CO_2 SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS SHIFT REACTION WITH CONCOMITANT FOR THE RECOVERY OF CO_2

Quarterly Report for the Period January 2002- March 2002

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Technical Summary

The reversibility study using TGA/MS has been completed. Our result shows that the hydrotalcite material we proposed exhibits a high degree of CO_2 reversibility. In addition, at higher temperatures (>200ºC), insignificant adsorption of water was observed. Combining these results, we conclude that the hydrotalcite we choose is an ideal candidate material for high temperature gas separations requiring hydrothermal stability. We also have focused on the optimization of membrane synthesis. The gel formed after combining the reagents is an ideal precursor for deposition within the porous membrane based upon the Al/Mg ratio analysis and impurity leaching study. Finally, we experimentally verify the crystal growth temperature ranging from 100 to 150ºC. The crystal growth is also highly dependent upon the time. Our study shows a general growth pattern from 0 to >4 hours. In the next quarter, we will utilize the information obtained here to initiate the optimization of membrane synthesis.

1. Reversibility of CO_2 Affinity vs. Temperature

Reversibility is an essential requirement for the proposed hydrotalcite as a candidate material for membranes. In this quarter, we have completed the reversibility studies based upon the adsorption/desorption behavior of hydrotalcite under isothermal conditions using thermal gravimetric analysis (TGA) in conjunction with mass spectrum (/MS). The experiments were carried out keeping the temperature constant in a humidified atmosphere of CO_2 (~3% H_2O) during the adsorption step, and under vacuum during the desorption step. The desorption step time was set as 1hour, while the adsorption step lasted for 3hour. For every temperature, 5 adsorption/desorption cycles were repeated. During the adsorption part of the cycle we monitor the weight change of the material, while during the desorption part of the cycle we monitor the weight change together with the composition of the gases evolved.

The results are summarized below:

Table 1 Cyclic CO_2 Adsorption and Desorption using TG/MS at 150° C

	Total weight loss at desorption (wt %)	Total weight gain at adsorption (wt %)	Composition of gases evolved determined by MS	
			CO_2 (wt %)	H_2O(wt %)
1st Cycle	1.98	1.91	0.017	1.883
2nd Cycle	1.88	1.83	0.015	1.865
3rd Cycle	1.79	1.77	0.016	1.774
4th Cycle	1.70	1.66	0.015	1.685
5th Cycle	1.66	1.61	0.013	1.647

Table 2 Cyclic CO_2 Adsorption and Desorption using TG/MS at 200° C

	Total weight loss at desorption (wt %)	Total weight gain at adsorption (wt %)	Composition of gases evolved determined by MS	
			CO_2 (wt %)	H_2O(wt %)
1st Cycle	2.23	2.01	2.212	0.018
2nd Cycle	1.99	1.93	1.975	0.015
3rd Cycle	1.91	1.86	1.895	0.015

4th Cycle	1.87	1.83	1.855	0.015
5th Cycle	1.81	1.79	1.795	0.015

Table 3 Cyclic Adsorption and Desorption Study using TG/MS at 250° C

	Total weight loss at desorption (wt %)	Total weight gain at adsorption (wt %)	Composition of gases evolved determined by MS	
			CO_2 (wt %)	H_2O(wt %)
1st Cycle	2.19	1.99	2.172	0.018
2nd Cycle	1.93	1.91	1.915	0.015
3rd Cycle	1.89	1.86	1.875	0.015
4th Cycle	1.83	1.80	1.815	0.015
5th Cycle	1.79	1.77	1.775	0.015

Table 4 Cyclic Adsorption and Desorption Study using TG/MS at 300° C

	Total weight loss at desorption (wt %)	Total weight gain at adsorption (wt %)	Composition of gases evolved determined by MS	
			CO_2 (wt %)	H_2O(wt %)
1st Cycle	1.52	1.47	1.516	0.004
2nd Cycle	1.46	1.33	1.457	0.003
3rd Cycle	1.26	1.17	1.256	0.004
4th Cycle	1.13	1.08	1.126	0.004
5th Cycle	1.05	0.86	1.047	0.003

