

Adsorptive desulfurization with metal-organic frameworks: A density functional theory investigation



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ABSTRACT

The contribution of each fragment of metal-organic frameworks (MOFs) to the adsorption of sulfur compounds were investigated using density functional theory (DFT). The involved sulfur compounds are dimethyl sulfide (CH_3SCH_3), ethyl mercaptan ($\text{CH}_3\text{CH}_2\text{SH}$) and hydrogen sulfide (H_2S). MOFs with different organic ligands (NH_2 -BDC, BDC and NDC), metal centers structures (M, M-M and M_3O) and metal ions (Zn, Cu and Fe) were used to study their effects on sulfur species adsorption. The results revealed that, MOFs with coordinatively unsaturated sites (CUS) have the strongest binding strength with sulfur compounds, MOFs with NH_2 -BDC substituent group ligand comes second, followed by that with saturated metal center, and the organic ligands without substituent group has the weakest adsorption strength. Moreover, it was also found that, among different metal ions (Fe, Zn and Cu), MOFs with unsaturated Fe has the strongest adsorption strength for sulfur compounds. These results are consistent with our previous experimental observations, and therefore provide insights on the better design of MOFs for desulfurization application.

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1. Introduction

The utilization of fossil resource, such as petroleum, coal and natural gas, produce sulfur containing compounds, e.g. hydrogen sulfide, sulfur dioxide, mercaptan, thioether, thiophene etc. These sulfur species are toxic to human health and environment as well as the catalyst in the gas treatment system, making desulfurization process necessary and very important.

In fact, various desulfurization technics have been developed in the past decades, such as hydrodesulfurization, oxidation and adsorptive desulfurization (ADS) [1–5]. Among these sulfur removal technics, ADS method is very popular. It has a mild operating condition, low cost, less harmful side products and facile regeneration. The ADS performance was determined by the adsorbent, which can be effected by its adsorption capacity, efficiency, durability and regenerability [6].

In the past few years, metal-organic frameworks (MOFs), due to its large surface area, tunable pore size, morphology and functional pore surface, have been widely used in hydrogen storage, gas separation and catalysis [7–12]. It is also a promising adsorbent for

sulfur removal. For example, Katie A. Cychosz et al. [13] studied the performance of MOFs for organosulfur compounds dibenzothiophene and 4,6-dimethyldibenzothiophene removal from model diesel fuel. They found that, MOFs have better fuel hydrodesulfurization performance than that of zeolites and activated carbon.

Sabine Achmann et al. [14] reported that MOF-199 has a very high efficiency for sulfur removal from low-sulfur model oils and fuels, it shows both the highest sorption rates and the fastest sorption characteristics. It was proposed that the smaller pores in MOF-199 provide a better stabilization of the Cu-adsorbed sulfur compound by Van-der-Waals forces, and therefore leads to its outstanding sulfur removal performance. Silvia Bordiga et al. [15] investigated the adsorption behaviors of H_2S on Ni-MOF-74. When compared with other MOFs for H_2S adsorption, Ni-MOF-74 shows the highest uptake and high H_2S adsorption enthalpy while maintaining its original structure and porosity. Ben Van de Voorde et al. [16] performed DFT study on the S-heterocyclic compounds adsorption behavior on MOF-74 series (Ni, Co, Mg, Cu, and Zn). In that study, it was reported that the metal ion has significant effect on the MOFs adsorption capacity and affinity for S-heterocyclic compounds, and it was predicted that Ni-MOF-74 has the best desulfurization performance. Loming Hamon et al. [17] studied the performance of MIL-series, e.g. MIL-53(Al, Cr, and Fe), MIL-47, MIL-100(Cr), and MIL-101(Cr), for H_2S adsorption at 303 K. It proposed that the $-\text{OH}$ groups in MIL-53 could facilitate H_2S adsorption. In

