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Interpreting the CO₂ Adsorption on Functionalized Organic Group of IRMOF-1: A B3LYP Density Functional Theory based Study

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A B S T R A C T

Density Functional Theory (DFT) calculations techniques are used to study CO_2 adsorption in NH_2-, OH-, COOH-, Br- and Cl-functionalized IRMOF-1. Geometry optimization, density of states (DOS), and energy analysis were performed to investigate the adsorption phenomenon. The binding properties have been calculated and analyzed theoretically for pristine H_2BDC and $X-H_2BDC$ as well as their complex forms with CO_2 molecule in terms of binding energies, band structures, total density of states, and Mulliken charges. The finding showed larger interaction energy in COOH-H_2BDC and somewhat in OH-H_2BDC and NH_2-H_2BDC complexes compared to less interaction energies in Br-H_2BDC and Cl-H_2BDC complexes.

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1. INTRODUCTION

Global warming as a result of greenhouse gases emission has gotten across the board consideration. Regarding the extraordinary emission amount of CO_2 than other the greenhouse gases, it has the high contribution of CO_2 (more than 60%) to global warming [1]. Sources from which the removal of CO_2 is desirable include natural gas power plants and other sources of H_2 production [2], post-combustion flue gases [3] and transport vehicle emissions [4]. There are various CO_2 capture technologies such as physical absorption [5], chemical absorption [6-9], adsorption [10-15] and membrane technology [16-20]. Due to the numerous endeavors in the study of CO_2 capture in the past decade, nanoporous solids have been considered as the promising candidates for capable adsorption of gaseous carbon derivatives to limit the CO_2 emission [21].

One of the novel materials to reach this goal is metal organic framework (MOF) family due to their fascinating sorption properties [22-24], extremely high porosity [25], characterized by large surface areas and pore diameters

[26]. A main reason is that for most of MOF structures, the coordination sphere of the inorganic clusters is fully completed by the organic linker which hampers the activation of reactants [27].

One of the most important MOFs is $Zn_4O_{13}C_{24}H_{12}$ framework called as IRMOF-1, which was invented in 1999 [28]. This framework has potential applications for H_2 storage, CO_2 capture and catalysts [29]. The IRMOF-1 consists of Zn_4O nodes which are linked in terephthalate anions (1,4-BDC (benzene dicarboxylate)) groups to form a porous material (Figure 1(a)) [28]. The BDC ligands form angles of 45° with the cell axes, resulting in two different pores being present. The BDC can be found oriented in both directions, inward and outward, relative to the pores (Figure 1(b)). Pore size can be achieved by selecting appropriate dicarboxylic linkers of various lengths (IRMOF series). Sarmiento-Perez et al. [30] showed that the organic ligands have an important role in the CO_2 adsorption on IRMOF-1. Several strategies have been deployed in order to enhance CO_2-framework interactions in these new classes of porous frameworks. Among various approaches, organic

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ligand (main site for CO_2 adsorption) functionalization [29, 31-33] of MOFs has been shown to be a powerful route in enhancing the CO_2-framework interaction, and offers several advantages, such as chemical flexibility of possible ligands and functional groups and the high accessibility of the functional groups to the adsorbates.

In the current study, we perform a systematic strategy in the search for functionalized organic ligands (H_2BDC) with strong affinity for CO_2 using DFT calculations. In other word, we investigate in detail the role of each type of functional group on the organic ligand, i.e. -OH, -NH_2, -COOH, -Br, and -Cl, in the adsorption of CO_2 by IRMOF-1. For this purpose, in the first time, we examined the geometrical as well as the electronic structures of organic functionalized IRMOF-1 (OF-IRMOF-1) before and after interaction with CO_2, in order to compare and comprehend the relationship between their chemical structure and their related properties. Then, the best functional group for synthesis of OF-IRMOF-1, for CO_2 adsorption, will be introduced. We have accomplished first-standards calculations to determine the interaction behavior of the CO_2 with OF-IRMOF-1. It is well-known that DFT is ableto accurately treat various systems because of having the exchange-correlation property [34-36].

