Strong Binding Site Molarity of MOFs and Its Effect on CO₂ Adsorption

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ABSTRACT: Metal organic frameworks (MOFs) with strong binding sites usually have remarkable CO₂ adsorption capacity at ambient conditions. A new material parameter, the strong binding site molarity, defined as the number of the strong binding sites divided by the molecular weight of the unit cell of MOF, is introduced to understand CO₂ adsorption on these MOFs. The CO₂ adsorption capacity can be correlated to the strong binding site molarity in 1:1 **ratio**. The strong binding site coverage by CO₂ molecules can also be correlated to the isosteric heat of CO₂ adsorption at a given pressure. The strong binding site molarity is used to predict CO₂ adsorption amount of several new types of MOFs to show its uses in selection or design of MOFs for CO₂ capture.

KEYWORDS: MOFs; CO₂ adsorption; Strong binding sites molarity; Site coverage

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Metal organic frameworks (MOFs) are known for their extraordinarily high surface area, tunable pore size and adjustable internal surface properties, and have shown good potential for the utilization in CO₂ capture [1]. Among all types of MOF materials, MOFs with unsaturated metal sites (or called open metal sites) are reported to exhibit remarkable CO₂ adsorption capacity at low pressures [2-4]. The unsaturated metal sites are usually obtained following desolvation of the MOF material, where one of the solvent molecules in the coordination sphere of the metal center is removed in vacuo at elevated temperatures [1]. Thus the unsaturated metal sites serve as charge-dense binding sites for CO₂, which is adsorbed more strongly on these sites owing to its greater quadrupole moment and polarizability compared with N₂ [1]. Neutron diffraction measurements and density functional theory (DFT) calculations have confirmed that the unsaturated metal sites are primary binding sites for CO₂ [5, 6]. Recent studies have also shown that amine modification on the unsaturated metal sites of MOFs can enhance the CO₂ adsorption capacity for the application of CO₂ capture from air or from stationary combustion sources [7-9]. A hydrogen-bonded complex involving two carbamic acid moieties was formed which results in 2:2 amine:CO₂ stoichiometry with higher capacity and weaker binding energy than the 2:1 stoichiometry observed in most amine-functionalized adsorbents [10]. Overall, both unsaturated metal cations or alkylamines inside the pores of MOFs can be considered as strong binding sites for CO₂ adsorption, resulting in high CO₂ adsorption capacity at low pressure range [1, 8, 9].

Many studies have investigated the nature of binding site and its effect on CO₂ adsorption at low pressure for a specific MOF [5-12]. However, there lacks effort to compare CO₂ adsorption on various MOF with strong binding sites. We analyzed CO₂ adsorption on various MOFs with strong binding sites and found that the CO₂ adsorption data can be correlated by one

parameter related to the amount of the strong binding sites per unit mass of MOF. Here we report analysis of the CO₂ adsorption on various MOFs by this parameter.

We define binding site molarity SM (mmol/g) for a MOF as:

$$SM = 1000 \cdot N_{\text{site}} / W_{\text{u.c.}} \quad (1)$$

where N_{site} and $W_{\text{u.c.}}$ (g/mol) are number of strong binding site and molecular weight per unit cell of MOF. N_{site} can be obtained by calculating the number of unsaturated metal cations or incorporated amines. For example, there are 18 unsaturated Mg cations in every unit cell of Mg/DOBDC. These 18 cations are considered as strong binding sites because all of them can strongly interact with CO₂ molecules. Thus N_{site} equals 18 for Mg/DOBDC materials. The binding site molality of reported MOFs with extremely strong binding sites is summarized in Table 1. One can see that the value of binding site molality varies considerably among different MOFs because of the variation of molecular weight and the number of strong binding sites in MOFs. For example, though the number of strong binding sites of M/DOBDC (M = Mg, Co, Ni and Zn) series is same, their molecular weight differ from each other due to different types of metals being used in these materials, resulting in very different values for the binding site molarity for these materials.