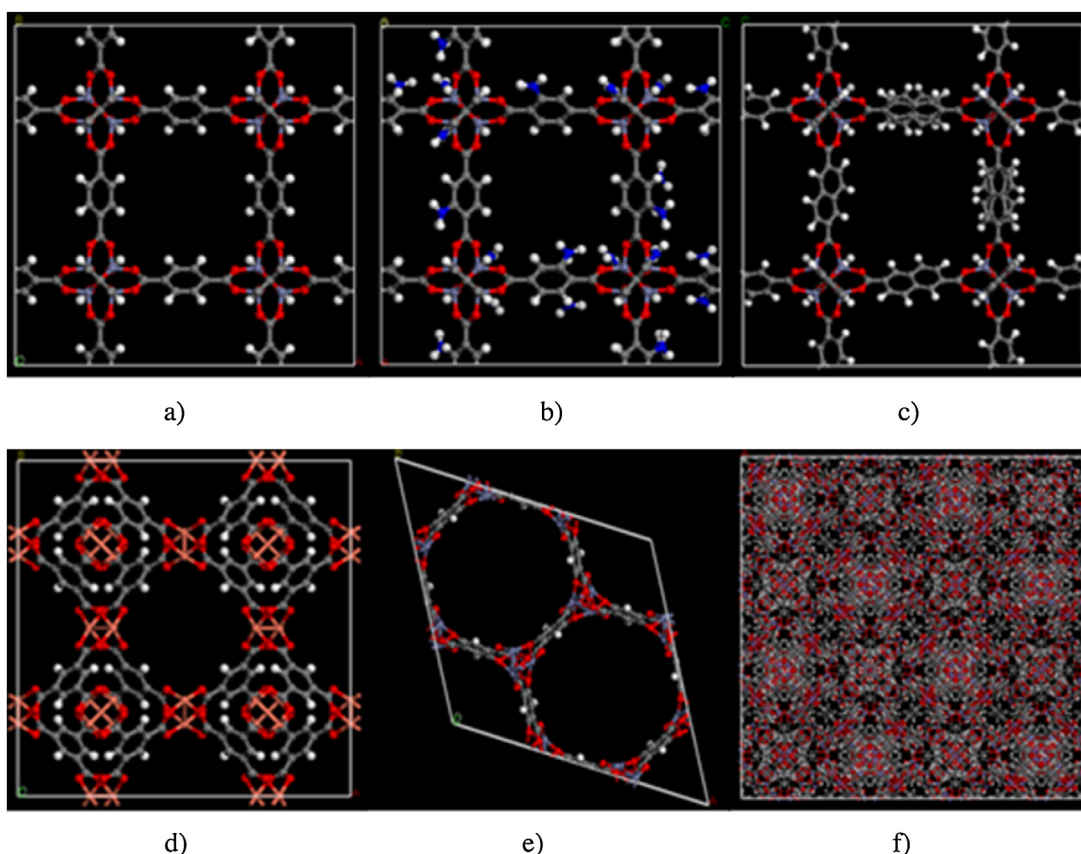
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Table 1

The characteristics of the materials IRMOF-1(Zn), IRMOF-3(Zn), IRMOF-8(Zn), MOF-199(Cu), MOF-74(Zn), and MIL-101(Fe).

material	Space group	Pore shape	Topology	$d_{\text{pore}}/\text{nm}$
IRMOF-1(Zn)	FM-3M	Cubic	PCU ^a	1.09/1.43
IRMOF-3(Zn)	FM-3M	Cubic	PCU	1.0/1.5
IRMOF-8(Zn)	FM-3M	Cubic	PCU	1.25/1.71
MOF-199(Cu)	FM-3M	pocket/channel	TBO ^b	0.5/0.9
MOF-74(Zn)	R-3	honeycomblike	ETB ^c	1.2
MIL-101(Fe)	FD-3M	–	MTN ^d	2.9/3.4

^a PCU: primitive cubic lattice net.^b TBO: three-dimensional twisted boracite framework.^c ETB: edge-transitive binodal structures.^d MTN: mobil thirty-nine.**Fig. 1.** Material structures of (a) IRMOF-1(Zn), (b) IRMOF-3(Zn), (c) IRMOF-8(Zn), (d) MOF-199(Cu), (e) MOF-74(Zn), (f) MIL-101(Cr) from the Cambridge Crystallographic Data Centre (CCDC).

another study, Loming Hamon et al. [18] reported that the –OH groups in MOFs can act as proton donors, and therefore enhances the adsorption of H_2S .

