

ADSORPTION SEPARATION OF METHANE AND CARBON DIOXIDE BY SILICALITE

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Introduction

The increasing concentration of carbon dioxide mainly from flue gas, automobile and landfill emissions in the atmosphere is the major contributor to global warming with more than 80% of total greenhouse gas (GHG) emissions. Also, methane is the most important non-CO₂ GHG responsible for global warming with more than 10% of total GHG emissions. The greenhouse warming potential (GWP) of this gas is 21% higher than carbon dioxide. Landfill gas (LFG) is a multi-component mixture containing mainly methane and carbon dioxide, which constitutes one of the main sources of methane and carbon dioxide emissions, and can be treated as an important resource of directly available methane. In this current work, adsorption separation of carbon dioxide and methane on silicalite was studied. Pure and binary isotherms were obtained by the constant volume and the concentration pulse chromatographic techniques. Additionally, the thermodynamic consistency tests between pure and binary gas adsorption systems were discussed.

Silicalite is one of the most important synthetic zeolites. It is widely used as a selective adsorbent. Its distinctive features include high thermal and hydrothermal stability, hydrophobic and organophilic adsorptive properties and an intermediate (ten-ring) pore size which leads to molecular sieve size selectivity. Its low aluminum content (the Si/Al ratio in the 1000's) is responsible for the hydrophobic nature of its surface.

The constant volume system has been used to determine pure adsorption isotherms of methane and carbon dioxide. This technique involves measuring the pressure change in a known volume of gas subjected to an adsorbent sample. Binary mixture adsorption isotherms have been determined by employing the dynamic method of analysis by using the concentration pulse chromatographic technique. This method, using the K_p -functions proposed in the literature for determining the binary isotherms from concentration pulse chromatographic data, has been given and shown capable of interpreting highly selective binary systems (Van der Vlist and Van der Meijden, 1973; Shah and Ruthven, 1977; Tezel et al., 1992; Harlick and Tezel, 2000 and 2001).

There are many models expressing adsorption isotherms for pure component systems. One of them is the empirical three-parameter Toth isotherm model that satisfies both low and high ends of the pressure range (Do, 1998):

$$\theta = \frac{q}{q_m} = \frac{BP}{\left[1 + (BP)^n\right]^{\frac{1}{n}}} \dots\dots\dots(1)$$

Models for mixed-gas adsorption are crucial for the design of adsorptive gas separation processes. They should be capable of predicting the equilibrium amount adsorbed from pure component isotherms. Because of the paucity of experimental data, however, none of the theories or models has been extensively tested. The simplest theory for binary system is the extended Langmuir model (Markham and Benton, 1931):

$$\theta_A = \frac{q_A}{q_{mA}} = \frac{B_A P_A}{1 + B_A P_A + B_B P_B} \dots\dots\dots (2)$$

where subscripts A and B refer to gases A and B, respectively.

Concentration pulse chromatographic technique was used for determining binary mixture adsorption isotherms of CO₂ and CH₄ gases with silicalite. In this technique, a pulse of the sample gas is injected into the carrier gas stream and passes through the column. From this response peak a mean retention time of the sample, defined as the first moment of the chromatogram, is determined experimentally (Shah and Ruthven, 1977). Dimensionless Henry's Law constant, K, can be determined from the corrected first moment of the response peak (Li and Tezel, 2005 and 2006; Li et al., 2005; Harlick and Tezel, 2000). The dimensionless Henry's Law constants, K, can be converted to a dimensional form, K_p, (Li and Tezel, 2005) and gives the slope of the adsorption isotherm for pure component systems. For a binary mixture, the relationship is given as follows (Shah and Ruthven, 1977):

$$K_p = (1 - y_1) \frac{dq_1}{dP_1} + y_1 \frac{dq_2}{dP_2} \dots\dots\dots (3)$$

Where $\frac{dq_1}{dP_1}$ and $\frac{dq_2}{dP_2}$ are the slopes of the adsorption isotherms for components 1 and 2, respectively. This method allows for the experimental evaluation of the binary mixture isotherms when K_p values are determined for different concentrations of the carrier gas (Shah and Ruthven, 1977). The binary K_p data has been treated by several methods in the literature (Van der Vlist and Van der Meijden, 1973; Triebe and Tezel, 1995; Harlick and Tezel, 2000 and 2001).