Fig. 1 plots CO₂ adsorption amount at 298 K and 1 bar versus corresponding binding site molarity for MOFs reported in the literature. It is remarkable to see that the CO₂ adsorption amount is determined by the binding site molarity in 1 to 1 ratio. This suggests that CO₂ adsorbed in a MOF would not occupy any other binding site unless the strong binding sites are fully occupied. The results show that every strong binding site inside the framework of these materials is occupied by one CO₂ molecule under such a condition due to the strong interaction forces between the strong binding sites and CO₂ molecules [5, 12]. For example, the binding

energy between CO₂ and Mg²⁺ cations of Mg/DOBDC is calculated to be over 40 kJ/mol [6]. Such strong binding strength will result in fast occupation of Mg²⁺ cations by CO₂ molecules at low pressure, which is evidenced by the sharp increase of CO₂ adsorption isotherm with increasing pressure in the low pressure range and at ambient temperature [13]. At room temperature, CO₂ adsorption reaches saturation for all these MOFs with strong binding sites with CO₂ pressure approaching 1 atm because they have similar high binding strength between different strong binding sites and CO₂ molecules [6]. It should be noted that the CO₂ binding strength at secondary binding sites, mainly organic linkers, are usually quite weak [5, 21, 22] and thus the CO₂ adsorption amount at these sites at 298 K and 1 bar is too small to be considered. Deviations are observed for several materials, as marked in Fig. 1, which is simply because of the limitation of surface area or pore volume. For instance, the bio-MOFs series have same number of strong binding sites, but their surface area are 1148 m²/g, 1008 m²/g, 412 m²/g and 17 m²/g for bio-MOF-11, 12, 13 and 14 respectively [18]. In the cases of bio-MOF-11 and 12, their surface area is large enough to accommodate sufficient CO₂ molecules and thus their experimental adsorption data agree very well with the binding site molarity. In contrast, the surface area of bio-MOF-13 and 14 is too low, which means there is no enough space for CO₂ molecules to occupy every strong binding sites. Thus reasonable surface area or pore volume is also an important consideration besides the binding site molarity.

Isosteric heat for CO₂ adsorption on various MOFs at different adsorption amount is plotted in Fig. 2.a versus site coverage defined as:

$$\theta_A = \frac{m_{ad}}{SM} \quad (2)$$

where m_{ad} (mmol/g) is the adsorption amount of CO₂ at a given pressure. One can see that at a given pressure value of θ_A gradually increases with the increasing of isosteric heat, in the

sequence Zn/DOBDC < Co/DOBDC < Ni/DOBDC < Mg/DOBDC < Mg/DOBPDC < mmen-Mg/DOBPDC < en-Mg/DOBPDC. However, such a relationship does not exist when using isosteric heat versus CO₂ adsorption amount, as shown in Fig. 2.b. Although the CO₂ adsorption capacity of Mg/DOBDC and Mg/DOBPDC differ from each other significantly [2, 8], the site coverage by CO₂ of these two materials are almost same at 1 kPa, which indicates the Mg²⁺ centers in these two materials have similar binding strength to CO₂. Considering that these two materials have a similar structure but different size linkers, one can conclude that the higher CO₂ adsorption capacity of Mg/DOBDC comparing to Mg/DOBPDC is due to its lower framework weight. However, the difference between these two values becomes larger as pressure increasing, as shown in Fig. 2. **This may be due to the different adsorption potential generated by different size of pores of these two materials.**