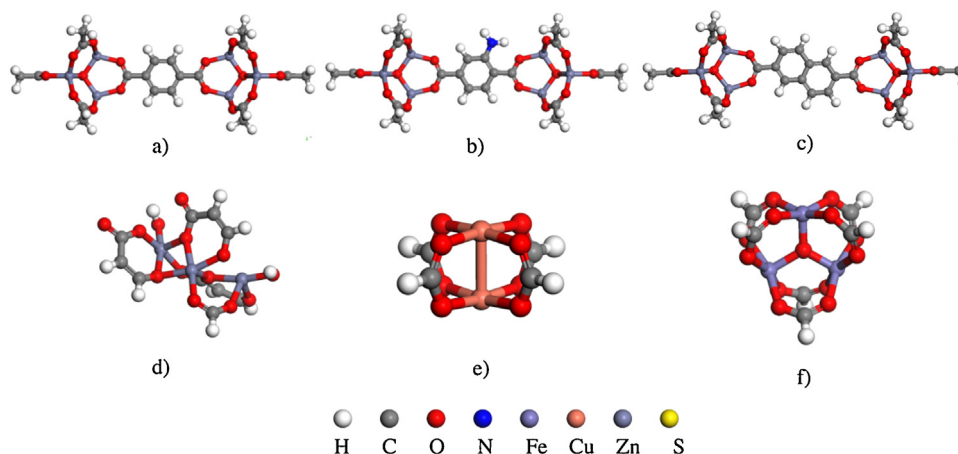
The previous studies indicate that the performance of MOFs can be affected by many factors, e.g. substituent group, metal ions and CUS, etc. Moreover, most studies have been focused on thiophene compounds removal from liquid fuel. To the authors' best knowledge, the desulfurization performance of MOFs for H_2S , especially mercaptan and thioether compounds are rarely reported. Therefore, in the present study, a systematic DFT study on the effect of MOFs metal centers (including structures and metal ions) and organic ligands (with or without substituent group) on H_2S , $\text{CH}_3\text{CH}_2\text{SH}$ and CH_3SCH_3 adsorption was performed. By comparing MOFs desulfurization performance predicted by DFT calculations with experimental results, the present study provides insights on the better understanding of MOFs' desulfurization mechanism.

2. Computational method

All the theoretical calculations were performed using the DFT method with DMol³ [19] program in Materials Studio 5.5 software. The generalized gradient approximation (GGA) [20] with Perdew-Burke-Ernzerhof (PBE) parametrization was used to describe the exchange-correlation interaction. Density functional semi-core pseudopotentials (DSPP) [21] fitted to all electron relativistic DFT results and a double numerical plus (DNP) polarization basis set was employed. A real-space orbital global cutoff of 4.4 Å was applied and the convergence threshold parameters for the optimization were set to 2×10^{-5} (energy), 4×10^{-3} (gradient), and 5×10^{-3} (displacement), respectively. Usually, the majority of standard DFT methods perform very well for geometric optimizations of MOFs. But, they have limitation to accurately describe the long-range electron correlations [22]. To overcome this shortcoming, empirically corrected functional DFT-D2 [23] was used for calculation in this work. More-

Table 2Binding energies of guest molecules across small and large cage of BDC, NH₂-BDC, and NDC.

Adsorbate	Adsorption site	BE (KJ/mol)		
		BDC	NH ₂ -BDC	NDC
H ₂ S	S	−12.30	−33.30	−16.98
	B	−13.54	−28.36	−16.16
CH ₃ CH ₂ SH	S	−16.26	−31.76	−23.84
	B	−21.25	−36.72	−25.29
CH ₃ SCH ₃	S	−16.78	−28.24	−22.29
	B	−19.59	−38.37	−23.69

**Fig. 2.** The structures for (a) BDC in IRMOF-1 (b) NH₂-BDC in IRMOF-3 (c) NDC in IRMOF-8 (d) M in MOF-74 (e) M-M in MOF-199 (f) M₃O in MIL-101.

over, the M06-L functional (with 6–311++g** basis set, including BSSE) which shows more accurate results than MP2 [24] in MOFs system, was employed to verify the reliability of DFT-D2 on two selected clusters for adsorbing three sulfur compounds mentioned in this work. The resulted binding energies from DFT-D2 are very close to that from M06-L (SI Table S1) indicating that the functional DFT-D2 is desirable for this system.