2. THEORITICAL METHOD

According to literature, adsorption of small molecules in IRMOF-1 occurs first in a site near the Zn cluster in the large pores (site A' in Figure 1(b)) [37-41]. Sarmiento-Perez et al. [30] introduced a similar site that is present in the smaller pore (site B' in Figure 1(b)) and presented three models containing; model A (whole structure), model B (only the inorganic unit) and model C (only the organic ligand). They showed that the site B' in Fig. 1b is main site for CO_2 adsorption and adsorption behavior in model C is better than model B. Then, they reported that the primary step in the abnormal CO_2 adsorption in IRMOF-1 (model A) is due to synergic and significant contributions from all the three models (A,B and C). Due to the inherent ability of the organic ligand to interaction with CO_2 and the ability to receive functional groups, the reinforcement of H_2BDC linker is reasonable and simple approach for increase the CO_2-framework interaction.
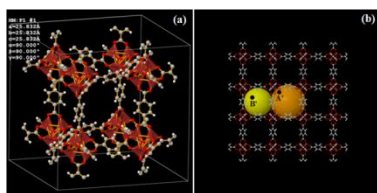
Figure 1. (a) 1 by 1 by 1 IRMOF-1 framework, and (b) the small and large pores of IRMOF-1 framework

As reported in the previous studies, calculation of the chemical properties of IRMOF-1 using a representative fragment is in good agreement with the experimental results [42-44]. In order to practical modelling of the IRMOF-1 structure via a DFT calculation, H_2BDC linker was separated from the large size of IRMOF-1 cell to reduce the calculation time and applied the modification by functionalizing various groups. Accordingly, in this paper, we considered the adsorption behavior of CO_2 molecule on the surface of pristine unit cell of IRMOF-1 and unit cell of the five linker (H_2BDC-X (X= NH_2, OH, COOH, Br, Cl). Geometry optimization, density of states (DOS), and energy analysis were performed to investigate the adsorption phenomenon using Gaussian 09 program package [45] with DFT at B3LYP/6-31G (d,p) functional/basis set. The temperature and pressure for all calculations were 298.15 K and 1.00 atm, respectively. The adsorption energy of X on H_2BDC is calculated by:

$$E_{ad} = E_{X-H_2BDC} - \left(E_{H_2BDC} + E_X\right) \tag{1}$$

where $E_{X-(H_2BDC)}$ is the total electronic energy of H_2BDC interacting with the X and E_{H_2BDC} is total energy of an pristine H_2BDC, and E_X is the total electronic energy of an pristine X. The interaction energy of CO_2 with pristine H_2BDC and H_2BDC-X is calculated by:

$$E_{ads(H_2BDC)} = E_{CO_2-H_2BDC} - \left(E_{H_2BDC} + E_{CO_2}\right) \tag{2}$$

$$E_{ads(Y)} = E_{CO_2-Y} - \left(E_Y + E_{CO_2}\right), \ Y = X - H_2BDC \tag{3}$$

where, $E_{ads(H_2BDC)}$ and $E_{ads(X-H_2BDC)}$ correspond to interaction energy of CO_2 with H_2BDC and X-H_2BDC, $E_{CO_2-H_2BDC}$ and $E_{CO_2-(X-H_2BDC)}$ are total electronic energies of H_2BDC and X-H_2BDC interacting with the CO_2, and E_{CO_2} is the total energy of an isolated CO_2.

All the mentioned energies of the equations related to equivalently relaxed minimum energy structures. Also chemical potential (μ), hardness (η), softness (S) and electrophilicity (ω) [46] are calculated by:

$$\mu = -\frac{(E_{HOMO} + E_{LUMO})}{2} \tag{4}$$

$$\eta = \frac{(E_{LUMO})}{2} - E_{HOMO} \tag{5}$$

$$S = \frac{\eta}{2} \tag{6}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{7}$$

where, E_{HOMO} and E_{LUMO} are the energies of HOMO and LUMO, respectively. The charge transferring between CO_2 and the surface of both H_2BDC and X-H_2BDC is calculated by Mulliken charge analysis [47].

