

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

Quarterly Report for the Period July 2001- September 2001

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Technical Summary

This quarterly report focuses on the two specific topics:

- Reversibility of CO₂ affinity of hydrotalcite materials
- In-situ crystallization of hydrotalcite on commercial tubular ceramic membrane as substrate.

The former relates to the foundation of the use of the hydrotalcite material as a membrane. The later addresses the first step of the membrane synthesis we propose. Our study concludes that the CO₂ affinity of the hydrotalcite material is reversible at 150°C and in the presence of water using TG/MS. Additional study at a high pressure and/or high temperature will be performed to scope the operating range of the membrane. On the other hand, the in-situ crystallization is proven to be an effective first step for the hydrotalcite membrane synthesis. Our result indicates that about hydrotalcite covers about 50% of the porosity of the substrate, ideal as a seed for the 2nd step involving in-situ crystal growth. Our next quarterly report will report the result from the study on the 2nd step.

1. Reversibility of CO₂ Affinity of Hydrotalcite

Hydrotalcite is known for its surface affinity to CO₂ in the presence of water at an intermediate temperature range, i.e., 150 to 450°C. However, this affinity must be reversible via pressure and/or temperature swing in order to become a viable steady state CO₂ separation process through the membrane. Although knowledge regarding adsorption fundamentals of hydrotalcite materials suggests its reversibility, no literature study (i.e., experimental study) is available to verify this reversibility, particularly in the presence of water. As part of this project, an experimental program has been conducted for this purpose. Up to this point, we have completed the reversibility study using a TG/MS. Due to the limitation of the instrument, pressure swing between vacuum to <1 atmospheric pressure has been performed. The experimental study involving the pressure > 1 atm is presently under study using a high-pressure adsorption test rig.

1.1 Experimental

Powder hydrotalcite material was used in this study. A thermal gravimetric analyzer (TGA) with MS is used for this purpose. Step by step experimental condition is listed as follows:

- (1) Evacuation for one day (below 50 mTorr)
- (2) Ramp to 250°C at 5°C/min (P: vacuum)
- (3) Isotherm 30 min at 250°C (P: Vacuum)
- (4) Ramp to 150°C at -5°C/min (P: Vacuum)
- (5) Isotherm 120 min at 150°C (P: atmosphere with humidified CO₂)
- (6) Ramp to 250°C at 5°C/min (P: Vacuum)
- (7) Repeat (3) thru (6)

In addition a MS is used to analyze the off-gas on-line. Due to time lag resulted from the gas sample traveling from the balance in TGA to the MS, possible sample mixing, and other factors, MS is used here as a semi-quantitative tool to determine the relative composition of water vs CO₂ evolved to indicate the CO₂ affinity in the presence of water.

1.2 Results

Table 1 lists the experimental result with TGA using humidified CO₂ (at room temperature) as a carrier gas. The reversibility of CO₂ affinity is demonstrated in this 4-cycle study. Further in a separate study, MS analysis indicates the presence of both water and CO₂ in the off-gas. Thus, the reversibility in the presence of water is evident.

In a previous run, a shorter adsorption cycle was performed, i.e., 30 instead of 120 minutes as in the above study. The result of this shorter cycle run is listed in Table 2.

The result indicates that the degree of reversibility could be suffered if the adsorption time is insufficient.

In summary, in a membrane configuration with a steady state transport process, CO₂ is expected to adsorb and desorb reversibly to achieve the selective removal of CO₂ based upon the affinity of the hydrotalcite material.

1.3 Recommendations

- A similar reversibility study with the high-pressure adsorption unit is underway and will be completed in the near future to prove the reversibility at a high-pressure condition similar to the operating condition of the membrane.
- A similar experimental study as described here will be repeated for temperature at 200 to 500°C to define the operating range of the hydrotalcite membrane.

2. Hydrotalcite Membrane Synthesis via In-situ Crystallization

In a previous quarterly report, we described the membrane synthesis technique involving in-situ crystallization as a first step. Then, in-situ crystal growth may be added as a 2nd step to reduce the residual pore opening prior to the post treatment by chemical vapor deposition (CVD). In the 1st quarterly report, we summarized the result of the in-situ crystallization on the outer surface of the 0.2 μ m and 500 Å porous ceramic tubular substrates. The result was promising. In this quarterly report we summarize the result using this similar technique; however, the crystal is deposited on the inner tubular surface, instead of the outer surface. For a tubular ceramic membrane, it is a common practice to deposit the selective layer on the inner tubular surface for many technical reasons. In this section, we present the result on the deposition of the inner tubular surface.