The binding energy (BE) between the adsorbates and MOFs was calculated as follows:

$$BE = E_{\text{MOFs/adsorbates}} - E_{\text{MOFs}} - E_{\text{adsorbates}}$$

where $E_{\text{MOFs/adsorbates}}$ is the total energy of the MOFs/adsorbates system, while E_{MOFs} and $E_{\text{adsorbates}}$ are the energy of MOF cluster and the adsorbates, respectively. A negative value of BE suggests an exothermic adsorption of the adsorbate over MOFs.

3. MOFs model complexes

In the present study, a series of IRMOF crystalline, e.g. IRMOF-1, IRMOF-3, IRMOF-8, were chosen to discuss the effect of ligands on sulfur compounds adsorption. These IRMOFs have a similar PCU topology: Zn₄O was connected with six organic linkers and forms body-centered cubic structure. IRMOF-1 contains 1, 4-benzenedicarboxylate (BDC) as the linker. For IRMOF-3 and IRMOF-8, the linkers are 2-amino-1, 4-benzenedicarboxylate (NH₂-BDC) and 2, 6-naphthalenedicarboxylate (NDC), respectively. Structural parameters [25,29] of these IRMOFs were listed in Table 1.

Three types of MOFs, named as MOF-199, MOF-74 and MIL-101, were chosen to investigate the effect of metal centers on sulfur compounds capture. They all have CUS but different structures (M-M, M and M₃O). Based on their different metal centers, they were referred as Cu-MOF-199, Zn-MOF-74 and Fe-MIL-101. Cu-MOF-199 has a face-centered-cubic crystalline structure, and it was characterized by the paddle-wheel unit assembled from one Cu dimer

and four BTC linkers [26]. Cu-MOF-199 have two types of cages: tetrahedron side pockets (about 5 Å in diameter) and the large square-shaped channels (9 × 9 Å) [27]. Zn-MOF-74 is centered by Zn ion, and it has a honeycomblake pore structure with a high concentration of open metal sites. Fe-MIL-101 is assembled from Fe₃O trimers and 1, 4-benzenedicarboxylic acids through corner-sharing super tetrahedral structure. Fe-MIL-101 contains both small and large cages with a diameter of 29 Å and 34 Å, respectively. The small cages was connected through pentagonal microporous windows with a 12 Å aperture, whereas the large cages were accessible through both hexagonal and pentagonal windows of 14.7 × 16 Å² aperture [28]. Fig. 1 shows the structure of these MOFs, and the corresponding characteristics [26–29] are presented in Table 1.

In the present study, the MOFs model clusters were cleaved from the matrix of each MOF and the dangling bonds were saturated by appropriate groups [22], e.g. CH₃ or H. Fig. 2(a–c) show the clusters of IRMOFs ligands saturated with methyl group [30]. Fig. 2(d–f) are the metal centers that were saturated with hydrogen atoms. The electronic states of the clusters with open-shell configurations (contain Fe and Cu) were shown in Table S2 of SI. The ones with Zn are all singlet.

4. Results and discussion

4.1. Sulfur compounds adsorption on MOFs organic ligands

The different orientations of the organic ligand plane in IRMOF result in two different sized pores [31]. These pores are the absorbing site in MOFs. For example, in IRMOF-1, the large pore has a diameter of 14.3 Å, in which the organic ligand is parallel to it; the small pore has a diameter of 10.9 Å and its ligand is vertical to it. The corresponding absorbing sites in the big and small pores are referred as B-site and S-site, respectively. The adsorption of H₂S, CH₃SCH₃, and CH₃CH₂SH at both B-site and S-site of different ligands of IRMOFs, e.g. BDC, NH₂-BDC, and NDC were studied.

