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CH_4 and CO_2 Adsorption Study in ZIF-8 and Al-BDC MOFs

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Abstract: CH_4 and CO_2 adsorption capacity at 25, 50 and 75°C was evaluated in two metal-organic frameworks: Al-BDC and ZIF-8, the later with zeolite topology. Adsorption experiments were carried out under static conditions using a gravimetric suspension balance until 40 bar of pressure. Adsorption isotherms of type I were obtained for both materials showing high adsorption capacity values. ZIF-8 exhibited the higher uptake value for both CH_4 and CO_2 (4.9 and 8.5 mmol g^{-1}, respectively). The Toth equilibrium model was used to fit experimental isotherms in order to obtain q_m (maximum adsorption capacity) and t (related to energetical heterogeneity of the surface). Isosteric heats of adsorption were also calculated by Clausius-Clapeyron equation.

Keywords: Adsorption, ZIFs, MOFs, adsorption heats, adsorption isotherm

1. Introduction

A new family of materials named metal organic framework (MOFs) has been developed principally in the last two decades. These novel crystalline materials attract the scientific interest because of it is possible to design rationally new structures as well as to monitor the empty spaces (pores and cavities) at nanometrical

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scale. The control of the empty spaces enables the manipulation capacity of the molecule chemistry trapped inside which represents a powerful tool for several important applications.

MOFs are composed of two blocks: (i) the connectors (ligands) and (ii) nodes (metallic ions with charge $^{2+}$ or $^{3+}$) which constitute open metal sites located at the cavities surface. The strength of the bond between the metal oxide cluster and the linker has been suggested to be important in determining the stability [1]. They are attractive for adsorption and separation applications [2-5] and gases storage [6, 7] due to their thermal and chemical stability, versatility and numerous structural design possibilities.

The framework structure of MIL-53-Al (also known as Al-BDC) is composed of infinite $AlO_4(OH)_2$ octahedra connected by a 1,4-benzenedicarboxylate ligand. Its chemical formula is $M(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$, in which M stands for either Al^{3+} [8]. This MOF is important in the field of gas adsorption [9, 10] and separation of organic compounds [11].

More recently a MOFs sub-family known as ZIFs (zeolitic imidazolate frameworks) has fascinated the scientific community. These materials own a zeolitic type structure given by their structure similarity with these inorganic compounds and possess even higher thermal stability. Their framework arises by the metallic node connected by imidazole derivatives with a tetrahedral environment [12].

The zinc 2-methylimidazolate [$Zn(C_4H_5N_2)_2$ or $Zn(MeIm)_2$], zeolitic imidazolate framework ZIF-8 [13, 14] is commercially available, highly stable MOF that is receiving great interest fora diverse variety of applications. ZIF-8 is constructed from corner-sharing $Zn(MeIm)_4$ tetrahedral units in which the MeIm-ligands bridge the Zn^{2+} ions to form a three-dimensional framework with the sodalite framework topology and a pore size of 3.4 Å. Separation of linear and branched alkanes, ethane/ethylene, hydrogen storage and carbon dioxide capture have been evaluated using ZIF-8 material [12, 15-17].

From an environmental and energy perspective, purification and recovery of carbon dioxide from flue gas and natural gas are of great interest. CO_2 is the main component of the greenhouse gases, and its accumulation in the environment is leading to global warming issues. Thus, the selective adsorption of CH_4 in the presence of other gas species, such as CO_2, is a property of fundamental interest. Methane adsorption and selectivity in ZIFs have been studied both experimentally [18] and computationally [19] for pure gases and gas mixtures relevant in the context of natural gas separations. Experimental studies in ZIFs have involved measurements of adsorption isotherms [18], breakthrough curves [20], and membrane selectivity [21]. The understanding derived from these studies has been complemented by relevant investigations in other related metal-organic framework (MOF) systems, [22, 23] featuring data on the time-resolved uptake of methane and carbon dioxide [24] as well as neutron scattering to characterize CH_4 and CO_2 binding sites and occupations [25, 26]. The studies of ZIFs have shown that these frameworks can exhibit adsorption

selectivities and uptakes that exceed the performance of commercial adsorbents used for natural gas separation and that performance depends on several factors, including the choice of linker, functionalization, pore size, and metal ion.