Different K_p functional forms have been suggested in the literature to determine the binary isotherms. One of them is the 3rd degree polynomial, MVV-CPM (modified Van der Vlist and Van der Meijden - concentration pulse method) (Van der Vlist and Van der Meijden, 1973; Tezel et al., 1992; Harlick and Tezel, 2000). This equation, together with corresponding binary isotherms and their derivatives are given as follows:

$$K_p = A_0 + A_1 y_1 + A_2 y_1^2 + A_3 y_1^3 \dots\dots\dots (4)$$

$$\frac{dq_1}{dP_1} = B_0 + B_1 y_1 + B_2 y_1^2 \dots\dots\dots (5)$$

$$\frac{dq_2}{dP_2} = C_0 + C_1 y_1 + C_2 y_1^2 \dots\dots\dots (6)$$

$$q_1 = \left(B_0 y_1 + \frac{B_1}{2} y_1^2 + \frac{B_2}{3} y_1^3 \right) P \dots\dots\dots (7)$$

$$q_2 = \left[C_0 (1 - y_1) + \frac{C_1}{2} (1 - y_1^2) + \frac{C_2}{3} (1 - y_1^3) \right] P \dots\dots\dots (8)$$

Another function, HT-CPM (Harlick and Tezel - concentration pulse method), for describing the binary K_p data was developed by Harlick and Tezel (2001). This 5-parameter function, together with corresponding binary isotherms and their derivatives are given as follow:

$$K_p = A_1 + A_2 y_1 + A_3 y_1^2 + A_4 \ln|y_1 + \lambda| \dots\dots\dots (9)$$

Where $\lambda \neq 0$.

$$\frac{dq_1}{dP_1} = B_1 + 2B_2 y_1 + \frac{B_3}{|y_1 + \lambda|} \dots\dots\dots (10)$$

$$\frac{dq_2}{dP_2} = C_1 + 2C_2 y_1 + \frac{C_3}{|y_1 + \lambda|} \dots\dots\dots (11)$$

$$q_1 = \left(B_1 y_1 + B_2 y_1^2 + B_3 \ln \left| \frac{y_1 + \lambda}{\lambda} \right| \right) P \dots\dots\dots (12)$$

$$q_2 = \left[C_1 (1 - y_1) + C_2 (1 - y_1^2) - C_3 \ln \left| \frac{y_1 + \lambda}{1 + \lambda} \right| \right] P \dots\dots\dots (13)$$

Binary gas adsorption behavior has been determined experimentally by using these equations and determining the A, B and C constants from the experimental data. More details on this technique are given in the literature by Harlick and Tezel (2000, 2001, 2002 and 2003) and Li and Tezel (2006a, b).

In this study, separation factors and phase diagrams are determined for the separation of methane and carbon dioxide gases by using silicalite as the adsorbent.

Experimental

Constant Volume System: An AccuSorb 2100E Physical Adsorption Analyzer supplied by Micromeritics Instrument Corporation was equipped with high precision pressure transducers and thermocouples. Data acquisition was performed using a National Instruments based data acquisition card and Labview 6.1 on an Intel based computer. The adsorbent sample was regenerated at approximately 350 °C under vacuum for approximately 20 hours before use.

Concentration Pulse Chromatography: The flow rates and compositions of the carrier gases were controlled by two MKS mass flow controllers, and set to a total flowrate of 15 cc/min. A mixing chamber was installed after the mass flow controllers to ensure a homogeneous mixture in the carrier gas. The carrier gas passed through the reference side of the thermal conductivity detector (TCD) in the system. It then went through the sample injection valve, which introduced a 1 cc pulse of adsorbate sample gas at atmospheric pressure into the mixed carrier gas stream. Then, the carrier and the sample passed through the packed column and the sample side of TCD, where the response of the column to the sample injection as a voltage was monitored as a function of time. Data acquisition was performed using a National Instruments based data acquisition card and Labview 6.1 on an Intel based computer. The adsorbent was regenerated at 101.3 kPa and 350 °C under helium purge for approximately 20 hours before use. The column was packed with zeolite silicalite adsorbent within a Varian 3300 gas chromatograph. When determining binary isotherms, mixed carriers were used without the He gas. For the CO₂-CH₄ system, CH₄ was used as the primary gas. Samples of each gas were injected into the column at different carrier gas concentrations.