3. RESULTS AND DISCUSSION

3. 1. Optimized Structure Geometries of isolated pristine H_2BDC, $X-H_2BDC$ and their interaction with CO_2 was optimized at B3LYP functional at 6-31G(d,p) basis set to allow them to be relaxed. Figure 2 shows that the optimized unit cell of the five linker design. There are two possible configurations for CO_2 (O end and C end) to be optimized.

The interaction of CO_2 molecules with H_2BDC and $X-H_2BDC$ through different routes has been studied using the aforementioned way and let them to be fully relaxed. In this manuscript we discuss the strongest adsorption site and use the more stable configurations to further studying (Figure 3). The values of adsorption energy as well as some important parameters for all relaxed systems are listed in Table 1. The geometric parameters of H_2BDC agree well with the already reported data [48]. According to obtained results, can conclude that the highest and lowest adsorption attribute to the $COOH-H_2BDC$ and $Br-H_2BDC$ respectively. According to Figure 3, polar functional groups such as COOH, NH_2 and OH introduce new specific CO_2 adsorption sites at the H_2BDC surface. Given that, after adsorption of CO_2 on pristine H_2BDC and $X-H_2BDC$ (X: COOH, NH_2, OH), the location of CO_2 was approximately similar for each of the three adsorbent.

In other word, these functional groups preserve the accessibility of the adsorption sites existing in the pristine H_2BDC. This has a beneficial impact on CO_2 uptake. By contrast, the Br and Cl functional groups did not enhance the number of adsorption sites, and partially hindered access to pristine H_2BDC adsorption sites (Figure 3e and f). Accordingly, because CO_2 adsorption in two locations

of adsorption (pristine H_2BDC and polar functional groups), we distinguish between polar functional groups (COOH, NH_2 and OH) and non-polar functional groups (Br and Cl) for future investigation.

Zero-coverage CO_2 enthalpies of adsorptions (E_{ads}) are lower (more negative) in $X-H_2BDC$ (X= COOH, NH_2 and OH), compared to the pristine H_2BDC indicating stronger CO_2-framework interactions in the polar functionalized materials (quite the contrary of $Br-H_2BDC$ and $Cl-H_2BDC$) (Table 1).
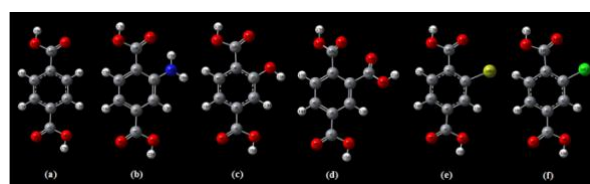
Figure 2. (a) Pristine H_2BDC and (b-f) optimized-modified $X-H_2BDC$ ligand (X=-NH_2, -OH, -COOH, -Br, and -Cl)
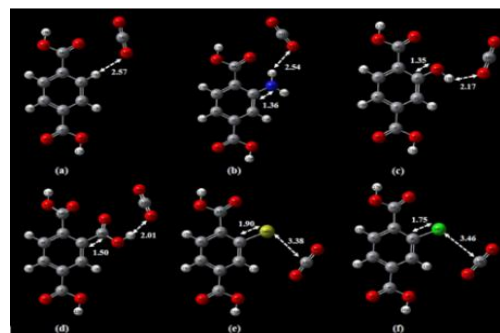
Figure 3. (a) Relaxed configuration of CO_2-H_2BDC and (b-f) CO_2-X-H_2BDC