In this work, a gravimetrical adsorption study of CH_4 and CO_2 using ZIF-8 and Al-BDC MOFs is exposed. Adsorption and desorption isotherms at 25, 50 and 75°C up to 40 bar of pressure were obtained. From the recorded isotherms the adsorption heats (Q_d) were estimated using the Clausius Clapeyron's equation. The Toth model was used to fit the experimental isotherms in order to obtain q_m (maximum adsorption capacity) and t (parameter related to energetical heterogeneity of the surface).

2. Materials and Methods

2.1 Materials

ZIF-8 and Al-BDC were supplied by Sigma-Aldrich (commercialized as Basolite Z1200 and Basolite A100; Cat. Nr.59061-53-9 and Cat. Nr. 185361, respectively). Table 1 summarizes some textural properties of both materials: specific surface area and micropore volume [27, 28].

Table 1. Textural properties.

Material	Specific Surface area and micropore volume		
	Surface area ($m^2 \cdot g^{-1}$)	Micropore volume ($cm^3 \cdot g^{-1}$)	Reference
Al-BDC	1100	0.350	[27]
ZIF-8	1813	0.663	[28]

2.2 Methods

Scanning electron microscope (SEM) observation was conducted on a Philips CM 200 Supertwin-DX4, from samples dispersed in ethanol. A drop of the suspension was put on a carbon coated Cugrid (300 mesh).

The conditions of sample regeneration and thermal stability were evaluated from thermogravimetric curves (TG) recorded using a thermal analyzer METTLER TOLEDO, model TGA/DSC 1 with software STARe version 10.00 from METTLER TOLEDO STAR^e system. The experiments were carried out in N_2 at flow of 50 $ml.min^{-1}$ with a rate of $10^oC.min^{-1}$.

CH_4 and CO_2 adsorption experiments were carried out using a magnetic suspension balance Rubotherm (Bochum, Germany). Adsorption measurements were performed at 25, 50 and 75°C until 40 bar. Prior to

each measurement samples were outgassed 200ºC (heating rate of 2ºC.min^{-1}) under vacuum (10^{-3} bar). Experimental data were obtained gravimetrically so it was necessary to take into account the effects of buoyancy during the experiments. For a given pressure P of surrounding gas, the adsorbed phase concentration in excess could be obtained according to (Eq. 1):

$$m_{ex}(P,T) = \Delta m\ (P,T) + (V_b+V_s)*\rho(P,T) \quad (1)$$

where:

m_{ex}: excess mass amount adsorbed (g.g^{-1} of sample)

Δm: mass difference recorded by the equipment (g.g^{-1} of sample)

V_b: specific volume of the balance suspended components (cm^3.g^{-1} of sample)

V_s: specific volume of the solid sample (cm^3.g^{-1} of sample)

ρ: gas density (g.cm^{-3})

P: pressure (bar)

T: temperature (K)

The absolute mass was estimated using the standard procedure reported by Myers et al. (Eq. 2) [29].

$$n_a = n_e + \rho v_p \quad (2)$$

where $v_p = V_{mp}/m_s$ is the specific micropore volume (cm^3.g^{-1}) of the solid.

Isosteric heats of adsorption were obtained using the Clausius Clapeyron's equation (Eq. 3):

$$d(lnP)/dT\ = \Delta H/RT^2 \quad (3)$$

Experimental isotherms were fitted to the Toth model as (Eq. 4) [30].

$$q = q_m \frac{bP}{(1+(bP)^t)^{1/t}} \quad (4)$$

where:

q_m: maximum adsorption capacity

b: parameter related to the affinity of the pair adsorbate-adsorbent

t: parameter related to energetical heterogeneity of the surface

Binary isotherms were predicted by the Toth extended model (Eq 5)

$$q_i = \frac{q_{max,i} b_i P_i}{(1+\sum_{i=1}^{j}(b_i P_i)^{t_i})^{1/t_i}} \quad (5)$$

