CO, CO_2 and CH_4 Gas Adsorption (Pure and Binary) on Cu-BTC and MIL-101 Metal Organic Frameworks (MOFs)

Pradip Chowdhury*

Department of Chemical Engineering, National Institute of Technology Rourkela
Rourkela-769 008, Odisha, INDIA
* Email: *chowdhuryp@nitrkl.ac.in*, Ph: *+91 661 2462269*, Fax: *+91 661 2462999*

ABSTRACT

In this research article, we present a comparative study on gas adsorption of CO, CO_2 and CH_4 on two of the most versatile MOFs reported till date: Cu-BTC (or, HKUST-1) and MIL-101 (or, Cr-BDC). The high pressure (0-100 bar) pure gas adsorption studies were carried out gravimetrically (Rubotherm, Magnetic Suspension Balance) at varying temperatures. Virial-Langmuir and Dual Site Langmuir models were found to suitable in explaining the experimental isotherm data on Cu-BTC and MIL-101 respectively. Isotherm studies showed that the electrical properties of the probe molecules (*viz*. dipole moment, quadrupole moment, polarizability etc.) as well as the nature of the adsorbent surfaces influencing the adsorption. The isotherm curves of all three probe molecules showed an interesting cross-over feature, independent of temperature. Finally, any realistic process development requires estimation / prediction of mixed gas adsorption. Here, we report a binary prediction for CO_2+CH_4 mixture using ideal adsorption solution theory (or, IAST) on Cu-BTC.

Keywords: MOFs, Cu-BTC, MIL-101, Virial-Langmuir, Dual Site Langmuir

1 INTRODUCTION

Metal Organic Frameworks (MOFs) which forms as a result of combination of an inorganic metal atom/ion as a node with an organic ligand as a linker can be classified to be a relatively new group of materials. Ever since initial reports on its synthesis, there has been a spurt in research activities owing to some of their characteristic features. The most important features include: extremely high specific surface area (*ca*. 800-5000 m^2 g^{-1}) and large pore volume (*ca*. 0.8-2.5 cc g^{-1}), uniform pore size distribution and tunable or tailor-made pores. A careful review of literature further shows that out of an excess of more than 2000 variants of MOFs reported till date: the Zn, Cu and Cr based MOFs have found a niche in the scientific community. In this present study we have opted for Cu-BTC and MIL-101 as the adsorbents and CO, CO_2 and CH_4 as the probe molecules. Very high specific surface area and moderate to high chemical and thermal stability are the reasons behind the choice of these adsorbents. The argument behind the choice of these specific probe molecules can be attributed to many factors. Not only each of these gases are environmentally and industrially important but also mixtures of them are found in many cases *viz*. partial oxidation/gasification of coals/hydrocarbons, steam reforming of naphtha, natural gas processing etc. Secondly, the adsorbate molecules are strikingly different in their electrical properties. CO has a permanent dipole, CO_2 possess a high quadrupole moment and CH_4 is non-polar. From a fundamental view point such a study is important to understand the adsorption behavior. Moreover, pure gas adsorption data is important to predict the mixed gas behavior using ideal adsorption solution theory (IAST). In this article, we report a binary prediction for CO_2+CH_4 mixture using IAST model on Cu-BTC.

2 EXPERIMENTAL

2.1 Synthesis and Characterization

Cu-BTC and MIL-101 were synthesized following standard recipes [1, 2]. The synthesized products were thoroughly characterized using various analytical measurement techniques [1, 2].

2.2 Gas Adsorption Measurements

Excess amount adsorbed for CO, CO_2 and CH_4 on Cu-BTC and MIL-101 were mesaured gravimetrically at varying temperatures and pressures ranging between 0-100 bar. All the measurements were carried out in a magnetic suspension balance (Rubotherm). Helium was used for calculating buoyancy volume. Standard protocols were followed during all measurements [3].