The supplier of CO₂ (99.9%), CH₄ (99.97%) and He (99.999%) was Praxair Inc., Ottawa. The silicalite adsorbent (HISIV 3000, 1/16 inch extrudate, Crushed to 20 x 60 mesh) was MOLSIV Adsorbents supplied by the Universal Oil Products, Des Plaines, IL, USA.

A non-linear regression was performed in order to determine the parameters for the pure component isotherm fits to the Toth isotherm as well as the K_p regressions. In order to solve the equations given by HT-CPM and MVV-CPM, a non-linear equation solver was used.

Results and Discussion

Pure Gas Adsorption of CO₂, and CH₄ by silicalite: Adsorption equilibrium isotherm data for CO₂, and CH₄ on silicalite pellets were obtained at three different temperatures for pressures up to 5 atm and are given in Figure 1 as data points. By non-linear regressions the parameters of different isotherm models were obtained and corresponding parameters for Toth are shown in Table 1.

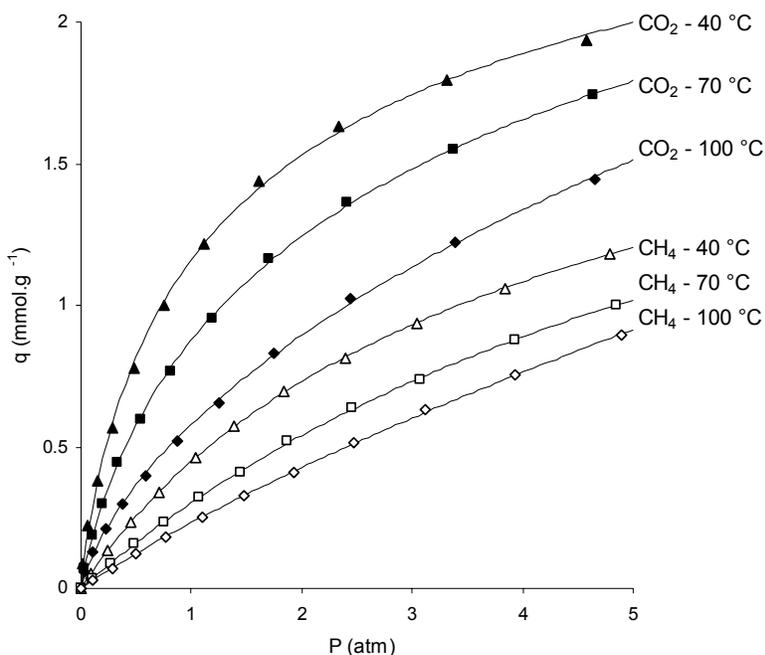


Figure 1. Isotherms for CO₂, and CH₄ on silicalite:
The points are experimental data and the curves are Toth isotherm model fits

In Figure 1, the experimental data are fitted by Toth isotherm. According to the isotherm data on silicalite, CO₂ is adsorbed more than CH₄ because the quadrupole moment of carbon dioxide. At low pressure, the slopes of the isotherms of carbon dioxide are very high, and then the slopes decrease rather fast with increasing pressure as the adsorbent sample is close to saturation. However, the slopes of the isotherms of methane hardly decrease as pressure increases in the range of low pressure near zero. On the other hand, at low pressure, the slopes of the isotherms are very high at low temperature, and then it decrease very fast with increasing pressure because of getting close to saturation, but the slopes at high temperature decrease

little with increasing pressure. Besides, the adsorbed amount decreases with increasing temperature for both adsorbates since physical adsorption is always exothermic.