The efficiency of carbon dioxide separation for these MOFs was estimated by the selectivity of CO_2 over CH_4 considering a scenario of 70% CH_4 and 30 % CO_2 (v/v). Selectivity was calculated from the ratios of mole fractions in the gas phase and in the adsorbed phase at equilibrium, as shown in (Eq. 6):

$$S_{i/j} = \frac{q_{i\,mixt}}{q_{j\,mixt}} * \frac{P_j}{P_i} \tag{6}$$

3. Results and Discussion

SEM images of the ZIF-8 and Al-BDC solids morphology are showed in Figure 1 (a) and (b), respectively. SEM study revealed the presence of clusters of spherical and uniform particles of size between 180-240 nm in the case of ZIF-8 sample, (Figure 1a). However, the Al-BDC material showed an irregular morphology of different size particles, (Figure 1b).

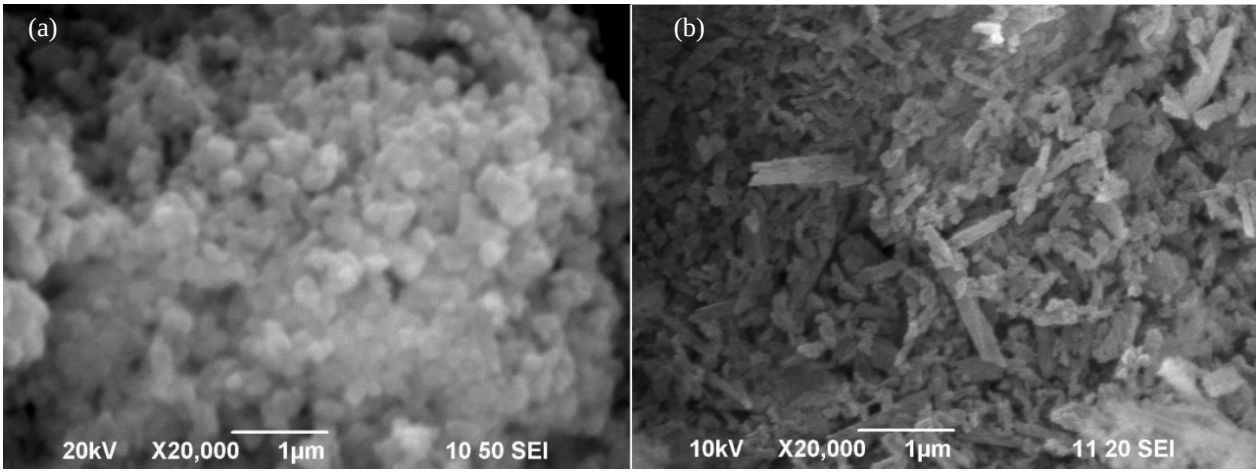

Fig. 1:SEM micrographs (a): ZIF-8 and (b): Al-BDC.

Thermal stability of ZIF-8 and Al-BDC was evaluated by thermogravimetric analysis (TGA). The weight loss percent of both materials as a function of the temperature is shown in Figure 2. For temperatures between 40-230°C; 230-420°C and 420-470°C continuous weight losses of 6 %, 6 % and 54 %,respectively, were observed for the ZIF-8 sample, which is attributed to water and residual solvent used in the synthesis process. On the other hand, the Al-BDC sample showed just two individual weight losses of 11 % and 49 %, within temperatures between 30-536°C and 536-677°C, respectively, attributed to the removal of water and the solvents used in the synthesis.