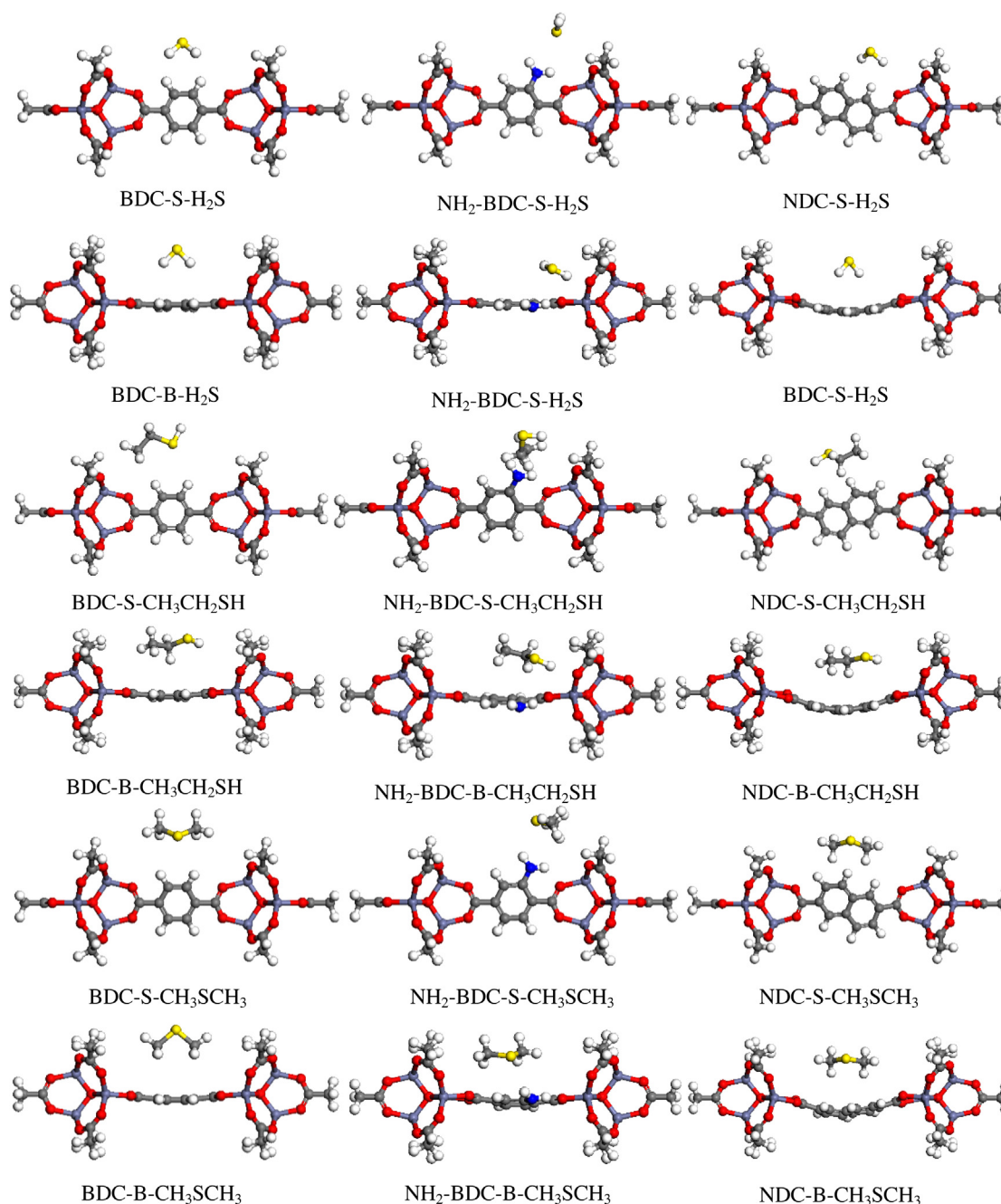


Fig. 3. The optimized geometries of ligand- adsorption site-sulfide compound complex (-S- means small cage; -B- mean large cage).

Fig. 3 shows the most stable adsorption configurations for ligands-sulfur compounds. Their BEs were listed in Table 2. The results show that the sulfur compounds adsorbed on NH₂-BDC has the largest binding energy at both S and B sites, followed by NDC and BDC. This indicates that, as compared with NDC and BDC ligands, sulfur compounds molecules prefer to adsorb over NH₂-BDC.

