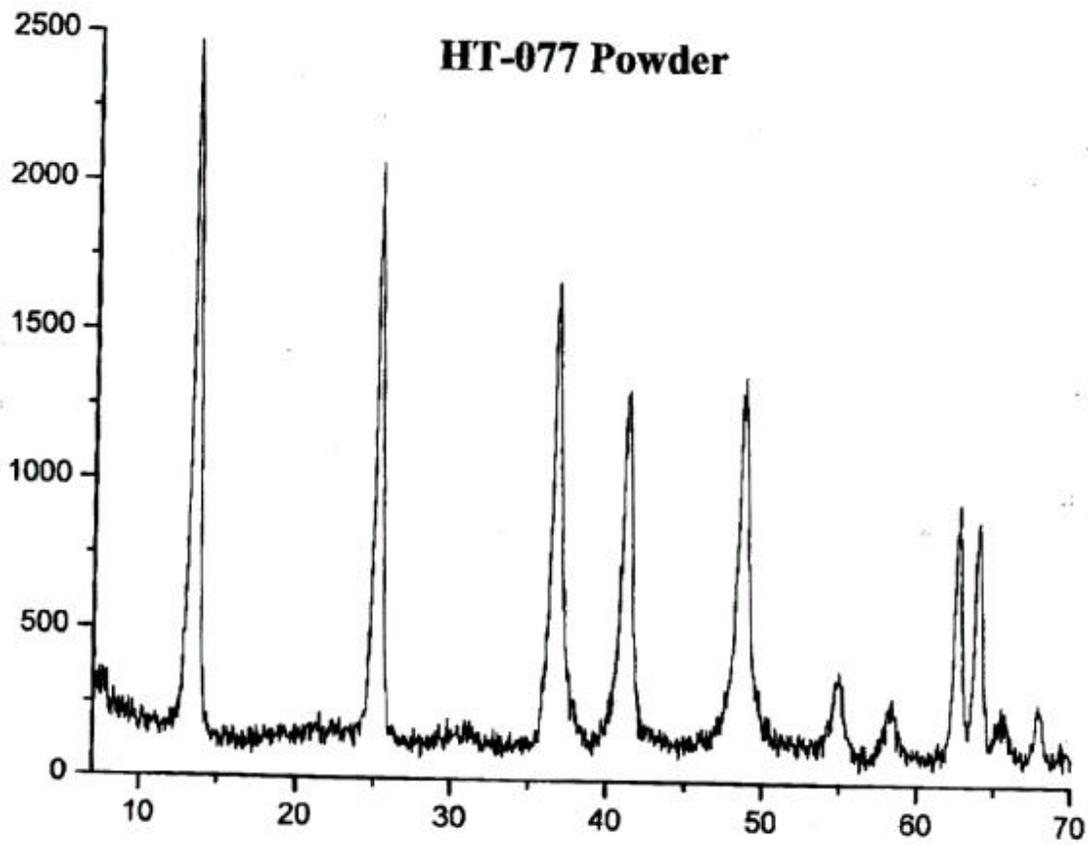


Figure 7: XRD of hydrotalcite prepared via co-precipitation at pH=10 and then aged at 150°C for 4 hours.