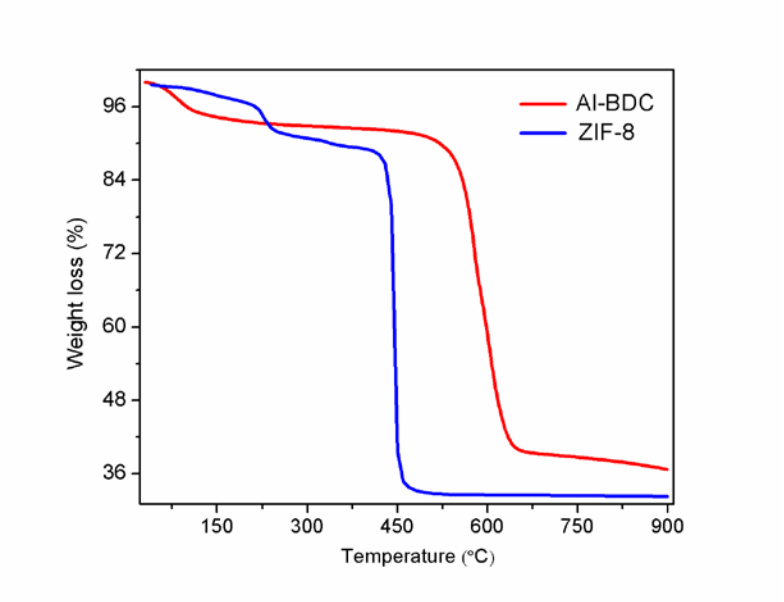

Fig. 2: Thermogravimetric curves of ZIF-8 and Al-BDC.

CO_2 and CH_4 single component adsorption and desorption isotherms at 25, 50 and 75ºC are shown in Figure 3 in the range of pressures between 0-40 bars. As expected, both samples exhibited preferential adsorption for CO_2 in relation to CH_4 over the whole pressure range for all measured temperatures. ZIF-8 sample exhibited the highest adsorption capacity of CO_2 under the studied conditions (8.5 mmol.g^{-1} for CO_2 and 4.7 mmol.$g^{-1}$for CH_4 at 25ºC and 40 bar). Additionally, it was appreciated that the ZIF-8 presented a higher CO_2 adsorption capacity than that observed for the Al-BDC sample (5 mmol.g^{-1} of CO_2 under the same conditions). This higher CO_2 capture capacity may be attributed to the combination of high specific surface area and micropore volume. Similar behavior has been reported in ZIF-69 and ZIF-76 at 30ºC [31]. All isotherms do not present hysteresis loop indicating the reversibility of process.