Since Fig. 1 shows that the CO₂ adsorption amount is determined by the binding site molarity, we can use the binding site molarity to predict the CO₂ adsorption capacity of MOFs with strong binding sites at ambient conditions. Table 2 shows that the molality of strong binding site in IRMOF-74 series materials. The CO₂ adsorption capacity of these materials at ambient conditions, most of which haven't been reported by far, were estimated based on the values of binding site molality, as shown in Fig. 3. One can see that the CO₂ adsorption capacity of IRMOF-74s series materials significantly decreases with increasing size of organic linkers. This is due to the limit of the number of strong binding site as well as the increase of molecular weight per unit cell of these MOFs, as shown in Table 2. After adding ethylenediamine (en) and *N,N'*-dimethylethylenediamine (mmen) into the pores of IRMOF-74s, the CO₂ adsorption capacity of these materials is significantly reduced comparing to the original materials but some of them are still among the best performance materials in the area of low pressure CO₂

adsorption. The decrease can be attributed to the fact that the number of strong binding site per unit cell has not been changed but the molecular weight per unit cell has been significantly increased by adding en and mmen groups, as shown in Table 2.

The CO₂ adsorption capacity of tri(2-aminoethyl) or bis(3-amino-propyl) amine functionalized IRMOF-74s are estimated to be dramatically improved comparing to the original materials, as shown in Fig. 3. The enhancement in the CO₂ adsorption capacity is due to the fact that the number of strong binding site per unit cell is doubled after functionalization even if the molecular weight is increased (see Table 2). It should be noted that attaching amine groups on unsaturated open metal sites of MOFs may not only increase CO₂ adsorption capacity, but also reduce the effect of water vapor on CO₂ capture in flue gas. McDonald et al. [20] found that the water vapor adsorption was significantly reduced in mmen-Mg/DOBDC. Here, we predict that a higher CO₂ adsorption capacity would be obtained by attaching amine groups on IRMOF-74-III material comparing to mmen-Mg/DOBPDC, meanwhile, retaining the similar working capacity under water presence.

In conclusion, the CO₂ adsorption amount of MOFs with strong binding site at ambient conditions is determined by the binding site molarity (SM) in 1 to 1 ratio. Meanwhile, a good correlation between the value of strong binding site coverage and isosteric heat is found. Our results show that the SM is a good parameter for estimating the CO₂ adsorption capacity of MOFs, and the binding site coverage obtained using SM is useful to estimate the binding strength between CO₂ and MOFs. Further work will be performed to extend the SM parameter for CO₂ adsorption on zeolites which have countable number of cations. We are also interested in verifying this parameter using the adsorption data of different gases in MOFs with strong binding sites in the future.

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Notes

The authors declare no competing financial interest.

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Table 1. Molecular weight ($W_{u.c.}$) and number of strong binding sites (N_{site}) per unit cell as well as binding site molality ($N_{site}/W_{u.c.}$) of reported MOFs with extremely strong binding sites.

material	$W_{u.c.}$ (g/mol)	N_{site}	$N_{site}/W_{u.c.}$ (mmol/g)
Mg/DOBDC	2178	18	8.26
Co/DOBDC	2807	18	6.41
Ni/DOBDC	2803	18	6.42
Zn/DOBDC	2923	18	6.16
Mg/DOBPDC	3816	24	6.29
HKUST-1	9696	48	4.95
MOF-505	4086	18	4.41
bio-MOF-11	4032	16	3.97
bio-MOF-12	5424	16	2.95
bio-MOF-13	4720	16	3.39
bio-MOF-14	4832	16	3.31
en-Mg/DOBPDC	5256	24	4.57
mmen-Mg/DOBPDC	5928	24	4.05
mmen-Mn/DOBPDC	6672	24	3.60
mmen-Fe/DOBPDC	6796	24	3.58
mmen-Zn/DOBPDC	6912	24	3.47

Table 2. Molecular weight ($W_{u.c.}$) and number of strong binding sites (N_{site}) per unit cell as well as binding site molality ($N_{site}/W_{u.c.}$) of unreported MOFs with extremely strong binding sites.