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2.3 Experimental Setup

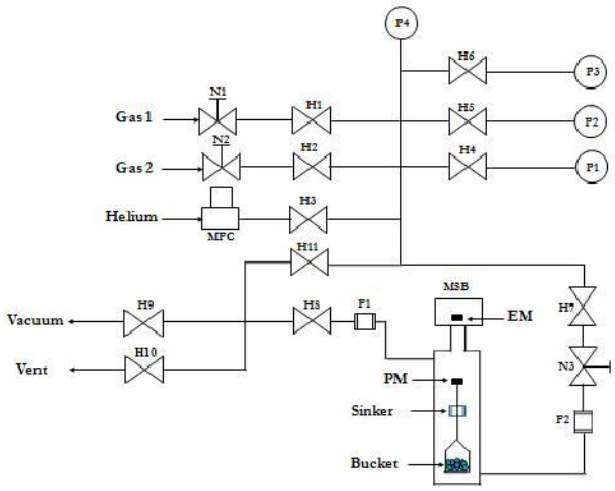

Figure 1: Schematic of gravimetric experimental setup used in the work

Nomenclature:

MSB−Magnetic suspension balance
H1-H11−Pneumatic valves**, N1-N3**−Needle valves
P1-P4−Pressure transducers, **MFC**−Mass flow controller, **F1-F2**−Filters, **PM**−Permanent magnet, **EM**−Electro magnet

The schematic of complete experimental setup is shown in Figure 1. For brevity, many auxiliaries are not shown in the figure. The balance can measure the weight of the sample and simultaneously the density of the surrounding gaseous atmosphere in the pressure range from 0-150 bar and temperature up to 523 K. The complete protocol may be easily outlined through macros; each macro consists of a pre determined series of valve operations.

3 RESULTS AND DISCUSSION

The isotherm data for all three gases on each of the adsorbents *viz*. Cu-BTC and MIL-101 are plotted in conventional [f vs. N] as well as in Virial domain [$\ln(\frac{f}{N})$ vs. N]. Fugacity is used to account for non-ideality at high pressures. The excess adsorption data along with their important significances have already been published [4]. A specific case with adsorption of CO (Virial domain plots) on both the adsorbents are shown in figures 2 and 3 respectively. For each of the gases including CO, isotherm data on Cu-BTC are best described by Virial-Langmuir model of the following form [4]:

$$f = \frac{N^{max}N}{\beta(N^{max}-N)} exp(bN + cN^2) \quad (1)$$

Where, β is Henry constant, N^{max} is saturation capacity, b and c are the second and third Virial coefficients respectively. The usual temperature dependency is considered for these parameters.

$$\beta = \beta_0 \, exp\left(\frac{\beta_1}{T}\right) \quad (2)$$

$$b = b_0 + \frac{b_1}{T} \quad (3)$$

$$c = c_0 + \frac{c_1}{T} \quad (4)$$

The saturation capacity N^{max} is also expressed by a similar temperature dependency.

$$N^{max} = \eta_0 + \frac{\eta_1}{T} \quad (5)$$

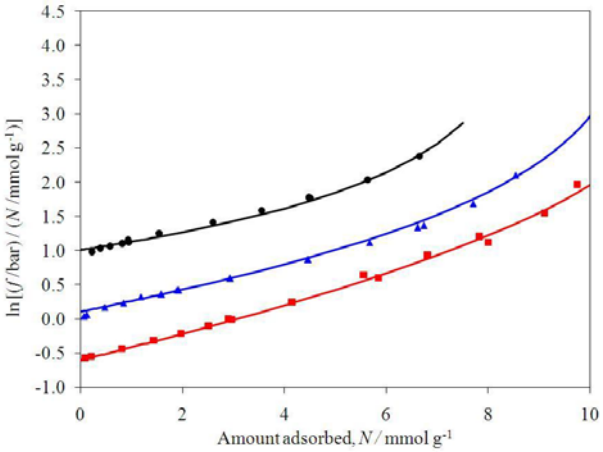

Figure 2: High pressure adsorption isotherms for CO on Cu-BTC. Symbols: Experimental points, Lines: Virial-Langmuir model fits. Squares: 295 K, Triangles: 318 K, Circles: 353 K