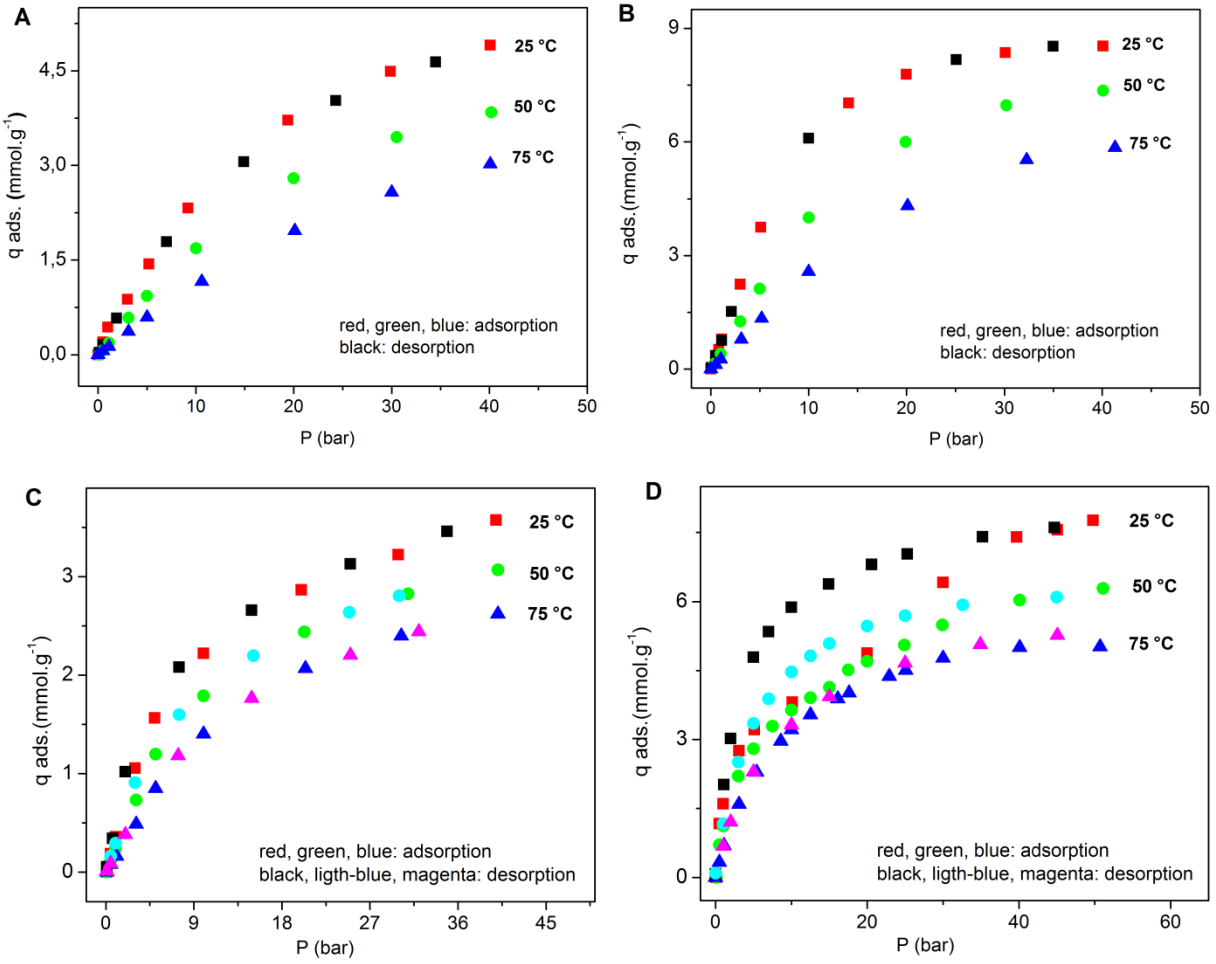

Fig. 3: Single component adsorption isotherms of A: CH_4, B: CO_2 in ZIF-8 and C: CH_4, D: CO_2 in Al-DBC at 25, 50 and 75°C until 40 bar of pressure.

The Toth parameters and the isosteric heats of adsorption for both samples are summarized in Table 2 and Figure 4. The parameter *b* (Eq. 4) indicates how strongly the adsorbate molecule is attracted onto adsorbent surface [30]. As expected, higher *b* values were obtained for CO_2 in comparison with CH_4. This behavior could be ascribed to the presence of a quadrupolar moment in the CO_2 molecule which could interact with the electric field gradient inside the pores and cavities. The CH_4 molecule presents octupolar moment which is smaller in magnitude than the quadrupolar moment of the CO_2 molecule (Qzz_{CO2} = 5.9x10^{-26} esu cm^2, Ω_{CH4} = 6 x 10^{-34} esu cm^3) [32]. For each sample, it can also be observed that higher values for q_{max} are obtained for CO_2. The isosteric heats of adsorption for CO_2 were higher than those for CH_4 in the two studied samples; and they were higher in the ZIF-8 material. These results could be related to the higher specific surface area as well as the higher micropore volume in this material. A lower heat of adsorption usually means an easier

regeneration and from the observed behavior, one can conclude that these MOFs have not only high capacity and apparent selectivity for CO_2 but also potentially a good regenerability.

Table 2. Parameters of Toth isotherm model, calculated selectivity (CO_2/CH_4) and isosteric heats of adsorption for ZIF-8 and Al-BDC MOFs.

Sample (V_{mp} ($cm^3.g^{-1}$))	Toth parameters					Selectivity (mol CO_2/mol CH_4)[a]	Adsorption heats
ZIF-8 (0.58)	*T*(ºC)	q_m(mmol.g^{-1})	*b* (bar^{-1})	*t*	r^2		*Qd*(kJ.mol^{-1})
	25	14.31	0.065	0.98	0.96543	2.21	
CO_2	50	14.02	0.040	0.98	0.97581	2.11	-19.5
	75	13.91	0.024	0.98	0.99012	1.71	
	25	9.98	0.043	0.93	0.98991		
CH_4	50	9.02	0.030	0.91	0.98753		-17.0
	75	8.01	0.025	0.90	0.98021		
Al-BDC(0.325)	*T*(ºC)	q_m(mmol.g^{-1})	*b* (bar^{-1})	*t*	r^2		*Qd*(kJ.mol^{-1})
	25	15.32	0.101	0.57	0.94565	2.33	
CO_2	50	13.21	0.094	0.57	0.95871	2.92	-15.0
	75	11.41	0.093	0.57	0.97244	3.68	
	25	5.17	0.084	1.00	0.99454		
CH_4	50	5.04	0.058	1.00	0.99956		-13.5
	75	5.01	0.041	1.00	0.99745		