Table 5 Cyclic Adsorption and Desorption Study using TG/MS at 350° C

	Total weight loss at desorption (wt %)	Total weight gain at adsorption (wt %)	Composition of gases evolved determined by MS	
			CO_2 (wt %)	H_2O(wt %)
1st Cycle	1.51	1.46	1.506	0.004
2nd Cycle	1.42	1.33	1.407	0.003
3rd Cycle	1.23	1.17	1.226	0.004
4th Cycle	1.10	1.08	1.106	0.004
5th Cycle	1.06	0.86	1.057	0.003

The TGA results are consistent with the previously presented results for the thermal behavior of the hydrotalcite under inert atmosphere. At low temperatures (as indicated by the TGA/MS result at 150°C) most of the gases evolved consist of H_2O, and little amount of CO_2 is evolved. At higher temperatures most of the gases evolved consist of CO_2 and little amounts of water. Below 300 ^oC the total adsorption averages ~ 2.2%. Above 300 ^oC the adsorption decreases, which is consistent with the studies of the thermal evolution of the structure of hydrotalcite, which indicate that the structure of hydrotalcite partially collapses in this temperature range. In addition, at these higher temperatures there is a significant decline in the adsorbed amount as a function of the cycle number indicating the decrease in the degree of reversibly adsorbed CO_2 as the temperature increases. In summary the CO_2 affinity of hydrotalcite material has been proven reversible via pressure swing under an isothermal condition, which simulates the CO_2 transport through the hydrotalcite membrane. This high degree of reversibility fulfills the essential requirement for a hydrotalcite-based membrane. In addition, the extremely low affinity to H_2O at a higher temperature (i.e., >200ºC) discourage the competition by water as in most oxides. This provides a fundamental basis fr the hydrothermal stability of the hydrotalcite.

2. Hydrotalcite Crystal Growth

During Year I of our feasibility study, we have proven <u>the seeding and in-situ crystal growth</u> is a viable hydrotalcite membrane synthesis technique. As part of our optimization study, we have concentrated on the verification of the crystal growth under the synthesis conditions selected by us in this quarter. This exercise provides the experimental evidence on the synthesis of the hydrotalcite membrane via crystal growth under the selected condition. The crystal growth conditions selected by us range from 100 to 150ºC and 0 to >4 hours. Powder hydrotalcite products generated under this condition were rinsed thoroughly and then examined with XRD. The XRD results are available upon request. Key conclusions drawn from this study include:

1. It appears that hydrotalcite crystal forms immediately after combining the two reagents together (based upon HT054 initial).
2. There is no obvious improvement in the crystal size via crystallization at a higher temperature (i.e., 140 vs 100ºC) although most literatures support the effect of temperature.
3. As a general trend the crystal size increases along with the crystallization time at a given temperature, indicative of the crystal growth with time under the selected condition. However, some XRD peaks obtained do not follow this trend. It may be dependent upon the sampling position from the autoclave. More study will be conducted in the future.

In summary the hydrotalcite crystal grows at temperature of 100 to 150C. The crystal size is a function of the crystallization time. Once the membrane is seeded, we plan to utilize this experimental condition for the crystal growth within the porous membrane structure.

3. Hydrotalcite Precursor as Seed for Membrane Synthesis

Based upon the results from Sec. 2, it is believed that the gel immediately formed after combining the two reagents (i.e., $AlNO_3$ and $MgNO_3$). In addition this gel is most likely is the precursor of the hydrotalcite. This gel can be used as the seed for deposition within the membrane substrate for crystal growth. The hydrotalcite membrane thus formed would be in the designated area, e.g., within the porous thin film, instead of indiscriminately deposition above, below and within the thin film. To verify the gel formed is indeed the precursor of hydrotalcite, two experiments described below were conducted in this month:

- <u>Performing the analysis of Al/Mg ratio of the gel (as a precursor) and the supernatant solution.</u> If the Al/Mg ratios were in line with the resultant hydrotalcite crystals, this gel would be qualified as a precursor. The result is presented in Table 6. The ratio (3.63) is close to the ratio based upon theoretical calculation (2.04). Thus, we conclude that he gel is most likely is the precursor for hydrotalcite.