Unlike in case of Cu-BTC, experimentally measured excess adsorption data on MIL-101 is best described by the Dual Site Langmuir model. The following equations are used [4]:

$$N = \frac{N_1^{max} b_1 P}{1+b_1 P} + \frac{N_2^{max} b_2 P}{1+b_2 P} \quad (6)$$

where, $N_i^{\max}$ and b_i denotes saturation capacity and affinity parameters for sites of type *i*. The temperature dependency is included through affinity parameters via

$$b_i = b_i^0 exp\left[\frac{-\varepsilon_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (7)$$

where, b_i^o is the affinity at reference temperature T_o and ε_i is the enthalpy of adsorption on site i with respect to temperature T_o .The Henry's constant β in this case is given by

$$\beta = N_1^{max} b_1 + N_2^{max} b_2 \quad (8)$$

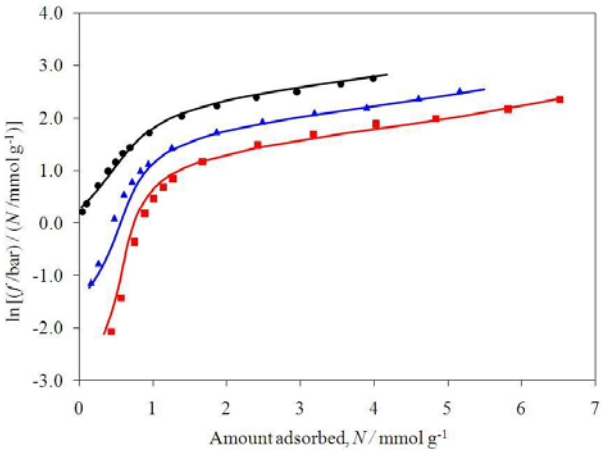

Figure 3: High pressure adsorption isotherms for CO on MIL-101. Symbols: Experimental points, Lines: Dual Site Langmuir model fits. Squares: 295 K, Triangles: 318 K, Circles: 353 K

The Virial domain plot for CO shows a distict knee in the low loading region for adsorption on MIL-101, an indication of surface heterogeneity whereas the effect is less pronounced on Cu-BTC. The effect of heterogeneity becomes more conspicuous for polar molecules like CO and CO_2 whereas for non-polar gases like CH_4 the effect is marginal [4].

A comparison of adsorption isotherms of CO, CO_2 and CH_4 shows interesting cross-overs. Figures 4 and 5 depicts the nature of the isotherms at 353 K in Virial domain.

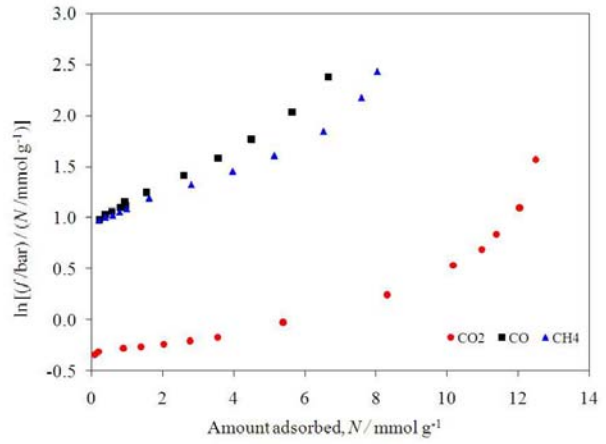

Figure 4: Comparison of adsorption isotherms of CO_2 (circle), CO (squares) and CH_4 (triangles) on Cu-BTC framework at 353 K (Virial domain plot)