[a]: average values calculated in the pressure range from 0.1 to 30 bar

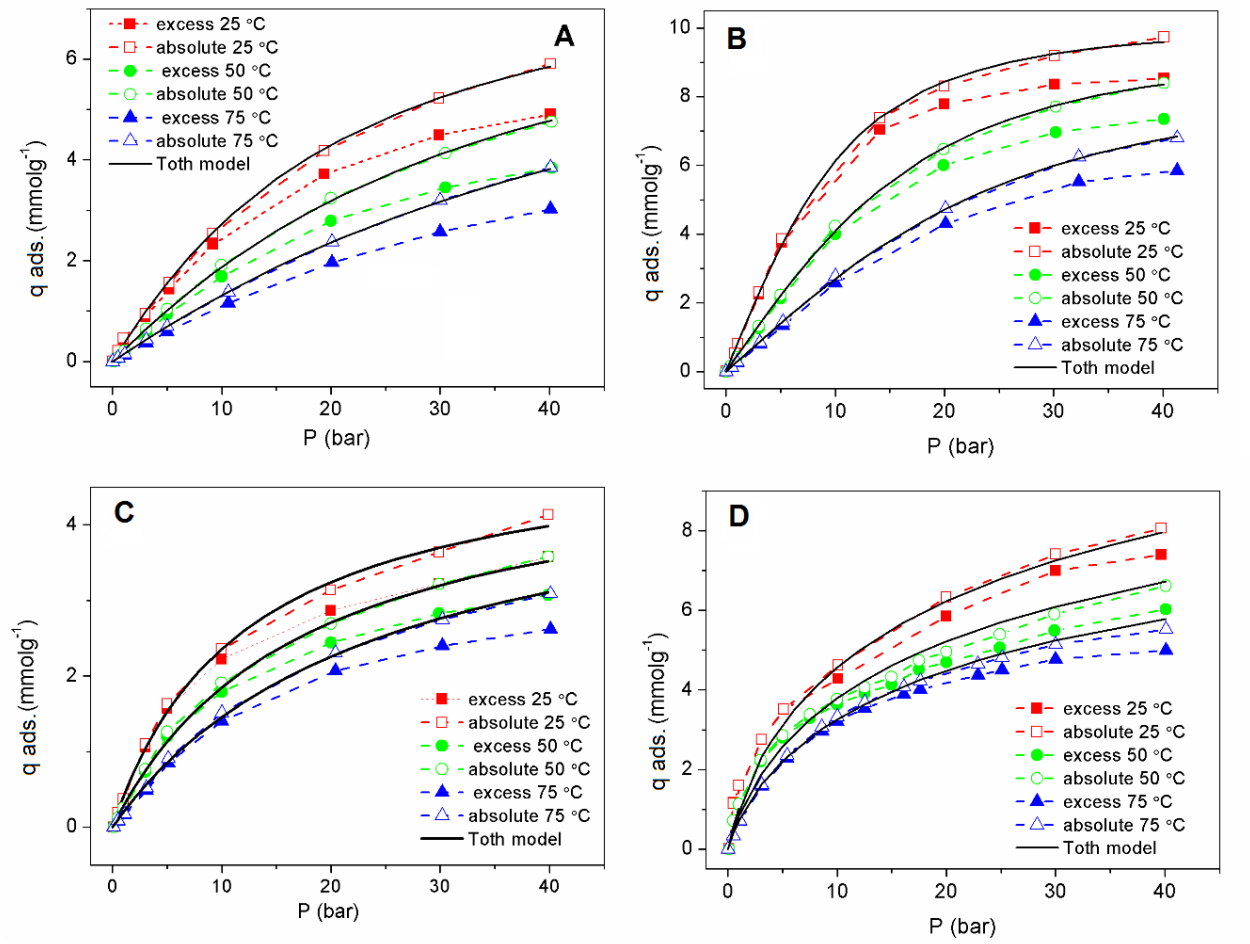

Fig. 4: Representation of Toth model for the obtained isotherms of CH_4 and CO_2 adsorbates in ZIF-8 and Al-BDC MOFs. A: CH_4 in ZIF-8, B: CO_2 in ZIF-8, C: CH_4 in Al-BDC and D: CO_2 in Al-BDC.

