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

Quarterly Report
For the period April 1, 2004 to June 30, 2004

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August 1, 2004

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Under Cooperative Agreement
No. DE-FC26-00NT40922

By
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ABSTRACT

For the purpose of process simulation and economic analysis of the proposed CO_2 selective membrane process, we began to generate the equilibrium and rate data at the operating condition interested to our applications. In this quarter, we have concentrated on the experiments at 200ºC and CO_2 pressure of 0 to 1 bar. In this report we present the equilibrium isotherm and transport rate data and the mathematical treatment using the commonly accepted Langmuir and linear driving force equations. The results from this analysis were then compared with the literature published data. In general, our equilibrium capacity is higher than the literature reported data while the linear driving force model is adequate to describe the rate data obtained from 0 to 1 bar CO_2 pressure. In the next month, we will begin the experimental study at higher temperatures (i.e., 300 and 400ºC) to complete our thermodynamic and kinetic database for process simulation.

TABLE OF CONTENTS

List of Graphical Materials

Figures

List of Graphical Materials

Tables

Introduction

In response to the recommendation by the review panel, we have had performed experimental and simulation study on the use of the hydrotalcite material for selective CO_2 removal in parallel to the development of the hydrotalcite membrane for CO_2 permeation. For future process development purpose, experimental data required include:

- Equilibrium capacities at 200 to 400ºC
- CO_2 uptake rate by the hydrotalcite material at the same temperature range.

In this report we summarize the batch equilibrium data, i.e., isotherms, and kinetic data, i.e., rate constant for CO_2 uptake by the solid phase, obtained from the experimental results. These parameters will be required for the mathematical model selected for the proposed CO_2 sequestration-related applications.

Executive Summary

For the purpose of process simulation and economic analysis of the proposed CO_2 selective membrane process, we began to generate the equilibrium and rate data at the operating condition interested to our applications. In this quarter, we have concentrated on the experiments at 200ºC and CO_2 pressure of 0 to 1 bar. In this report we present the equilibrium isotherm and transport rate data and the mathematical treatment using the commonly accepted Langmuir and linear driving force equations. The results from this analysis were then compared with the literature published data. In general, our equilibrium capacity is higher than the literature reported data while the linear driving force model is adequate to describe the rate data obtained from 0 to 1 bar CO_2 pressure. In the next month, we will begin the experimental study at higher temperatures (i.e., 300 and 400ºC) to complete our thermodynamic and kinetic database for process simulation.

Experimental

1. Adsorption isotherm was obtained from the measurement of weight pick-up using TGA at 200ºC and a given CO_2 pressure. CO_2 pressures ranging from 0.05 to 0.8 bar (with the balance of argon) were selected in this study. The equilibrium capacity was determined when the CO_2 weight pick-up reached steady state. In addition, the adsorption rate data were obtained from the weight uptake vs. time for a given CO_2 pressure. In order to obtain an average rate data, virgin materials were used for each CO_2 pressure. The adsorbent was pretreated with Ar at 200ºC before the introduction of CO_2 for adsorption rate and equilibrium study. The total feed flow rate is 60 cc/min. 200ºC was chosen here to simulate the low temperature shift (LTS) of the water gas shift (WGS) operating condition.

2. The adsorbent selected in this study is Al/Mg-based hydrotalcite with the formula as $Mg_{0.645}Al_{0.35}(OH)_2(CO_3)_{0.178}.0.105(H_2O)$. The particle size is ~100µm. The material shows a typical XRD pattern of hydrotalcite as shown in Figure 1. The weight loss vs.

temperature of the material as received is presented in Figure 2 in terms of the total weight and the CO_2 loss. Table 1 lists the fraction of water and CO_2 loss vs. temperature. In summary, the sample used in this study shows typical hydrotalcite properties based upon XRD, TGA, and TG/MS results.