Fig. 4 shows the highest occupied molecular orbitals (HOMOs) on BDC, NH₂-BDC, and NDC ligands. It can be seen that, the electron densities in NH₂-BDC, especially the *ortho*- and *para*-region of the amino-group, are much higher than that in BDC. The resulted high polarity in the ligand supposed to be beneficial to the adsorption of sulfur compound through the enhanced interaction with molecular orbitals of sulfur [32]. Moreover, Fig. 4 also shows that the HOMOs of NDC reveals higher electron density over the linker ring as compared with that in BDC, which also provide an explanation

Table 3

LUMO-HOMO gap of BDC, NH₂-BDC and NDC. The fermi energy is located at 0 eV.

Adsorption site	LUMO/Ha	HOMO/Ha	LUMO-HOMO Gap/eV
BDC	-0.1036	-0.2336	3.537
NH ₂ -BDC	-0.0911	-0.1848	2.550
NDC	-0.1022	-0.2092	2.912

for the stronger binding energies for NDC-sulfur compounds than BDC (Table 2).

To provide further evaluation of the ligands activities, the LUMO-HOMO gaps, for BDC, NH₂-BDC, and NDC were also calculated (Table 3). Small LUMO-HOMO gap implies high chemical activity [33]. The result shows that the gap of NH₂-BDC (2.550 eV) is smaller than that of NDC (2.912 eV) and BDC (3.537 eV). This

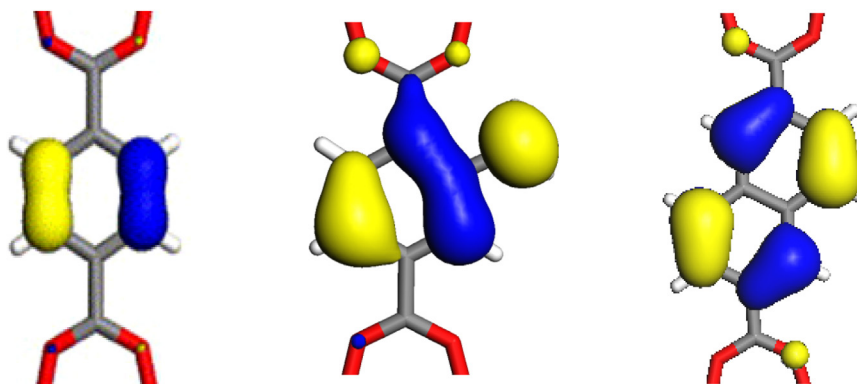
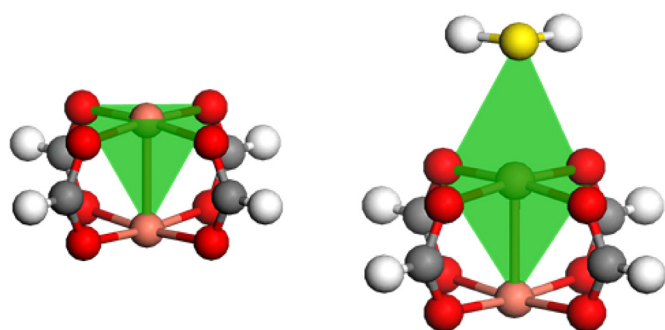


Fig. 4. HOMO of organic ligands of IRMOFs: BDC, $\text{NH}_2\text{-BDC}$, and NDC.



a) Square pyramidal

b) Octahedral

Fig. 5. Before and after adsorbing H_2S over CUS of MOF-199.

observation is also consistent with that binding energies reported in Table 2.

It should be noted that the observed binding strength between sulfur compounds and the organic ligands is relatively weak (> -50 kJ/mol). Therefore, the adsorption of sulfur compounds over these ligands can be considered as physical adsorption [34]. Furthermore, it was found that generally the adsorption strength of CH_3SCH_3 and $\text{CH}_3\text{CH}_2\text{SH}$ is stronger than H_2S . However, when sulfur compounds were adsorbed on the S-site of $\text{NH}_2\text{-BDC}$, the BEs of H_2S is stronger than that of CH_3SCH_3 and $\text{CH}_3\text{CH}_2\text{SH}$, shown in Table 2. This indicates the trend of acid-base interaction between amino-group and H_2S .