From the fit of the Toth model, several mixture isotherms were simulated at different temperatures (Figure 5). From this, binary gas equilibrium adsorption isotherms were obtained at 25, 50 and 75°C for an ideal gas natural composition (30% CO_2 and 70% CH_4). The aim of this study is to check if these materials have the same trend when the mixture evolves towards higher temperatures. Al-BDC and ZIF-8 samples showed, as expected, a decrease in the gravimetric uptake as the temperature increases, especially in the case of ZIF-8. In terms of selectivity, the Toth extended model predicts for ZIF-8 a decreasing selectivity as temperature increases while for the Al-BDC material this behavior is not observed, the selectivity increases as the temperature increases. The highest CO_2 affinity of this MOF balances the loss of CO_2 capacity when the temperature increases, remaining a high CO_2/CH_4 selectivity and even improves it.

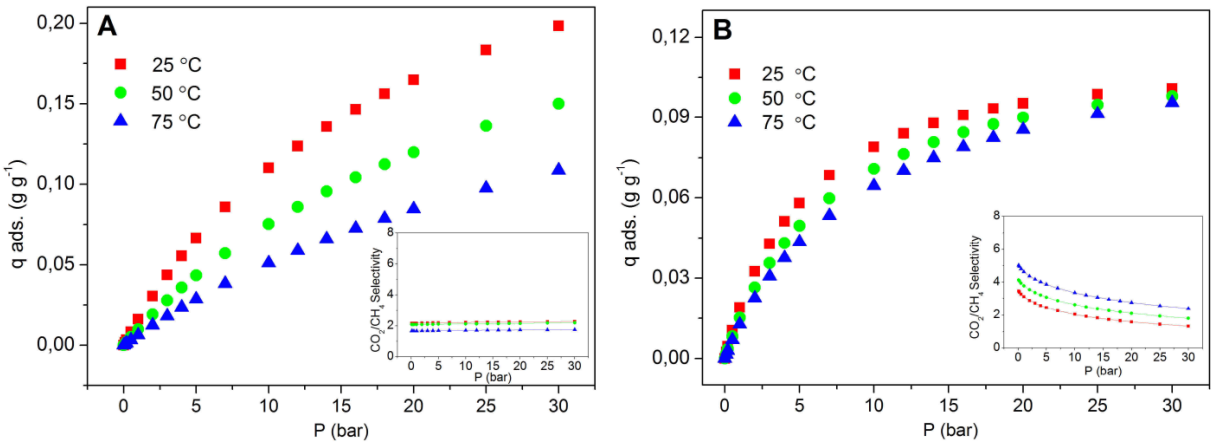

Fig 5: CO_2/CH_4 (30/70 v/v) binary isotherms predicted by Toth Extended model for A**:** ZIF-8 and B**:** Al-BDC. CO_2/CH_4 selectivity values are also plotted.

4. Conclusion

CH_4 and CO_2 adsorption at 25, 50 and 75°C up to 40 bar of pressure were carried out using Al-BDC and ZIF-8 MOFs as adsorbents. Both materials showed optimal levels of adsorption; therefore the two evaluated adsorbents seem to be attractive for CH_4 and CO_2 adsorption. However ZIF-8 exhibited higher CO_2 capture capacity under the studied conditions. This fact may be attributed to the combination of high specific surface area and micropore volume. Experimental isotherms were fitted to the Toth model from which higher *b* values were obtained for CO_2 in comparison with CH_4. Since the *b* parameter indicates how strongly the adsorbate molecule is attracted onto the adsorbent surface this could be related to the presence of a quadrupolar moment in the CO_2 molecule which would interact more strongly with the electric field gradient inside the pores and cavities.

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