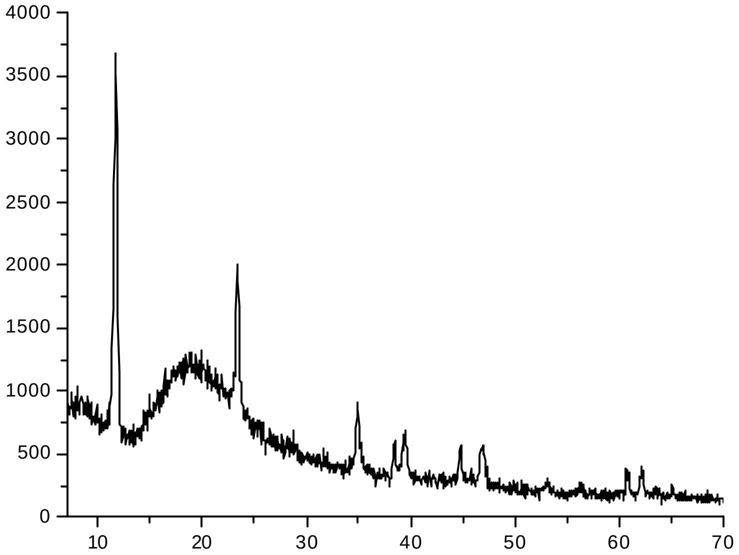


Figure 1 XRD spectra of the LDH sample used in this study.

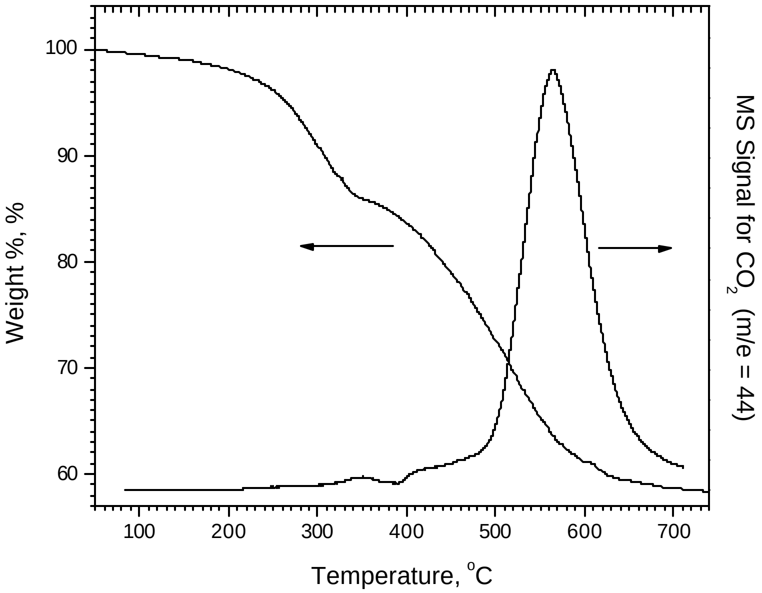


Figure 2 TGA spectra and MS signal generated with a scan rate of 5° C/min. (for the LDH sample)

Table 1. Fractions of H_2O and CO_2 (Percent of the Total Sample Weight) that are evolved in different temperature ranges

Temp Range	LDH2		
(ºC)	Total	H_20	CO_2
RT[a] - 100	0.59	0.59	
100 - 200	1.48	1.46	0.02
200 - 300	7.41	7.33	0.08
300 - 400	8.31	8.04	0.27
400 - 500	10.42	9.91	0.51
500 - 600	11.38	2.69	8.69
600 - 750	1.49		1.49
Total	41.08	30.02	11.06

[a] Room Temperature

Results and Discussions

1. Adsorption isotherms

The adsorption isotherm obtained from this experimental study is presented in Figure 3. The adsorption capacity appears level off at 0.24 mmole/g when the CO_2 pressure is beyond 0.25 bar. A typical Langmuir adsorption isotherm was selected to describe the relationship between the equilibrium solid phase loading vs. the gas phase pressure. The best fitted parameters using the langmuir equation are presented in Figure 3. We also performed the linear curve fitting of $1/g^*$ vs. $1/P_{co2}$ to obtain M_{CO2} and b_{CO2} as shown in Figure 4. Unfortunately, the M_{CO2} (~0.30) this obtained is much higher than the data presented (~0.24). Evidently, the experimental data obtained were insufficient to fit the Langmuir isotherm. More data should be obtained for 1/P in the range of 10 to 20. In the meantime using a two parameter equation, the experimental data were fitted extremely well as shown in Figure 5.