2.1 Experimental

An experimental technique described in the 1st quarterly report for the deposition on the outer tubular surface is adapted here with minor modifications. The ceramic tube with one end sealed with epoxy was immersed into a MgCl₂ solution; then, the AlCl₃ solution is quickly added into the inner tubular space to initiate the crystallization in the interface immediately. The tube after this treatment is then subject to permeation flow rate measurement as an indication of the degree of the pore filling by the crystal. This in-situ crystallization was repeated up to 7 times to determine the improvement of the pore filling along with the number of the crystallization. In addition, to determine

qualitatively the residual opening size, an initial flow measurement is conducted to quantify the % of flow contribution by the pore size in the order of $>100\text{\AA}$. The pore size $>100\text{\AA}$ according to our previous experience is too big for developing a high quality CVD thin film. Thus, the degree of initial flow remained offers some guidance in terms of the requirement of the in-situ growth as a second step.

2.2 Results

The permeation rate of the tubes with crystallization up to 7 times is summarized in Table 3 and Figure 3. The permeance of the membrane decreases along with the increase of the number of the crystallization. However, the initial flow measurement shown in Table 3 exhibits a similar degree of the remaining initial flow (i.e., ~50 to 60%) for the four samples prepared. Combining these results, one concludes that the crystal deposition after the 1st time likely settles on the top of the previous crystals to form an additional layer, instead of filling the residual gap. Thus, we conclude that one time in-situ crystallization may be adequate as seed for the subsequent growth to fill ~50% of the residual opening. The membrane sample is also examined under SEM as shown in Figures 1&2. In comparison with the bare substrate (Figure 5 of the quarter report, Jan-March 2001), the crystal formation on the inner membrane surface is evident. However, the penetration of the crystal cannot be deciphered by merely SEM examination. In fact the surface cracks as observed in these figures is supportive to the notion that the deposited layer >the 1st time may be too thick.

In a separate experiment with the 0.2 μ substrate, the initial flow measurement shows a much-improved coverage by the crystal. However, the residual initial flow did not stabilize throughout the experimental study as shown in Figure 4, indicating that some artifact may be present. The result from this 0.2 μ substrate study will be repeated in the near future for selecting an ideal substrate for membrane synthesis in Year II.

2.3 Recommendation

- The in-situ growth with the 0.2 μ pore size will be completed for determining its suitability as substrate in comparison with the 500 \AA substrate.
- An surface analysis by EDX is currently undertaken. EDX analysis will be able to verify the presence of the hydroxalcite crystal and also determine the degree of the crystal penetration into the substrate. The results will be reported in the next quarterly report.

Table 1 **CO₂ Affinity in a Multiple Cyclic Study (with A Longer Adsorption Cycle)**

Cycle	Wt loss via vacuum (%)	Wt gain via adsorption (%)
2 nd	2.83	2.76
3 rd	2.67	2.61
4 th	2.57	2.52

Table 2 **CO₂ Affinity in a Multiple Cyclic Study (with a Shorter Adsorption Cycle)**

Cycle	Wt loss via vacuum (%)	Wt gain via adsorption (%)
2 nd	2.00	1.75
3 rd	1.69	1.66
4 th	1.21	0.50

Table 3 Initial flow measurement of the 500A membrane after in-situ crystallization of hydrotalcites (8/27/2001)

HT-027-500A-1			HT-027-500A-3			HT-027-500A-5			HT-027-500A-7		
Time (hr)	Permeance	Initial Flow(%)	Time (hr)	Permeance	Initial Flow(%)	Time (hr)	Permeance	Initial Flow(%)	Time (hr)	Permeance	Initial Flow(%)
0.00	28.3	100	0.00	12.2	100	0.00	6.3	100	0.00	2.3	100
0.18	21.2	75	0.15	9.4	77	0.20	4.9	78	0.03	2.1	89
0.43	20.7	73	0.35	8.3	68	0.73	3.9	62	0.15	1.8	75
0.87	20.3	72	0.52	7.8	64	1.03	3.6	56	0.35	1.6	69
			1.02	7.0	57				0.53	1.5	65
			1.10	6.9	57				0.77	1.4	61
									0.98	1.4	58
<u>Before water Permeation</u>											
He permeance	28.6	He Permeance	12.3	He Permeance	6.4	He Permeance	2.0				
N2 Permeance	11.7	N2 Permeance	5.0	N2 Permeance	2.6	N2 Permeance	0.8				
Selectivity	2.44	Selectivity	2.47	Selectivity	2.46	Selectivity	2.60				

Table 4 Initial flow measurement of the 0.2 micron membrane after in-situ crystallization