TABLE 1. Calculated parameters for all systems

System	d_e [a] (Å)	$Q^O_{Mulliken}$ (e)	$Q^C_{Mulliken}$ (e)	E_{HOMO} (eV)	E_{FL} (eV)	E_{LUMO} (eV)	E_g (eV)	μ_D (Debey)	Total Energy (a.u.)	E_{ads} (kJ/mol)
CO_2	-	-0.720[b]	0.719[b]	-10.07	-4.63	0.81	10.88	0.0000	-188.5809	-
Pristine H_2BDC	-	-	-	-7.38	-4.75	-2.12	5.26	0.0012	-609.4108	-
NH_2-H_2BDC	1.36	-	-	-5.80	-3.84	-1.88	3.92	2.0489	-664.7767	-
$OH-H_2BDC$	1.35	-	-	-6.61	-4.34	-2.06	4.56	1.7253	-684.6239	-
$COOH-H_2BDC$	1.50	-	-	-7.41	-4.81	-2.21	5.20	1.1217	-797.9722	-
$Br-H_2BDC$	1.90	-	-	-7.00	-4.67	-2.35	4.65	1.1825	-3180.5034	-
$Cl-H_2BDC$	1.75	-	-	-7.19	-4.77	-2.36	4.83	1.3860	-1068.9933	-
CO_2-H_2BDC	2.57	-0.742	0.742	-7.41	-4.79	-2.18	5.23	0.2563	-797.9963	-12.0750
$CO_2-NH_2-H_2BDC$	2.54	-0.749	0.746	-5.68	-3.86	-1.92	3.89	1.8734	-853.3625	-12.8625
CO_2-OH-H_2BDC	2.17	-0.732	0.750	-6.63	-4.32	-2.01	4.62	1.8087	-873.2096	-12.6000
$CO_2-COOH-H_2BDC$	2.01	-0.750	0.759	-7.43	-4.82	-2.22	5.21	0.9115	-986.5616	-22.3125
CO_2-Br-H_2BDC	3.38	-0.730	0.733	-7.06	-4.71	-2.36	4.70	1.2562	-3369.0882	-10.2375
CO_2-Cl-H_2BDC	3.46	-0.725	0.734	-7.22	-4.77	-2.33	4.89	1.3746	-1257.5765	-6.0375

[a]The distance of X to H_2BDC (for X adsorption) and the distance of CO_2 to X (for CO_2 adsorption).
[b]Mulliken charge for free optimized CO_2

The strong local interactions of CO_2 with the polar functional groups include the CO_2 quadrupole-lone pair polar interactions with the NH_2, OH and COOH groups, where a strong electrostatic potential stabilizes the CO_2 quadrupole at the adsorption site. The basic amino groups (NH_2) have a high affinity toward acidic CO_2, mainly through the interaction with the lone electron pair on nitrogen. Also, hydrogen bond-like interactions between O (CO_2) and acidic hydrogen in the COOH and OH groups are important, are responsible for a strong polarization of the CO_2 in the main adsorption sites. Also the long distance for Br-H_2BDC and Cl-H_2BDC shows the interaction is very weak and the adsorption mostly happened because of the van der Waals interaction between CO_2 and X-H_2BDC (X: Br and Cl).

3. 2. Mulliken Charge Analysis b   Since CO_2 is known as a Lewis acid which tends to gain electrons in reactions, the CO_2 adsorption change the electronic properties of H_2BDC and X-H_2BDC via charge transfering. Because of positive carbon center and negative oxygen ends of the CO_2 molecule, an electron donation from C atom and electron back-donation from O atoms, occurs (donation/back-donation mechanism). The Mulliken electron charges distribution of C and O atom before and after interaction with the H_2BDC and X-H_2BDC depicted in Table 1. The obtained results showed that the interaction of CO_2 with H_2BDC and X-H_2BDC is due to the electrons transferring from C and O atom to H_2BDC and X-H_2BDC.

3. 3. Orbital Analysis   To understand the electronic properties of CO_2 during adsorption, the density of states (DOS) as the electron density of HOMO-LUMO was calculated for pristine H_2BDC and also X-H_2BDC as well as their complex forms with CO_2 molecule and the data are listed in Table 1. Quantum mechanically, the interaction between two reactants takes place for the reason that of interaction of frontier molecular orbitals [49]. HOMO has the aptitude to contribute electrons, while LUMO has the aptitude detract electron. However, if a molecule has high HOMO energy, then it will be more unstable and vice versa because of more reactivity [50, 51]. After functionalization of H_2BDC and adsorption of CO_2 molecule on the surface of pristine H_2BDC and X- H_2BDC, some changes occur in its HOMO and LUMO energies. According to results, among various functional groups the COOH-H_2BDC has high HOMO energy and more unstable structure, because of more reactivity. The HOMO-LUMO energy gap (E_g) is one of the key parameter to recognize the stability as well as conductivity of resulted adsorptions. Higher E_g (larger distance between the HOMO and LUMO) which results more stability and less conductivity of resulted complex. The band gaps of the pristine H_2BDC and X-