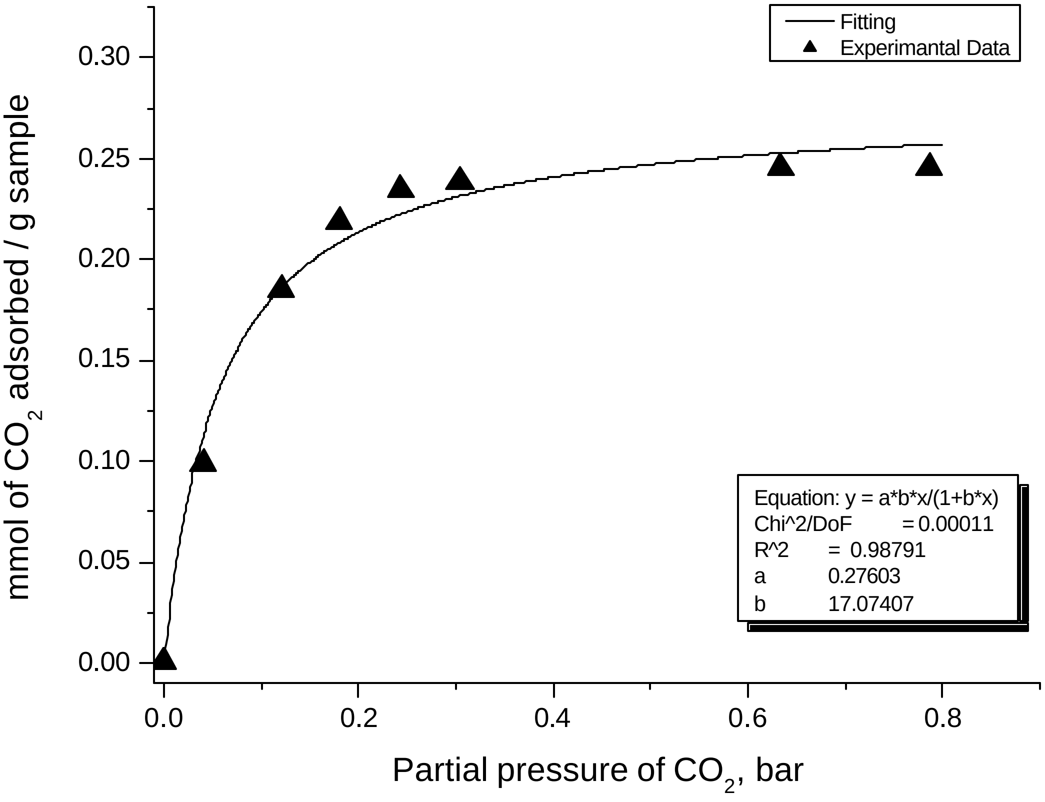


Figure 3 Equilibrium Capacity and the Best Fitted Langmuir Isotherm

Equation of Langmuir adsorption;