Table 1. Parameters of Toth adsorption model by non-linear regression

Parameters	CO ₂			CH ₄		
	40 °C	70 °C	100 °C	40 °C	70 °C	100 °C
B (atm ⁻¹)	1.397	0.678	0.100	0.257	0.136	0.009
q _m (mmol.g ⁻¹)	3.122	3.908	31.12	2.385	2.533	31.88
n	0.604	0.537	0.260	0.864	0.991	0.455

Binary Isotherms: After regenerating the silicalite adsorbent, the binary isotherms were determined by increasing the CO₂ mole fraction in CO₂-CH₄ carrier gas from 0% up to 100%. The samples were injected after attaining equilibrium after each concentration change for various compositions of the carrier gas. The results of the series of runs of the binary study are shown with HT-CPM and MVV-CPM in Figure 2, where all the end-points of the binary isotherms were combined with the Toth isotherms of pure gases determined by the Volumetric method:

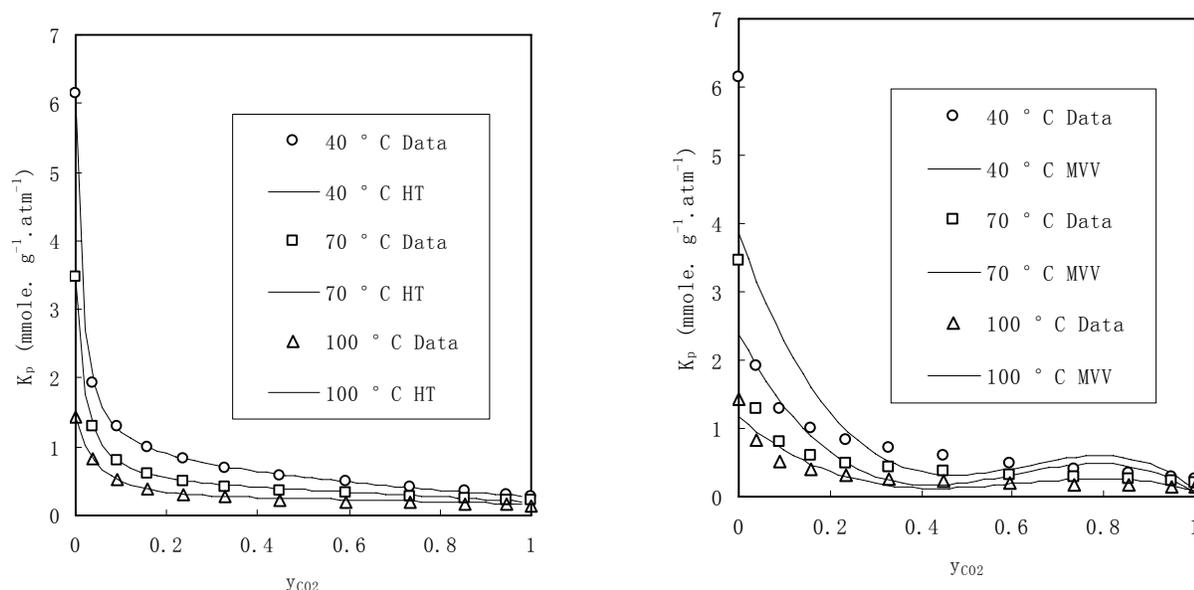


Figure 2. Regressions for CO₂/CH₄, binary K_p with silicalite by HT-CPM and MVV-CPM

For estimating and comparing the quality of the non-linear regressions from the concentration pulse methods, the RMS (root mean square) deviations were used. In comparison with the isotherms from the methods, according to Figure 2, the isotherms obtained by the HT-CPM match the experimental data very well. Those obtained by the MVV-CPM show oscillations and do not represent the experimental data obtained very well, as can be seen in Figure 2,. Therefore, HT-CPM was used to describe these systems for further study. The binary isotherms