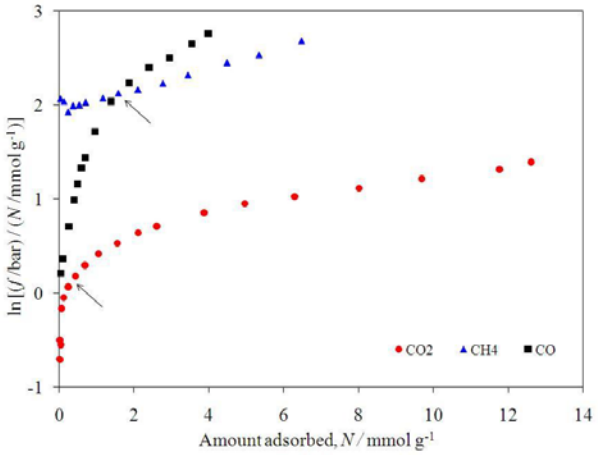

Figure 5: Comparison of adsorption isotherms of CO_2 (circle), CO (squares) and CH_4 (triangles) on MIL-101 framework at 353 K (Virial domain plot)

It is noteworthy to mention that this cross-over feature is independent of temperature. A detailed illustrative resaoning is given in our published article [4]. The avialability of metal centers or sites, polarity of the probe molecules influences the nature of the adsorptive forces *viz.* electrostatic and/or dispersion. It can also be concluded that the effective total pore volume of the adsorbents measured (~0.75 mmol g^{-1} for Cu-BTC and ~1.38 mmol g^{-1} for MIL-101), crystal purities of the MOF matrix (i.e. presence or absence of solvated molecules within the MOF motif) play a deciding role in the shape of the isotherm, since in the low-coverage region, the amount adsorbed is strongly correlated to the heat of adsorption and in the high loading region, the adsorption capacity is a function of pore volume whereas, surface area dictates terms in the intermediate coverage.

Finally, any realistic process development requires to estimate / prediction of mixed gas adsorption. Here, we report our findings on CO_2+CH_4 mixture using IAST model on Cu-BTC. The binary prediction is calculated from individual pure gas adsorption data of CO_2 and CH_4 on Cu-BTC. Figures 6 and 7 represents IAST predictions for CO_2+CH_4 mixture. The selectivity plots are shown in figures 8 and 9 respectively.

In fact IAST was used in several works in literature earlier for estimation of binary adsorption properties of gas mixtures on this type of frameworks. The selectivity values predicted by IAST varied between 5.7 and 7.2. This selectivity for CO_2/CH_4 mixture thus shows promise for effective separation using Cu-BTC.

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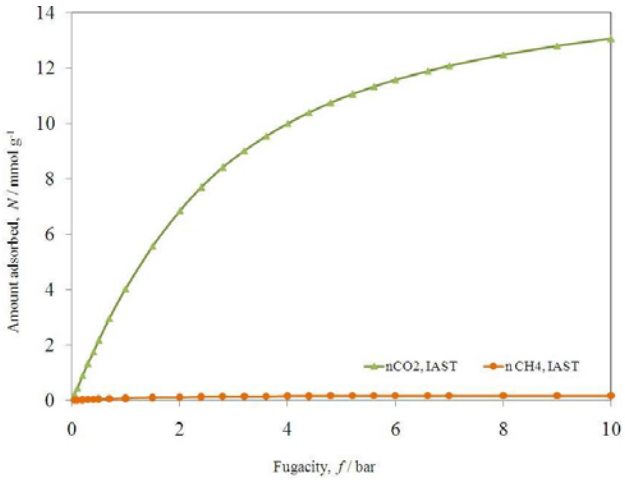

Figure 6: Variation of amount adsorbed from CO_2+CH_4 mixture at 305 K, yCH_4 = 0.1