$$q^*_{CO_2} = \frac{m_{CO_2} b_{CO_2} P_{CO_2}}{1 + b_{CO_2} P_{CO_2}}$$

$$m_{CO_2} = 0.27603\ [mol/kg]$$

$$b_{CO_2} = 17.07407\ [bar^{-1}]$$

$chi^2 = 1.1 \times 10^{-4}$

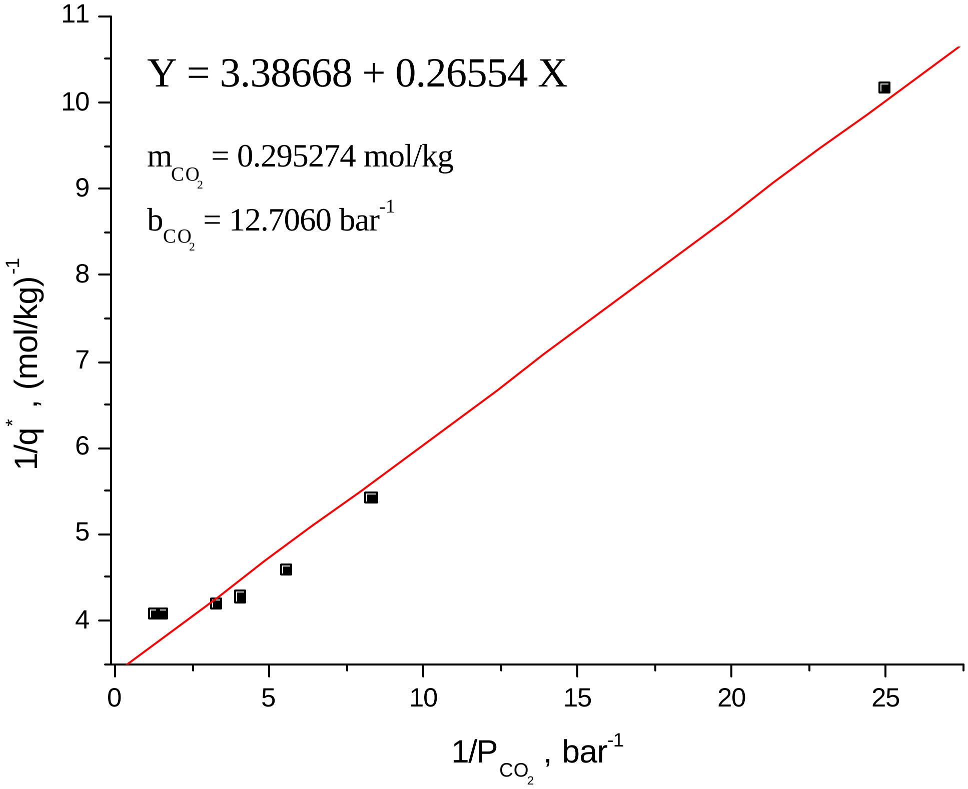


Figure 4 Parameters obtained for Langmuir Equation.