for CO₂ - CH₄ with silicalite were obtained at 40, 70 and 100°C. 40°C data are shown in Figure 3a. When y_{CO_2} increases, the CO₂ adsorption capacity, q_{CO_2} , increases and the CH₄ adsorption capacity, q_{CH_4} , decreases as expected. The total adsorbed capacity, q_{total} , has a minimum when y_{CO_2} is smaller than 0.2 at different temperatures. The y_{CO_2} value at the minimum increases with increasing temperature. At low y_{CO_2} values, increase of q_{CO_2} is less than the decrease of q_{CH_4} since CH₄ isotherm has a steep slope. After the minimum of the total adsorbed capacity, increase of q_{CO_2} is larger than the decrease of q_{CH_4} , causing the total adsorbed capacity to increase. For landfill gases, whose y_{CO_2} is around 0.5, the CO₂ adsorption capacity is much higher than that of CH₄. Therefore, this trend in adsorption capacities for CO₂ and CH₄ is very promising for silicalite as an adsorbent for applications in CO₂ removal from landfill gases. Also, q_{CO_2} , q_{N_2} and q_{total} increase with decreasing temperature since adsorption is exothermic, so temperature is a very important factor for separation of CO₂ and CH₄. The x-y diagrams for this binary system with silicalite are shown in Figure 3b for 3 different temperatures studied. The separation is very easy when y_{CO_2} is small as the slopes of curves are large in this region, while the system is difficult to separate when y_{CO_2} is high. When x – y diagrams are compared in Figure 3b, it can be seen that experimental results and Extended Langmuir are quite different. Experimental results give better separation than Extended Langmuir predictions, since Extended Langmuir model is an ideal one and can not take into account the non-idealities in the system. In this particular application, the non-idealities seem to work to the advantage of the separation of CO₂ and CH₄ with silicalite.

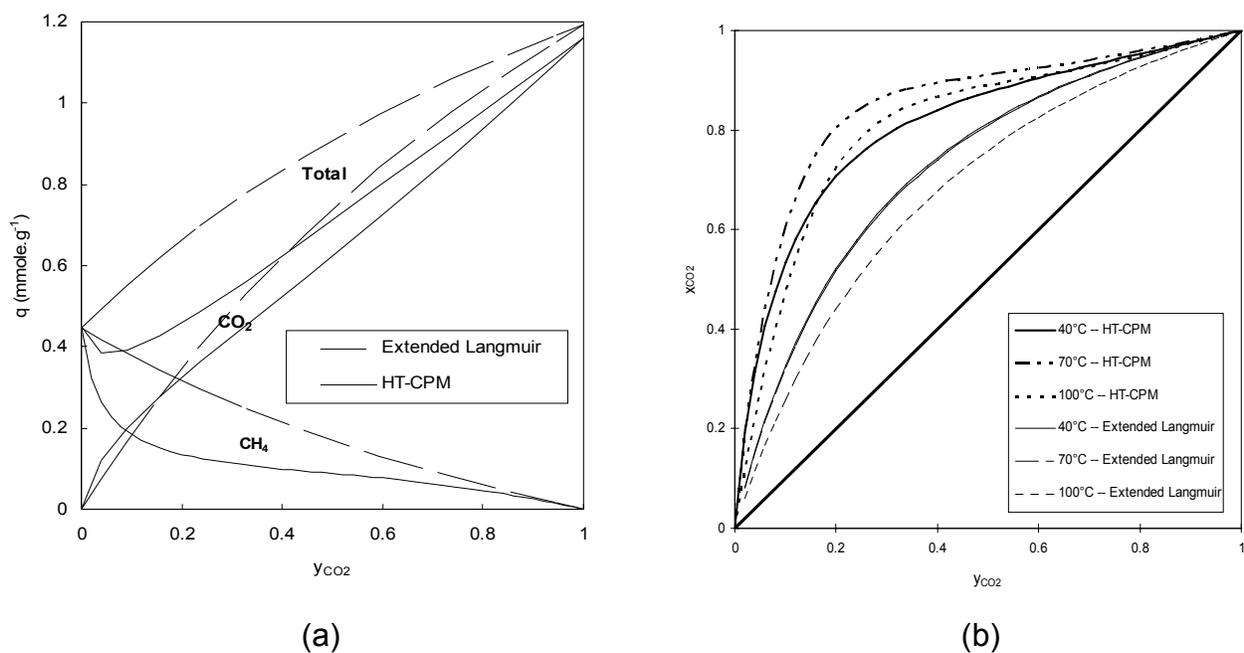


Figure 3. Binary adsorption behavior of methane and carbon dioxide with silicalite:
a) CO₂ / CH₄, Isotherms with silicalite by HT - CPM and Extended Langmuir at 40 °C
b) x – y diagram for CO₂ / CH₄ binary system with silicalite at 3 different temperatures

