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

Quarterly Report
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Abstract

CO_2 diffusivity through hydrotalcite materials at 200 to 250°C was determined based upon the weight pick-up vs time. D/r^2 (diffusivity/radius^2) for CO_2 ranges from 3 x 10^{-4} to 1 x10^{-3} depending upon the temperature. This range of diffusivity is consistent with the diffusivities through nanoporous materials, such as pillard clays and carbon molecular sieve, reported in the literature. Further the activation energy calculated based upon the diffusivity as a function of temperature is ~12 kcal/mole CO_2**,** indicating activated diffusion for CO_2 transport through the intracrystalline region of hydrotalcite. More importantly nitrogen diffusivity determined based upon the same methodology is negligible. This implies that the hydrotalcite materials have a strong affinity to CO_2, but not nitrogen although the kinetic diameters for both molecules are similar. This result supports our proposed concept on the use of the hydrotalcite membrane for selective permeation of CO_2. In the next quarter, we will conduct more calculation to determine the CO_2 permeability of an ideal hydrotalcite membrane. This theoretical analysis will provide a quantitative basis for the design of a hydrotalcite membrane. Further, the theoretical diffusivity thus obtained can be used as a tool to (i) gauge the degree of defects of experimental membranes prepared, and (ii) direct the future membrane synthesis and improvement.

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1.   Introduction

While we are actively pursuing the development of a hydrotalcite membrane via experimental study, we have invested some effort in characterizing the intrinsic transport properties of the hydrotalcite materials. These properties can be used with the mathematical model to estimate the permeability of an ideal hydrotalcite membrane, i.e., defect free. Then, the permeance of a hydrotalcite membrane with a realistic layer thickness, such as one to several microns, can be estimated. This exercise is extremely useful during the membrane development stage. The performance estimation based upon the intrinsic properties will give us guidance on the reasonable thickness of the membrane required in order to deliver the CO_2 enhancement. This quarterly report summarizes the diffusivity of CO_2 measured from the hydrotalcite materials. In the next report we will estimate the performance based upon this diffusivity and the solubility determined by TGA.

2.   Executive Summary

The CO_2 diffusivity (D/r^2) of the hydrotalcite materials obtained from this study ranges from 3×10^{-4} to 1×10^{-3} at 200 to 250°C, depending upon the range of the weight pick-up selected. This range of diffusivity is consistent with the diffusivities through nanoporous materials, such as pillard clays and carbon molecular sieve, reported in the literature. Further the activation energy calculated based upon the diffusivity as a function of temperature is ~12 kcal/mole CO_2, indicating activated diffusion for CO_2 transport through hydrotalciate. More importantly nitrogen diffusivity determined with the same methodology is negligible. This implies that the hydrotalcite materials have a strong affinity to CO_2, but not nitrogen. This unique transport property supports our proposed concept on the use of hydrotalcite for the CO_2 selective membrane construction. In the next quarter, we will conduct more calculation to determine the CO_2 permeability of an ideal hydrotalcite membrane. This theoretical analysis will provide a quantitative basis

for the design of a hydrotalcite membrane, and further direct out future membrane synthesis and improvement.

3.   Experiment

In order to measure the diffusivity of carbon dioxide and nitrogen in hydrotalcite (HTc) materials in a powder form, we have measured the uptake rates for these two gases thermogravimetrically using the Cahn TGA-121 system. The measurements were carried at USC with the sample provided by us. Prior to the initiation of the experiments, the HTc material was sieved; particles with radii in the range between 80 ~120μm were collected. About 60~70 mg of the fresh HTc powder sample collected was loaded into the bowl-shaped quartz sample holder at room temperature. The sample was then heated to the pre-set temperature in an argon atmosphere (flow rate of 30 sccm) with a heating rate of 5 ^{o}C/min. When the predetermined temperature was reached, the sample was kept at this temperature for a period of time, typically from 60~100 min, until its weight stabilized in the microbalance. After the microbalance was stabilized (changes in the reading <10μg), the flowing gas was changed from argon to carbon dioxide or nitrogen, depending on the experiment, while the flow rate was maintained constant at 30 sccm.