HT-026-0.2um-1			HT-026-0.2um-3			
Time (hr)	Permeance	Initial Flow(%)	Time (hr)	Permeance	Initial Flow(%)	
0	107.0		88	0	59.4	100
0.01	90.0		74	0.07	40.6	68
0.12	86.4		71	0.22	37.8	64
0.41	61.7		51	0.37	37.0	62
1.04	43.0		36	0.59	32.2	54
1.32	34.6		29	1.36	122.8	22
1.51	33.6		28	2.09	3.8	6
				2.29	2.1	3

Before Permeation

HT-026-0.2um-1	HT-026-0.2um-3	
He Permeance	121 He Permeance	58.5
N2 Permeance	61.5 N2 Permeance	32.5
Selectivity	1.96 Selectivity	1.8

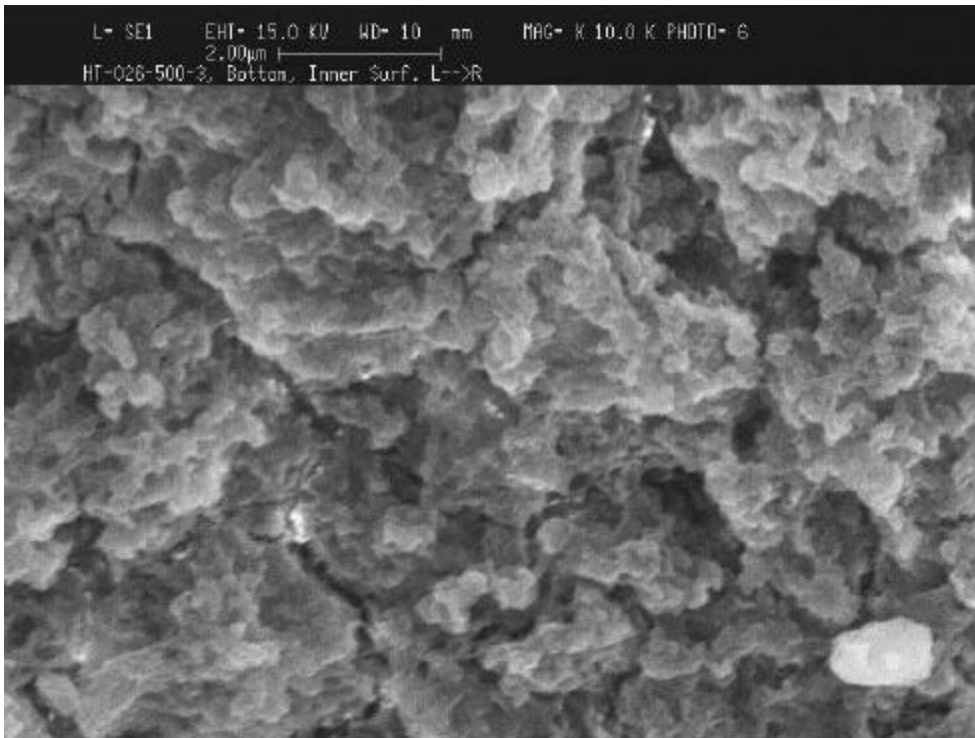


Figure 1 SEM photomicrograph of 500Å membrane deposited with hydrocalcite crystals via in-situ crystallization (3 times) – bottom of the inner tubular surface.