Conclusions

- According to the pure gas isotherm data on silicalite, carbon dioxide is adsorbed more than methane due to its quadrupole moment.
- The pure gas adsorption capacity decreases with increasing temperature in the systems of carbon dioxide and methane on silicalite.
- Among the two concentration pulse chromatographic methods used, HT-CPM is the better one, since MVV-CPM did not apply well for the binary behaviour of CO₂/CH₄ on silicalite.
- The adsorption capacities for CH₄ and CO₂ are very promising for silicalite as an adsorbent in applications for CO₂ removal from landfill gases.
- Extended Langmuir cannot describe the real binary adsorption system accurately for CO₂/CH₄ system with silicalite.
- Experimental data suggest that the selectivity is very good for the CO₂/CH₄ binary system on silicalite.

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Nomenclature

A_i = constants, dimensionless ($i = 0, 1, 2, 3$)

B = adsorption affinity constant, usually atm⁻¹ (units depending on models)

B_A = adsorption affinity constant of Component A, atm⁻¹

B_B = adsorption affinity constant of Component B, atm⁻¹

B_i = constants, dimensionless ($i = 0, 1, 2, 3$)

C_i = constants, dimensionless ($i = 0, 1, 2, 3$)

K = dimensionless Henry's law constant, dimensionless

K_P = dimensional Henry's law constant, mmole. g⁻¹.atm⁻¹

n = adsorption exponents or number of active sites, dimensionless

P = total pressure, atm

P_1 = partial pressure of Component 1, atm

P_2 = partial pressure of Component 2, atm

P_A = partial pressure of Component A, atm

P_B = partial pressure of Component B, atm

q = amount adsorbed, mmol.g^{-1}
 q_A = amount adsorbed of Component A, mmol.g^{-1}
 q_B = amount adsorbed of Component B, mmol.g^{-1}
 q_1 = amount adsorbed of Component 1, mmol.g^{-1}
 q_2 = amount adsorbed of Component 2, mmol.g^{-1}
 q_m = adsorption saturation capacity or maximum amount adsorbed, mmol.g^{-1}
 q_{mA} = adsorption saturation capacity of Component A, mmol.g^{-1}
 x = mole fraction in adsorbed phase at equilibrium, dimensionless
 x_A = mole fraction of Component A in adsorbed phase at equilibrium, dimensionless
 x_B = mole fraction of Component B in adsorbed phase at equilibrium, dimensionless
 y = mole fraction in fluid phase at equilibrium, dimensionless
 y_A = mole fraction of Component A in fluid phase at equilibrium, dimensionless
 y_B = mole fraction of Component B in fluid phase at equilibrium, dimensionless
 y_1 = mole fraction of Component 1 in fluid phase at equilibrium, dimensionless

Greek letters

$\alpha_{A/B}$ = adsorption separation factor (ratio of Component A over Component B), dimensionless
 $\alpha_{i,A/B}$ = ideal adsorption separation factor (ratio of Component A over B), dimensionless
 θ = fraction of monolayer coverage, dimensionless
 θ_A = fraction of monolayer coverage of Component A, dimensionless
 λ = constant parameter, dimensionless

Abbreviations

GHG = green house gases
GWP = greenhouse warming potential
HT-CPM = Harlick and Tezel - Concentration Pulse Method
LFG = landfill gas
MVV-CPM = Modified Van der Vlist and Van der Meijden - Concentration Pulse Method
PSA = pressure swing adsorption
RMS = root mean square

TCD = thermal conductivity detector
TSA = temperature swing adsorption

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