In order to interpret the experimental data, we have utilized the analytical solution of Fick's law of diffusion for isothermal diffusion into a homogeneous spherical particle of radius r, originally containing no adsorbed gas, and at t=0 being exposed to a gas atmosphere with a fixed concentration C. The solution is described for the following equation, with D being the diffusivity constant, M_t the amount uptaken at time t, and M_∞ being the amount uptaken at complete saturation.

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{p^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \cdot p^2 \cdot \frac{D}{r^2} \cdot t) \tag{1}$$

For small time ($M_t/M_\infty < 0.25$) Eqn. 1 approximates to:

$$\frac{M_t}{M_\infty} = \frac{6D^{1/2}t^{1/2}}{p^{1/2}r} \tag{2}$$

and the plot of M_t/M_∞ versus $t^{1/2}$ for sufficiently small times should give a straight line. However, for small times complications arise from the fact that the gas atmosphere may not be completely 100% CO_2 or N_2, (due to the transition of changing the following gas component) and the sample itself may contain Ar. We have instead opted here to utilize the form of Eqn. 1 valid for larger times ($M_t/M_\infty > 0.5$), where the higher-order terms in Eqn. 1 become negligible, so that the expression simplifies to:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{p^2} \exp(-p^2 D \cdot t / r^2) \qquad (3)$$

4.   Results/Discussions

1. When using Eqn. 3, the plot of $\ln(1 - M_t/M_\infty)$ vs. t should be linear with a slop of - $\pi^2 D/r^2$ and with an intercept of $\sim \ln(6/\pi^2)$. The following figures, Figures 1a&b, 2a&b, and 3a&b, present the weight pick-up data for three different temperatures, namely 200, 225, and 250 ^oC. Note that linear fit is generally good, but the intercept is $\sim$ -0.6 which somewhat larger than -0.5 or $\ln(6/\pi^2)$ indicating the approximate nature of the fit.

2. The diffusivities (D/r^2) calculated based upon the weight pick-up shown in Figures 1a&b, 2a&b, and 3a&b are listed below:

Table 1   Calculated CO_2 diffusivity (D/r^2) through hydrotalcite materials

Selected Weight Pick-up Range Temperature (°C) (M_t/M_8)	0.5 to 0.75	0.5 to 0.85
200	3.07 x 10^{-4}	3.61 x 10^{-4}
225	7.56 x 10^{-4}	8.90 x 10^{-4}
250	1.11 x 10^{-3}	1.33 x 10^{-3}