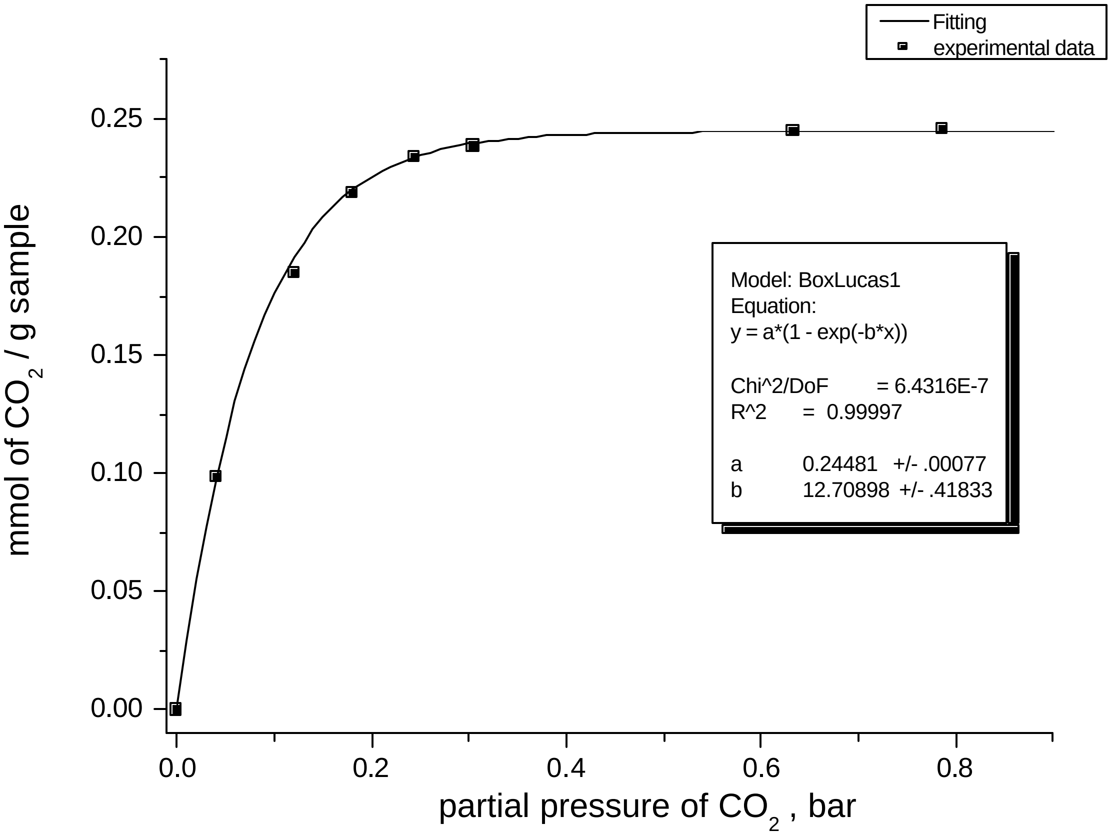


Figure 5 Adsorption Isotherm based upon of boxLucas Equation

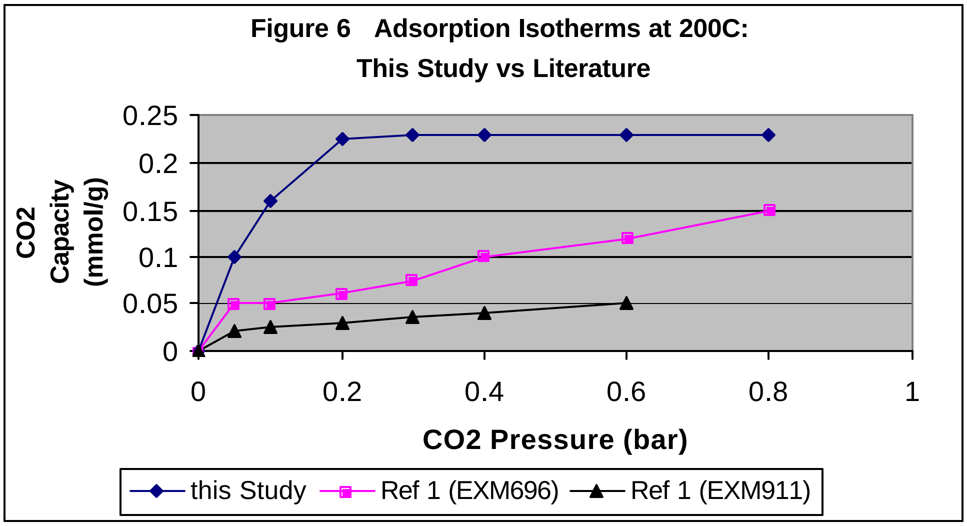
Equation of boxLucas fitting;

$$q^*_{CO_2} = m_{CO_2}(1 - \exp(-kP_{CO_2}))$$

$$m_{CO_2} = 0.24481\ [mol/kg]$$

$$k = 17.07407\ [bar^{-1}]$$

chi^2=6.43 x 10^{-7}



Literature data at the same temperature range were presented along with our result in Figure 6. According to Figure 6, our adsorption capacity reaches the maximum at a rather lower temperature, i.e., ~0.25 bar, than those reported in the literature. In addition, the adsorption capacity from our study is much higher than the literature published data at the same temperature, 200ºC (Ref. 1 &3). Since Al/(Al + Mg) of our material is 0.35 (close to the high end of the ratio reported in the literature), the higher CO_2 capacity reported here could be attributed to (i) surface adsorption of CO_2 by alumina, and/or (ii) the higher intercalated capacity. Finally literature indicates that the adsorption capacity of hydrotalcite increases significantly at 300 to 400ºC in comparison with the 200°C. Thus we expect the capacity increases significantly at temperatures >200°C. In the next month, we will undertake a similar study at the higher temperature.

2. Adsorption Kinetic Study

CO_2 uptake rate by the solid adsorbent can be expressed in terms of intrinsic mass transfer rate, such as diffusivity, or other simplified rate expression. The advantage of use of the intrinsic rate, i.e., diffusivity, is its independent of the particle size. In this study, we plan to use the same particle size for adsorption rate determination and future process simulation study. Thus, a simplified mathematical expression, e.g., linear driving force (LDF) model, is selected. The LDF model has been used by the literature (Ref. 2) for CO_2 adsorption by hydrotalcite successfully. We expected that this simplified model can adequately describe the rate uptake.

To verify the adequacy of the LDF model, the rate data were fitted with the equation below with the two parameters, “n” and “k”:

$$\frac{dC}{dt} = k(C_{eq} - C)^n$$

$$\ln\left[\frac{dC}{dt}\right] = \ln k + n\ln\left[(C_{eq} - C)\right]$$

Then the best fitted "n" and "k" for a given partial pressure was obtained as shown in Figure 7. Then "n" and "k" for the entire pressure range were presented in Table 2 and Figure 4. Excellence of fittings with the mathematical model chosen is indicated by in Figure 8. Further, both n and k are relatively independent of the partial pressure. "n" is found to be close to 1, indicating the adequacy of the LDF model. The best fitted k(i.e., lnk) for n=1 as shown in Figure 9 will be selected for our future simulation.