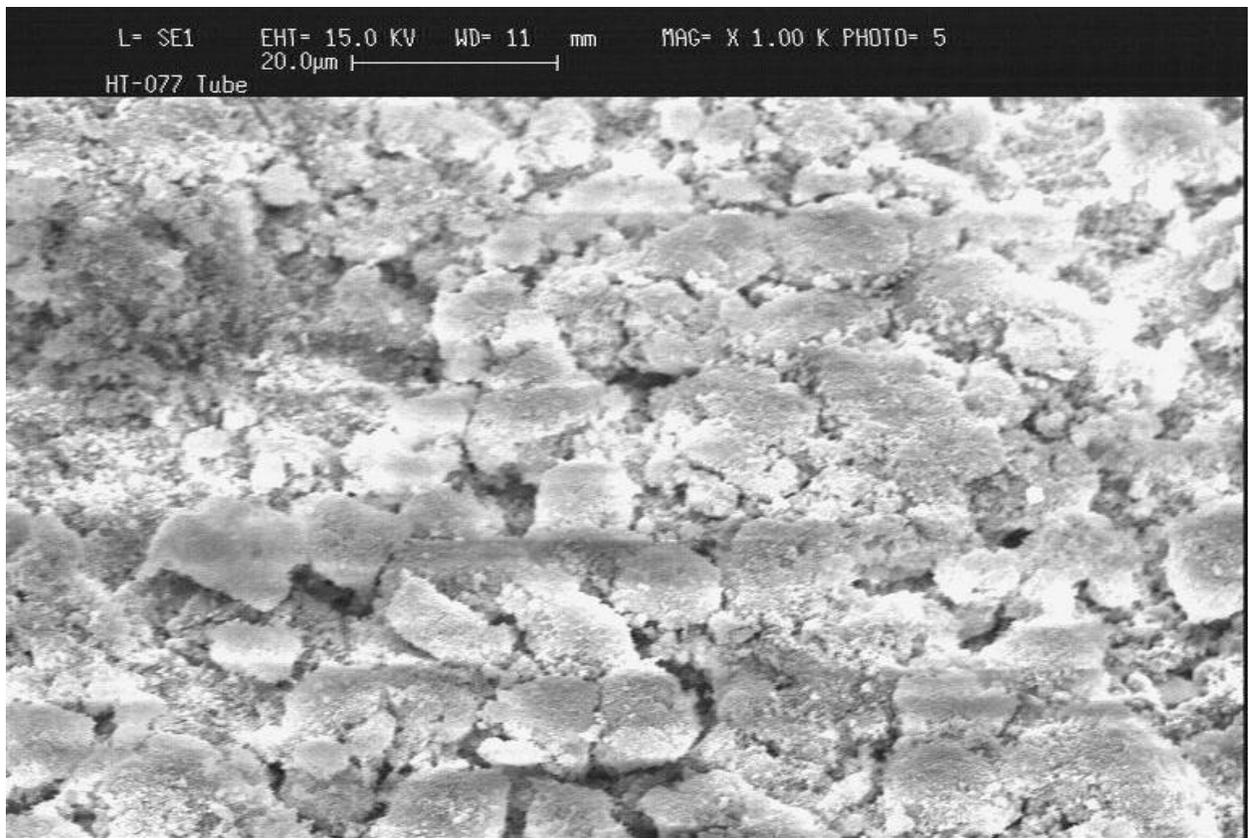


Figure 8: SEM photomicrograph of hydrotalcite prepared in a co-precipitate pH=10 and aged at 150°C for 4 hours.