Although difference between the two weight pick-ranges selected, the difference is very small in terms of the diffusivity calculation. As expected, the diffusivity increases along with the temperature range studied here. The Arrhenious plot is presented in Item #3 below while the comparison of these diffusivities with the literature values are presented in Item #4.
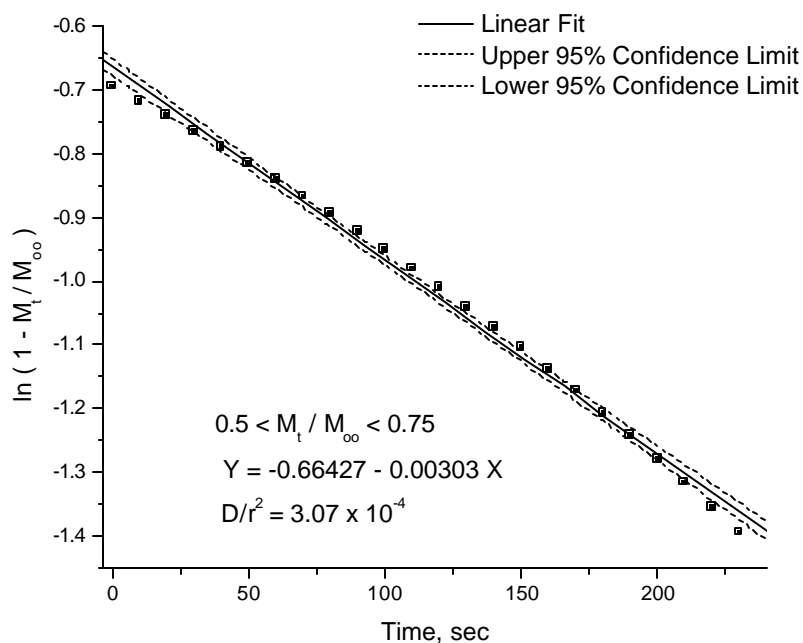
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Figure 1a CO_2 weight pickup on hydrotalcite materials at 200°C and the diffusivity (D/r^2) calculated based upon the $0.5 < M_t/M_8 < 0.75$.
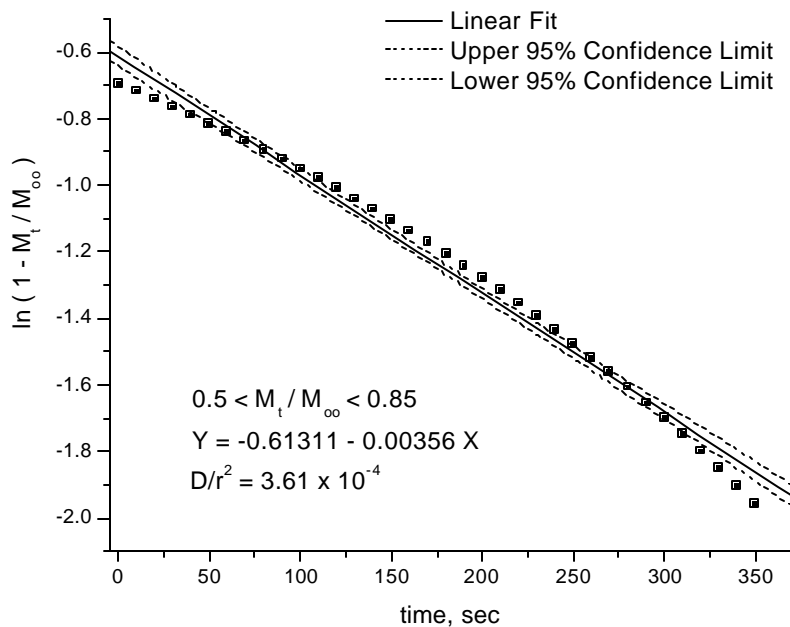

Figure 1b CO_2 weight pickup on hydrotalcite materials at 200°C and the diffusivity (D/r^2) calculated based upon the $0.5 < M_t/M_8 < 0.85$.