Table 2 "n" and 'k" best fitted for the CO_2 pressure range studied

Partial Pressure of CO_2 [bar]	n	lnk
0.04	0.8655	-4.44507
0.12	0.87339	-4.41067
0.18	0.90572	-4.3359
0.24318	0.88924	-4.16629
0.30398	0.91003	-3.90351
0.63328	0.93681	-.53962
0.78625	0.96062	-3.53364

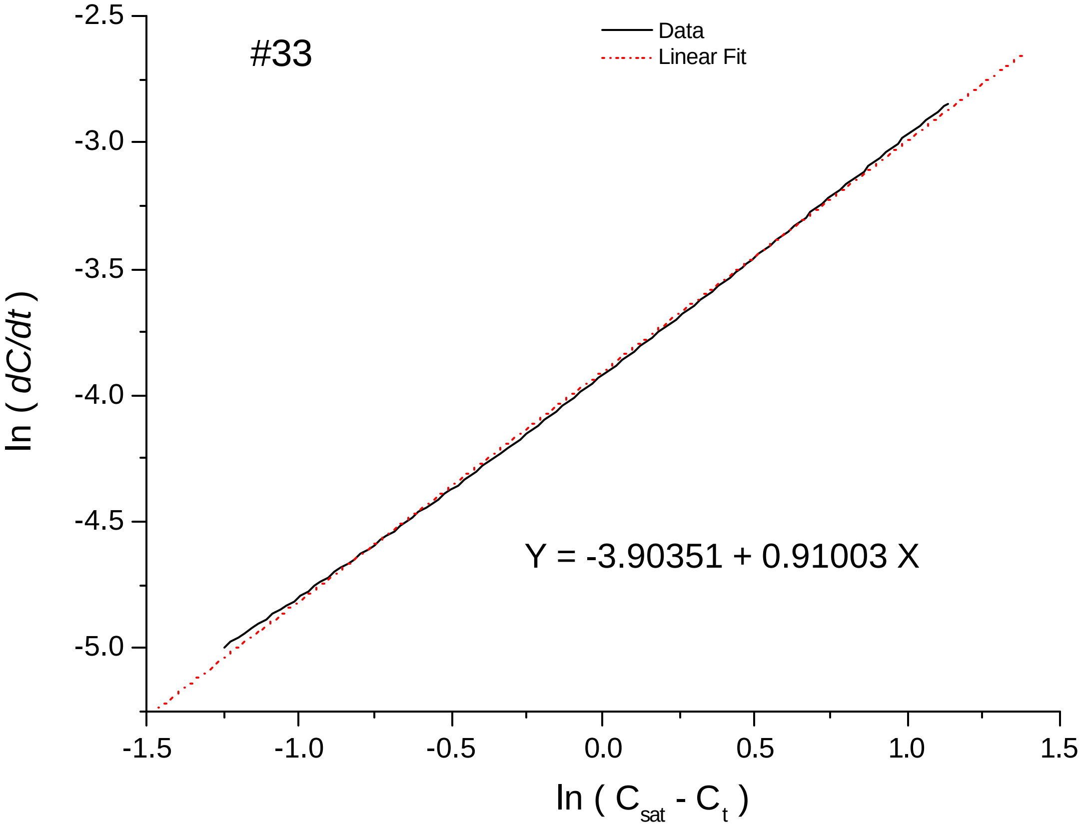


Figure 7 Determination of effective mass transfer coefficient for the LDF model

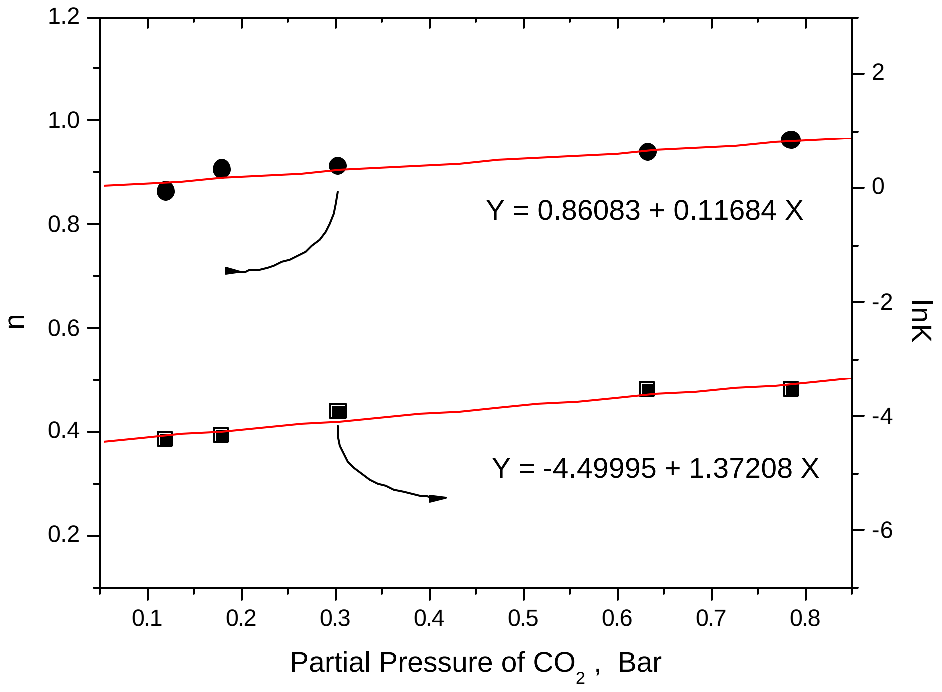


Figure 8 Best Fitted "n" and "k" for Entire CO_2 Pressure Range.

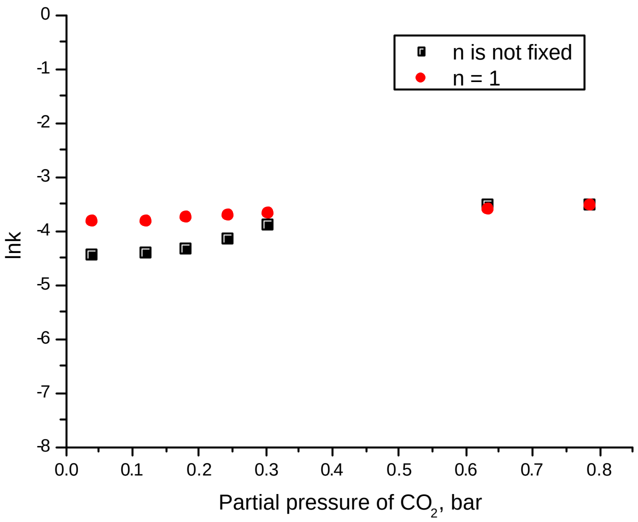


Figure 9 Comparison of lnK for n= 1 vs. not fixed.

Conclusions

We have concentrated on the activity to generate the thermodynamic and kinetic parameters required for future process simulation in this quarter. Key conclusions are summarized below:

- The equilibrium capacity of CO_2 on the hydrotalcite material was obtained at 200ºC and up to 1 bar. The results were fitted reasonable well with the Langmuir equation. However, the parameters obtained from the linear fitting were unsatisfactory. More data will be obtained to improve the curve fitting in the next quarter.
- In comparison with the literature data at the same temperature range, our material reaches the maximum capacity at a lower pressure, i.e., 0.25 bar, than the literature data. In addition, the maximum adsorption capacity of our material is higher than that of the literature data.
- The rate of CO_2 weight pick up by the hydrotalcite material is also determined at 200ºC and the pressure of 0 to 1 bar. The linear driving force model appears adequate for the entire pressure range. The effective mass transfer coefficients are found relatively insensitive to the pressure range we studied.

In the next quarter, we will begin to generate the thermodynamic and kinetic data at 300 and 400ºC using the same material and the methodology adopted in this report.

Bibliography

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Acronyms

LDF: Linear driving force
LDH: Layered double hydroxide
LTS: Low temperature shift
MS: Mass spectrum
TGA: Thermogravimetric analysis
WGS: Water gas shift reactive
XRD: X-ray diffraction