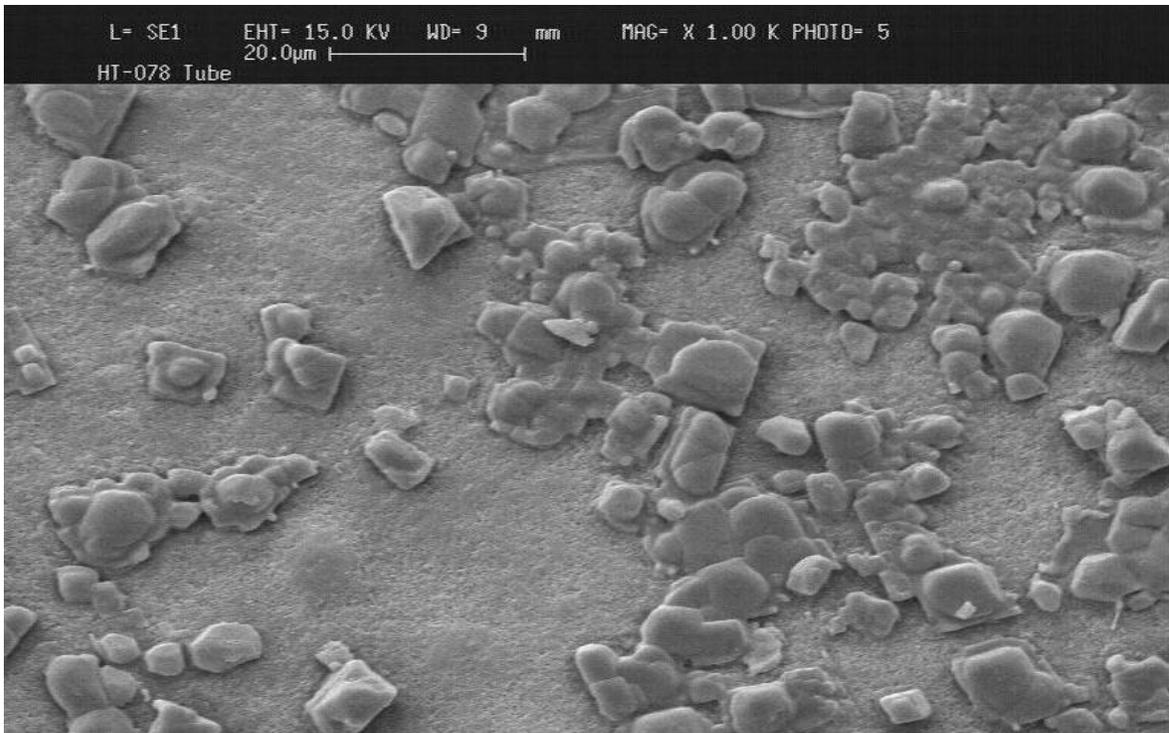


Figure 9: SEM photomicrograph of hydrotalcite prepared via co-precipitate at pH=8 and then aged at 150°C for 4 hours.