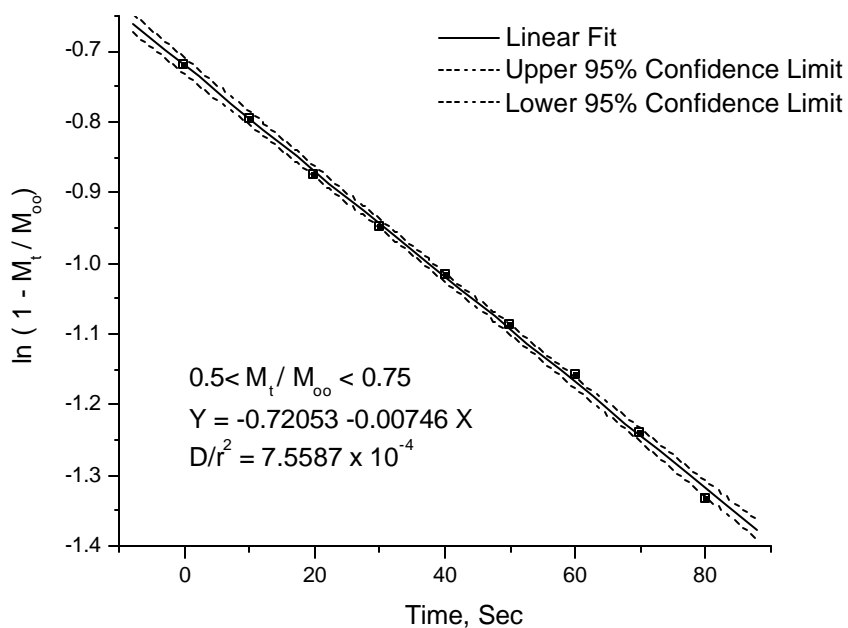Figure 2a CO_2 weight pickup on hydrotalcite materials at 225°C and the diffusivity (D/r^2) calculated based upon the $0.5 < M_t/M_8 < 0.75$.
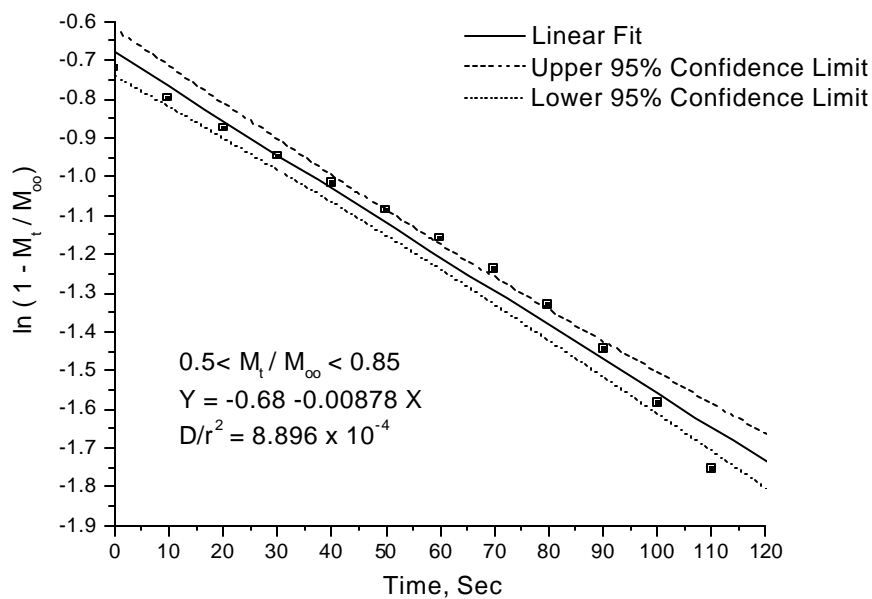

Figure 2b CO_2 weight pickup on hydrotalcite materials at 225°C and the diffusivity (D/r^2) calculated based upon the $0.5 < M_t/M_8 < 0.85$.

Figure 3a CO_2 weight pickup on hydrotalcite materials at 250°C and the diffusivity (D/r^2) calculated based upon the $0.5 < M_t/M_8 < 0.75$.

Figure 3b CO_2 weight pickup on hydrotalcite materials at 250°C and the diffusivity (D/r^2) calculated based upon the $0.5 < M_t/M_8 < 0.85$.
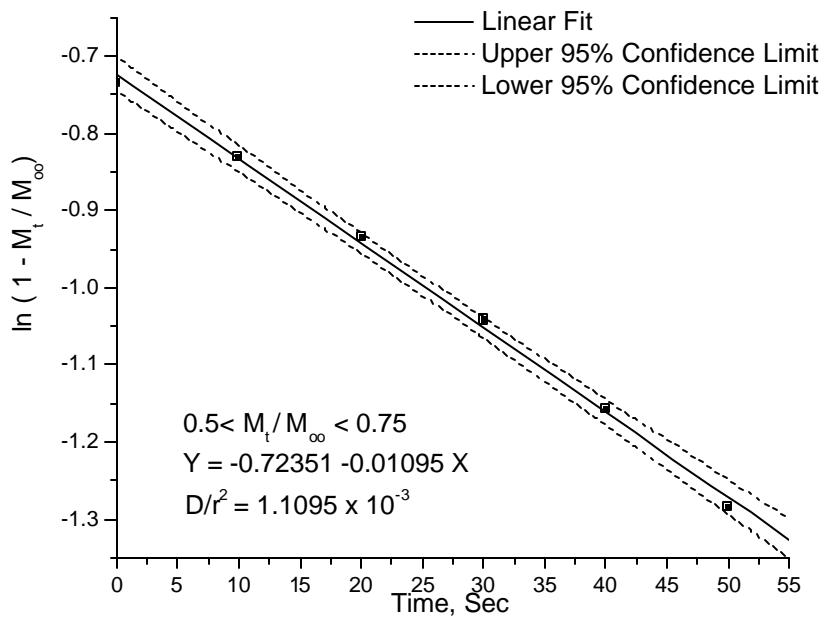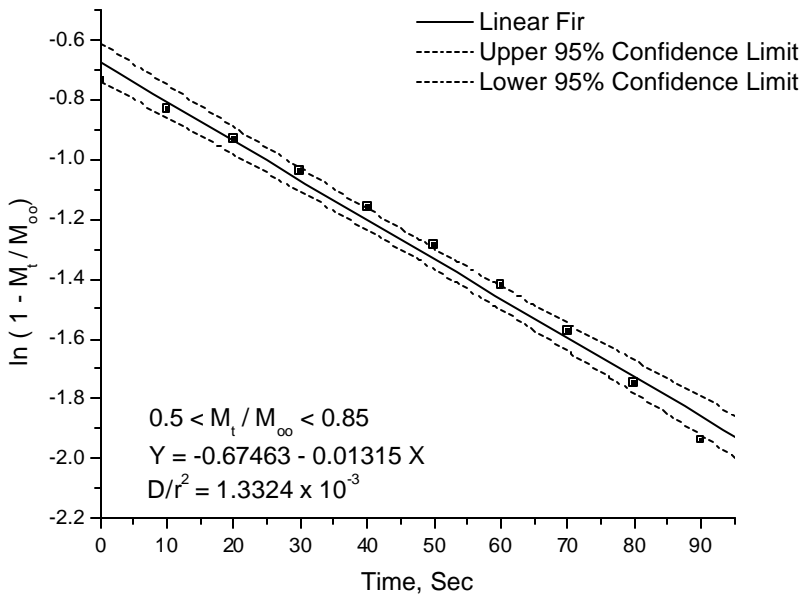
3. In order to calculate the activation energy of diffusion, we utilize the Arrhenious equation:

$$\ln D = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$$

$$R = 8.312 J / mol \cdot K = 1.987 cal / mol \cdot K$$

(4)

A plot of ln D versus (1/T) is shown below and it is linear with a slope of $-E/R$. $E_{act} =$ 52.857 kJ/mol = 12.635 kcal/mol. This activation energy is typical of activated diffusion processes, and it proves that the transport determining step is neither Knudsen nor bulk diffusion in the intracrystalline (in between the microcrystals) region.
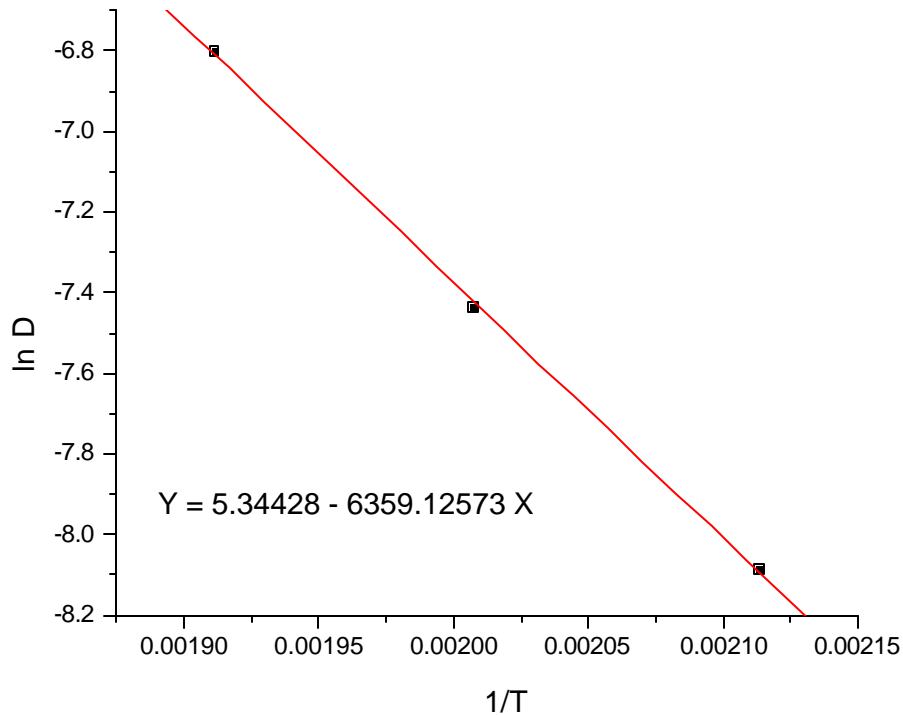

Figure 4   Arrhenious plot of the CO_2 diffusivity measured at 200 to 250°C.