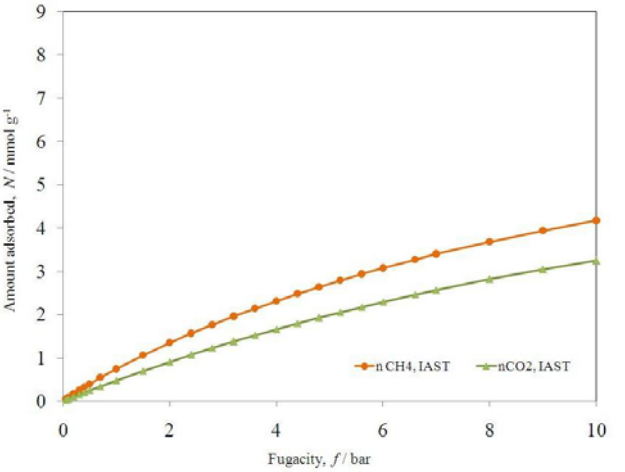

Figure 7: Variation of amount adsorbed from CO_2+CH_4 mixture at 305 K, yCH_4 = 0.9

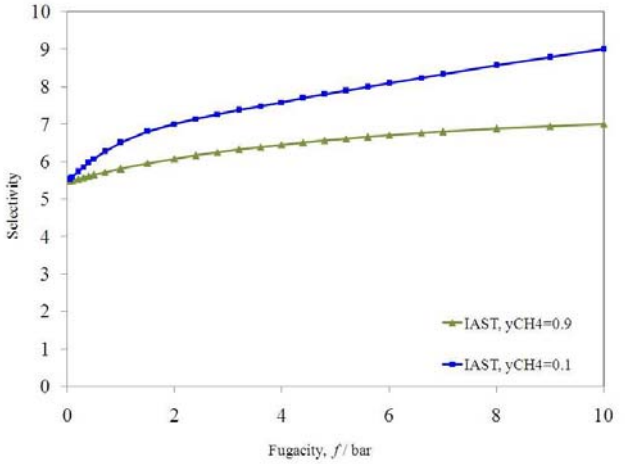

Figure 8: Variation of selectivity of CO_2+CH_4 mixture at 305 K with fugacity

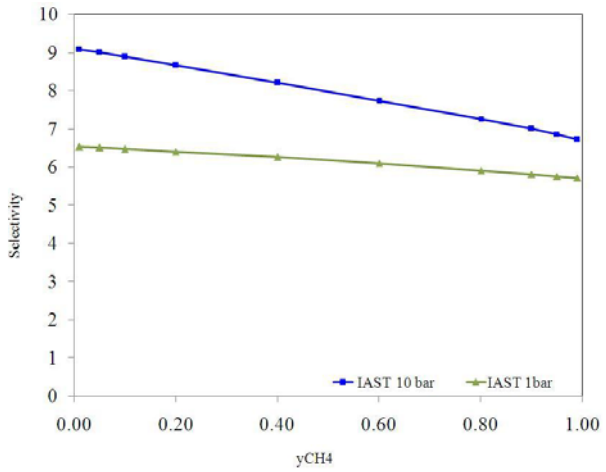

Figure 9: Variation of selectivity of CO_2+CH_4 mixture at 305 K with composition (in mole fraction)

4 CONCLUSIONS

We have successfully measured the adsorption isotherms of CO, CO_2 and CH_4 on Cu-BTC and MIL-101. Adsorbate polarity and sorbent surface characteristics largely determine the excess loading and nature of isotherms. Interesting cross-over features are also observed between isotherms. Finally, IAST model is used to predict the binary adsorption behavior of CO_2+CH_4 mixture on Cu-BTC. The selectivity values predicted by IAST varied between 5.7 and 7.2. This selectivity for CO_2+CH_4 mixture thus shows promise for effective separation using Cu-BTC. Although IAST is highly recognized method but its validity is still required to be tested. In our approach we have been trying to develop an infinite dilution solution technique along with Virial-Langmuir isotherm model to obtain binary interaction parameters. The data we obtained during our study is inconclusive and further experiments are required to be carried out for a concrete validation.

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