- To use this precursor as seed, it is highly desirable to eliminate extraneous precipitate along the crystal growth. Here we conduct a leaching study using the impregnated membrane rinsed with distil water. The control is the membrane deposited with the solution without containing aluminum and maganisiu. Based upon the gas permeance presented in Tables 7&8, it is believed that most impurity can be rinsed away.

The above two experiments confirm the potential of using the gel initially formed as a precursor for hydrotalcite synthesis and more importantly the impurities formed during the synthesis can be rinsed away with distill water.

Table 6 Aluminum/Magnisium Ratios of Gel, Supernatant and Crystals.

Samples / Analysis		Gel (HT-061)	Supernatant (HT-061)	Crystals (HT-062)	Solutions (by calculation)
Concentration determined by ICP	**Mg(ppm)**	513	233	75.8	NA
	Al(ppm)	157	31	33.0	NA
Concentration (mole)	**Mg**	21.1	9.58	3.12	NA
	Al	5.82	1.15	1.22	NA
Molar Ratio	**Mg/(Mg+Al)**	0.784	0.89	0.719	0.67
	Mg/Al	3.63	8.3	2.56	2.04

Table 7 Impurities Removal from Hydrotalcite Membranes (o.2 micron) Prepared via Crystallization

<table>
<tr><td colspan="5">HT-051: Samples impregnated with the standard hydrotalcite solution without Al and Mg components (i.e., NaOH and Na2CO3 solution). HT-051-10 for 10 minute impregnation of the membrane, and HT-051-60 for 60 minute impregnation</td></tr>
<tr><td>Sample ID</td><td>Leaching Method and Condition</td><td>He permeance (m3/m2/hr/bar)</td><td>N2 permeance (m3/m2/hr/bar)</td><td>Selectivity</td></tr>
<tr><td>HT-051-10</td><td>After impregnation and drying</td><td>0.031</td><td>0.0175</td><td>1.72</td></tr>
<tr><td>HT-051-10</td><td>After rinse and soak overnight</td><td>15</td><td>9</td><td>1.67</td></tr>
<tr><td>HT-051-10</td><td>After tube side rinse with pump</td><td>15.3</td><td>8.6</td><td>1.78</td></tr>
<tr><td>HT-051-10</td><td>After boiling water</td><td>No effect</td><td>No effect</td><td>-</td></tr>
<tr><td>HT-051-10</td><td>After acid leaching (1% HNO3)</td><td>111</td><td>62</td><td>1.79</td></tr>
<tr><td>HT-051-60</td><td>After impregnation and drying</td><td>0.87</td><td>0.52</td><td>1.67</td></tr>
<tr><td>HT-051-60</td><td>After rinse and soak overnight</td><td>6.8</td><td>2.8</td><td>2.43</td></tr>
<tr><td>HT-051-60</td><td>After tube side rinse with pump</td><td>3.97</td><td>2.35</td><td>1.69</td></tr>
<tr><td>HT-051-60</td><td>After boiling water</td><td>No effect</td><td>No effect</td><td>-</td></tr>
<tr><td>HT-051-60</td><td>After acid leaching (1% HNO3)</td><td>108</td><td>63</td><td>1.71</td></tr>
<tr><td>Control</td><td>Without impregnation</td><td>~110</td><td>~60</td><td></td></tr>
</table>

Table 8 Impurities Removal via Water Rinse

<table>
<tr><td colspan="2">Sample 04012-1: Membrane impregnated with Na2CO3 then rinsed in distil water for 2 hours and then dried at 115ºC</td></tr>
<tr><td>N_2 Permeance (m3/m2/hr/bar)</td><td>He Permeance (m3/m2/hr/bar)</td></tr>
<tr><td>29.552</td><td>77.669</td></tr>
<tr><td colspan="2">Sample 04012-2: Membrane impregnated with Na2CO3 then rinsed in distil water for 2 hours and then dried at 115ºC</td></tr>
<tr><td>N_2 Permeance (m3/m2/hr/bar)</td><td>He Permeance (m3/m2/hr/bar)</td></tr>
<tr><td>73.7</td><td>136.1</td></tr>
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