4. In order to provide a comparison, listed below are some values for D/r^2 of carbon dioxide reported in the literature with other nanoporous materials:

- 8.0 x 10^{-2} (Zr PILC-2 at 298°K; Yang et al., *AIChEJ*, **37**, 679, 1991)

- 9.0 x 10^{-4} (carbon molecular sieve; Kapoor et al., *Chem Eng Sci,* **44**, 1723, 1989)

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- 1.06 x 10^{-3} (carbon molecular sieves; in-house experimental data at USC)

The D/r^2 obtained from this study in the range of 3.1 x 10^{-4} to 1.3 x 10^{-3} is in-line with the data reported in the literature for nanoporous materials.

5. Experiments with N$_2$ in the same region of temperatures showed that the nitrogen is not transported through the intracrystalline region of the HTc. Figure 5 below for example, presents some of the raw uptake data. As expected the hydrotalcite has a strong affinity to CO$_2$. The negligible diffusivity to nitrogen (its kinetic diameter is close to CO$_2$) substantiates the surface affinity of the hdyrotlcite to CO$_2$.
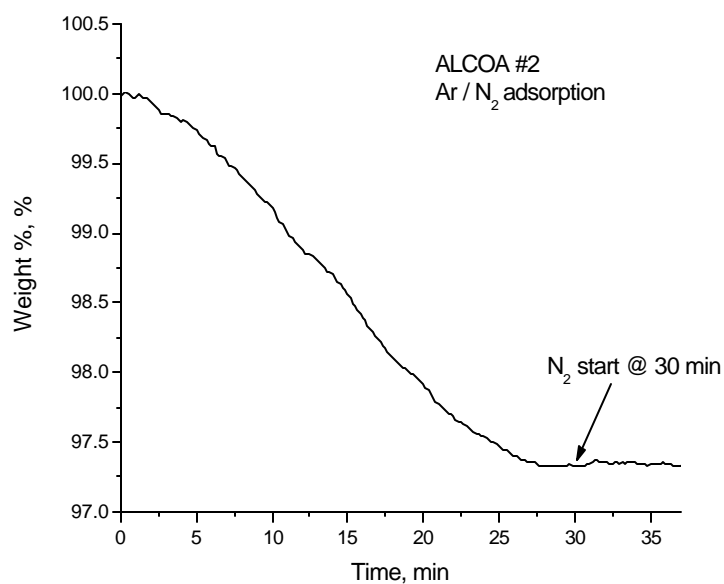

Figure 5   Weight uptake of nitrogen with the hydrotalcite material.

5. Conclusions

- The CO_2 diffusivity (D/r^2) obtained from this study ranges from 3×10^{-4} to 1×10^{-3}, which are consistent with the diffusivities reported in the literature for nanoporous materials, indicating the methodology selected by us to measure the diffusivity is acceptable.

- The diffusivity for nitrogen for hydrotalcite measured from this study is negligible in the same temperature range, i.e., 200 to 250°C. Since the kinetic diameter of N_2 is very close to CO_2, the negligible diffusivity implies that the hydrotalcite materials have a strong affinity to CO_2 in the intracrystalline region, but not to N_2. This intrinsic property provides experimental evidence to support our proposed concept of developing a hydrotalcite membrane for selective CO_2 transport.

- The activation energy obtained from the calculated diffusivity vs temperature is in the range of ~12 kcal/mole CO_2, which is typical of diffusion via activated transport through the intracrystalline region. The unique surface affinity and transport property of CO2 offer the theoretical basis of selective CO_2 transport through the hydrotalcite membrane.

List Of Acronyms and Abbreviations

D: Diffusivity
Mt: amount uptaken at time, t
M_∞:   amount uptaken at complete saturation
R: gas constant
T: temperature
E: activation energy
A: Arrhenious constant