H_2BDC as well as complex form of different H_2BDC(-X)-CO_2 are calculated and are listed in Table 1. According to Table 1, upon functionalization of H_2BDC with X (X: NH_2, OH, COOH, Br and Cl), the energy gap decreased which corresponds to higher conductivity of X-H_2BDC. The calculated band gaps showed not much different between the band gaps of the pristine H_2BDC and X-H_2BDC (X: NH_2, OH, COOH, Br and Cl) after and before of CO_2 adsorption. For X-H_2BDC, the calculations revealed the highest E_g value (5.21 eV) for interacted COOH-H_2BDC with CO_2, which again correlates well with the high adsorption energies of CO_2 in COOH-H_2BDC compared to X-H_2BDC.

Dipole moment (μD) is another key factor in orbital analysis. The amounts of the size and structures of the dipole moment (μD) for CO_2 on the H_2BDC and X-H_2BDC molecules are listed in Table 1. The dipole moment relates to a particular property of a molecule that considers data in the case electronic and geometrical properties [52]. The dipole moment for CO_2 is 0.0 Debye and related to their intrinsic symmetrical shapes. Also small quantities of μD value for pristine H_2BDC represent a relatively asymmetric structure. From comparing the dipole moments of the H_2BDC(-X) with ones after the CO_2 is adsorbed, it is clear that, the values of dipole moments do not change significantly which is a confirmation for physical sorption.

To understand the electronic properties of functional groups (X: OH, NH_2, COOH, Br and Cl) during adsorption, the density of states (DOS) was also calculated for isolated and complex (with CO_2) form of pristine H_2BDC as well as X-H_2BDC near the Fermi level (E_{FL}). After comparing the DOS of isolated H_2BDC and X-H_2BDC to that of their interacted forms, it was found that some change evidence of hybridization (shifting HOMO-LUMO) in the case of X-H_2BDC systems as listed in Table 1.

4. CONCLUTIONS

As a conclusion, the introduction of additional specific adsorption sites for CO_2, via polar functional groups such as -OH, -NH_2 and -COOH, enhances the affinity for CO_2 resulting in more negative molar enthalpies of adsorption. The principal intermolecular forces involved are hydrogen bonding and polar lone pair CO_2 quadrupole interactions. CO_2 can also become appreciably polarized in the vicinity of these groups. By contrast, the -Br and -Cl groups did not enhance the number of adsorption sites, and partially hindered access to IRMOF-1 framework adsorption sites. Our research showed that -COOH and -OH containing materials are worthy of further investigation, with COOH-IRMOF-1

and OH-IRMOF-1 outperforming the other materials in CO_2 adsorption.

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Interpreting the CO$_2$ Adsorption on Functionalized Organic Group of IRMOF-1: A B3LYP Density Functional Theory based Study

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چکیده

تکنیک تئوری نظریه چگال به منظور مطالعه جذب CO$_2$ بر روی IRMOF-1های عامل‌دار شده به وسیله Br، COOH، OH، NH$_2$ و Cl مورد استفاده قرار گرفت. برای بررسی پدیده جذب، بهینه سازی هندسه، چگالی حالات و آنالیز انرژی مورد استفاده قرار گرفت. خواص جذبی برای H$_2$BDC و X-H$_2$BDC اولیه و همچنین فرم‌های کمپلکس آن با مولکول CO$_2$ بر اساس انرژی‌های اتصال، ساختارهای باند، چگالی حالات کلی و بار Mulliken محاسبه شده و مورد تجزیه و تحلیل قرار گرفته است. یافته‌ها نشان می‌دهد که انرژی جذبی در COOH-H$_2$BDC و همچنین تا حدودی در -OH H$_2$BDC و NH$_2$-H$_2$BDC در مقایسه با انرژی‌های جذبی در Br- H$_2$BDC وCl-H$_2$BDC بیشتر است.

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