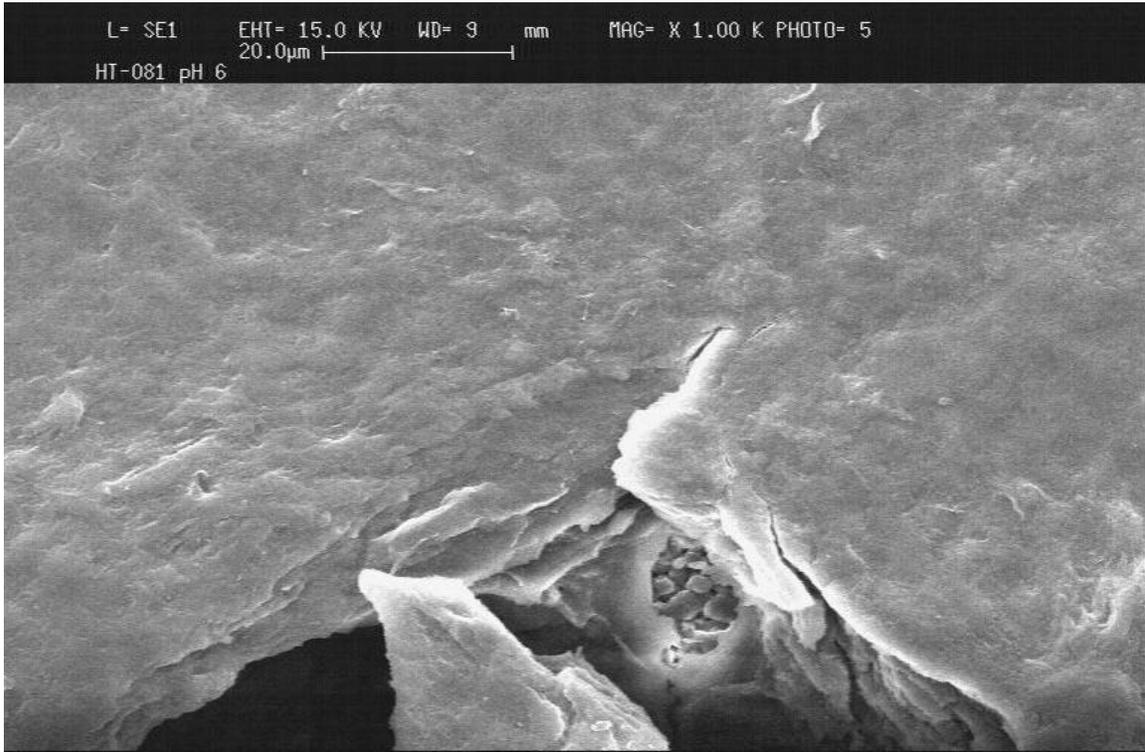


Figure 10: SEM photomicrograph of hydrotalcite prepared via co-precipitate at pH=6 and then aged at 150°C for 4 hours.

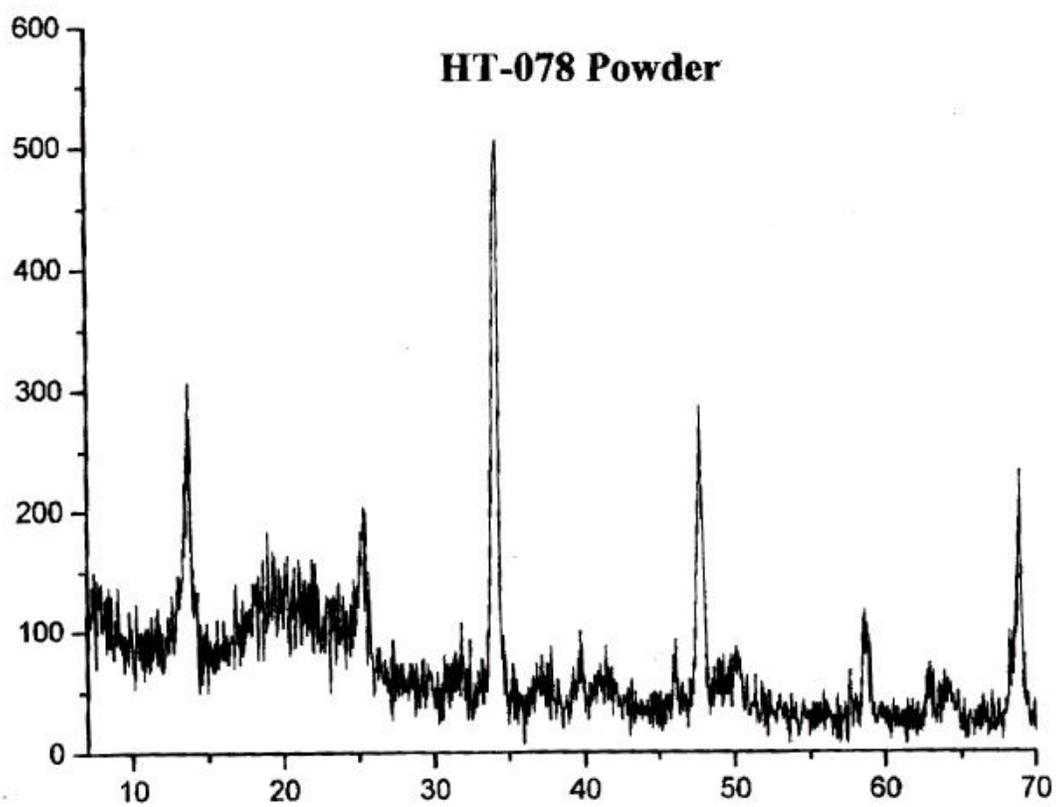


Figure 11: XRD of hydrotalcite prepared via co-precipitation at pH=10 and then aged at 150°C for 4 hours.