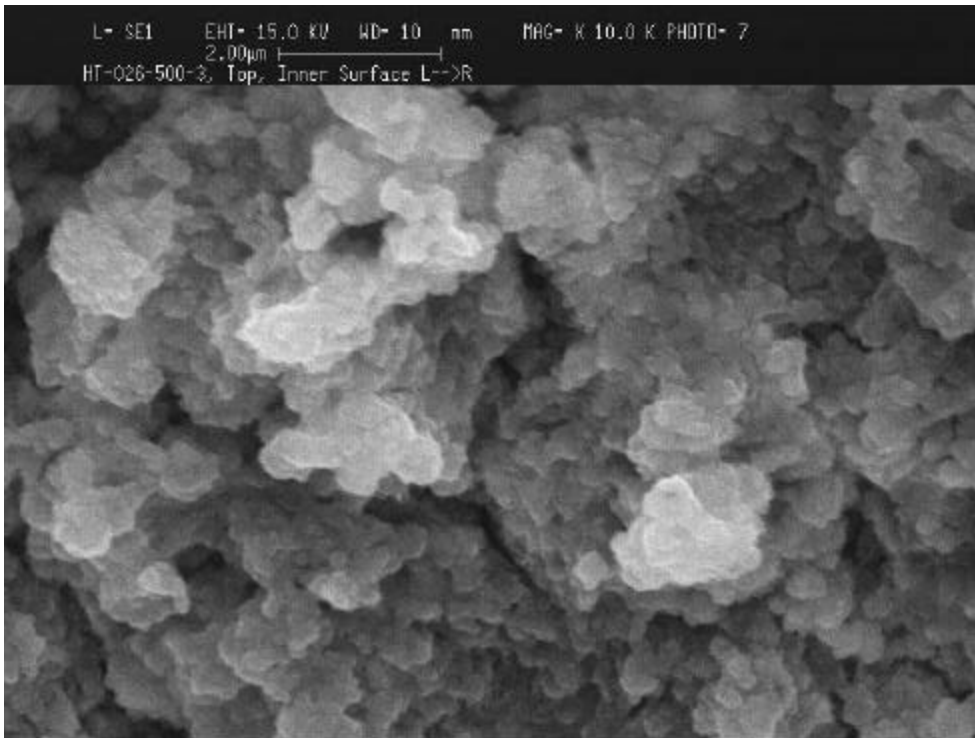


Figure 2 SEM photomicrograph of 500Å ceramic membrane deposited with hydrotalcite crystals via in-situ crystallization – top of the inner tubular surface.

Figure 3 Initial Flow of HT Membranes

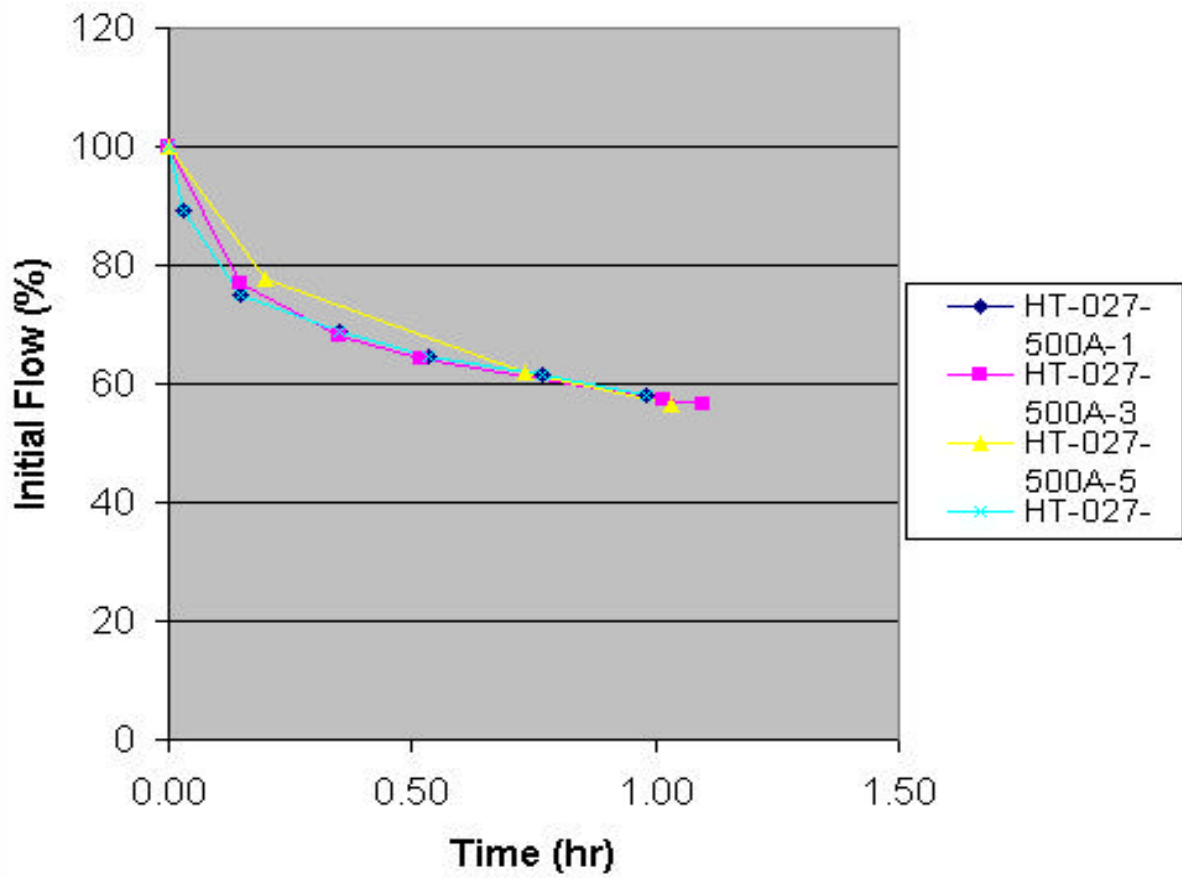


Figure 4 Initial flow measurement of 0.2 micron ceramic membrane depoisted with hydrotalcite