material	$W_{u.c.}$ (g/mol)	N_{site}	$N_{site}/W_{u.c.}$ (mmol/g)
IRMOF-74-III	3798	18	4.74
IRMOF-74-IV	4734	18	3.80
IRMOF-74-V	5670	18	3.17
IRMOF-74-VI	6606	18	2.72
IRMOF-74-VII	8802	18	2.04
en-IRMOF-74-III	4878	18	3.69
en-IRMOF-74-IV	5814	18	3.10
en-IRMOF-74-V	6750	18	2.67
en-IRMOF-74-VI	7686	18	2.34
en-IRMOF-74-VII	9882	18	1.82
en-IRMOF-74-VIII	11754	18	1.53
en-IRMOF-74-IX	14886	18	1.21
mmen-IRMOF-74-III	5382	18	3.34
mmen-IRMOF-74-IV	6318	18	2.85
mmen-IRMOF-74-V	7254	18	2.48
mmen-IRMOF-74-VI	8190	18	2.20
mmen-IRMOF-74-VII	10386	18	1.73
mmen-IRMOF-74-VIII	12258	18	1.47
mmen-IRMOF-74-IX	15390	18	1.17
bis(3-amino-propyl)-IRMOF-74-III	6156	36	5.85

bis(3-amino-propyl)-IRMOF-74-IV	7092	36	5.08
bis(3-amino-propyl)-IRMOF-74-V	8028	36	4.48
bis(3-amino-propyl)-IRMOF-74-VI	8964	36	4.02
bis(3-amino-propyl)-IRMOF-74-VII	11160	36	3.23
bis(3-amino-propyl)-IRMOF-74-VIII	13032	36	2.76
bis(3-amino-propyl)-IRMOF-74-IX	16164	36	2.23
tri(2-aminoethyl)-IRMOF-74-III	6426	36	5.60
tri(2-aminoethyl)-IRMOF-74-IV	7362	36	4.89
tri(2-aminoethyl)-IRMOF-74-V	8298	36	4.34
tri(2-aminoethyl)-IRMOF-74-VI	9234	36	3.90
tri(2-aminoethyl)-IRMOF-74-VII	11430	36	3.15
tri(2-aminoethyl)-IRMOF-74-VII	13302	36	2.71
tri(2-aminoethyl)-IRMOF-74-VII	16434	36	2.21

Fig. 1. Comparison of binding site molality and experimental CO₂ uptake amount in MOFs with strong binding sites, including Zn/DOBDC [4], Co/DOBDC [14], Ni/DOBDC [15], Mg/DOBDC [13], Mg/DOBPDC [8], HKUST-1 [16], bio-MOF-11 [17], bio-MOF-12 [18], bio-MOF-13 [18], bio-MOF-14 [18], MOF-505 [19], en-Mg/DOBPDC [9], mmen-Mg/DOBPDC [8], mmen-Mn/DOBPDC (blue) [20], mmen-Fe/DOBPDC (purple) [20], mmen-Co/DOBPDC (green) [20] and mmen-Zn/DOBPDC [20] which are numbered from 1-17 respectively in the figure. The experimental data are obtained at 298 K and 1 bar.

Fig. 2. The relationship between isosteric heat of CO_2 adsorption on MOFs with strong binding sites and (a) site coverage or (b) CO_2 uptake amount at 1, 5 and 10 kPa, 298 K. The numbers from 1-6 in the figures mean Zn/DOBDC [4], Co/DOBDC [14], Ni/DOBDC [15], Mg/DOBDC [13], Mg/DOBPDC [8], mmen-Mg/DOBPDC [8] and en-Mg/DOBPDC [9] respectively.

Fig. 3. Predicted CO₂ adsorption amount in IRMOF-74s as well as their amine modified forms at ambient conditions. The experimental data of IRMOF-74-I (Mg/DOBDC) [13], IRMOF-74-II (Mg/DOBPDC) [8], en-IRMOF-74-II (en-Mg/DOBPDC) [9] and mmen-IRMOF-74-II (mmen-Mg/DOBPDC) [9] are also shown in open symbol.

Graphic Abstract

**CO₂ adsorption
capacity depends on
positions**