4.2. The adsorption of sulfur compounds on metal centers with CUS

The CUS in MOFs is usually obtained by desolvation of the material, where the solvent molecules in the coordination sphere of the metal center can be removed in *vacuo*. It was reported that these CUS facilitate guest molecules adsorption. It raises the adsorption enthalpy and therefore enhances gases storage density [35]. When a guest molecule is adsorbed on CUS, configuration transition occurs. For example, Fig. 5 shows the configuration transition of CUS in MOF-199 before and after H_2S adsorption. The bare MOF-199 framework has a quasi-square-pyramidal symmetry, and the metal atom is five-fold-coordinated. It provides exposed metallic Lewis acid sites on metal center. After H_2S adsorption on the metal site, the metal coordination geometry was transformed from square-pyramidal to octahedral, as shown in Fig. 5. The same configuration transition also occurs in MOF-74 and MIL-101 when adsorbing H_2S , as well as CH_3SCH_3 and $\text{CH}_3\text{CH}_2\text{SH}$.

Fig. 6 shows the most stable adsorption configurations for sulfur compounds adsorption over MOF-199, MOF-74 and MIL-101 with various metal ions (Fe, Cu and Zn) and structures of metal centers (M-M, M and M_3O). The corresponding binding energies were also presented this figure. The results show that, for H_2S adsorption on the M-MOF-199, Fe-Fe has the strongest binding energy (-118.6 kJ/mol), followed by Zn-Zn (-94.3 kJ/mol) and Cu-Cu (-51.8 kJ/mol). Similar results were observed for H_2S adsorption on M-MOF-74, the binding energies for Fe, Cu and Zn were calculated to be -126.2 kJ/mol, -66.1 kJ/mol and -64.8 kJ/mol, respectively. The same is true on MIL-101, but its adsorption capability is less than M-MOF-199 and M-MOF-74. These results indicate that Fe ion based MOFs can be good absorbent for H_2S removal.

$\text{CH}_3\text{CH}_2\text{SH}$ and CH_3SCH_3 adsorption over CUS of MOF-199, MOF-74 and MIL-101 were also investigated (Fig. 6). In the case of $\text{CH}_3\text{CH}_2\text{SH}$ and CH_3SCH_3 adsorption, similar results were obtained in terms of their BEs, as revealed in H_2S adsorption. The binding capability of sulfur compounds over the same CUS of MOFs follows the order of $\text{CH}_3\text{SCH}_3 > \text{CH}_3\text{CH}_2\text{SH} > \text{H}_2\text{S}$. This might result from their different polarities. The dipole moment for CH_3SCH_3 is 1.40 D, it is slightly larger than that of $\text{CH}_3\text{CH}_2\text{SH}$ (1.39 D), and H_2S has the smallest dipole moment (1.1 D) [36]. This is consistent with their polarities tendency.

Mulliken population analysis was also conducted to investigate the charge transfer process between sulfur compounds and metal centers. As shown in Fig. 6, $q_{\text{S-tra}}$ is the transferred Mulliken charge of the sulfur species; $q_{\text{M-tra}}$ is the transferred Mulliken charges of the metal atom which is nearest to sulfide atom. The analysis shows that the adsorbing metal atoms are all negatively charged (0.089–0.407 e), indicating that electrons were transferred from S to metal substrate. Meanwhile, it was found that the more electrons transferred from S to metal atom, the stronger the binding energy between sulfur compounds and metal site.

4.3. Adsorption of sulfur compounds on MOFs

In the above two sections, the effect of ligands and coordination unsaturation metal centers on sulfur adsorption were investigated using a series of IRMOFs and other three MOFs with CUS, respectively. However, sulfur compounds adsorption on complete MOFs with both ligand and metal center is missing. To make a clear understanding of how sulfur compounds adsorb on each fragment of MOFs. S-compounds adsorption on the metal center (Zn_4O) of IRMOFs and organic ligands of MOF-199, MOF-74 and MIL-101 were studied in this section.

The results in Table 4 show that the BEs of sulfur compounds on these three organic ligands are ranged from -22.51 kJ/mol to -8.52 kJ/mol, whereas that on saturated metal center Zn_4O are less

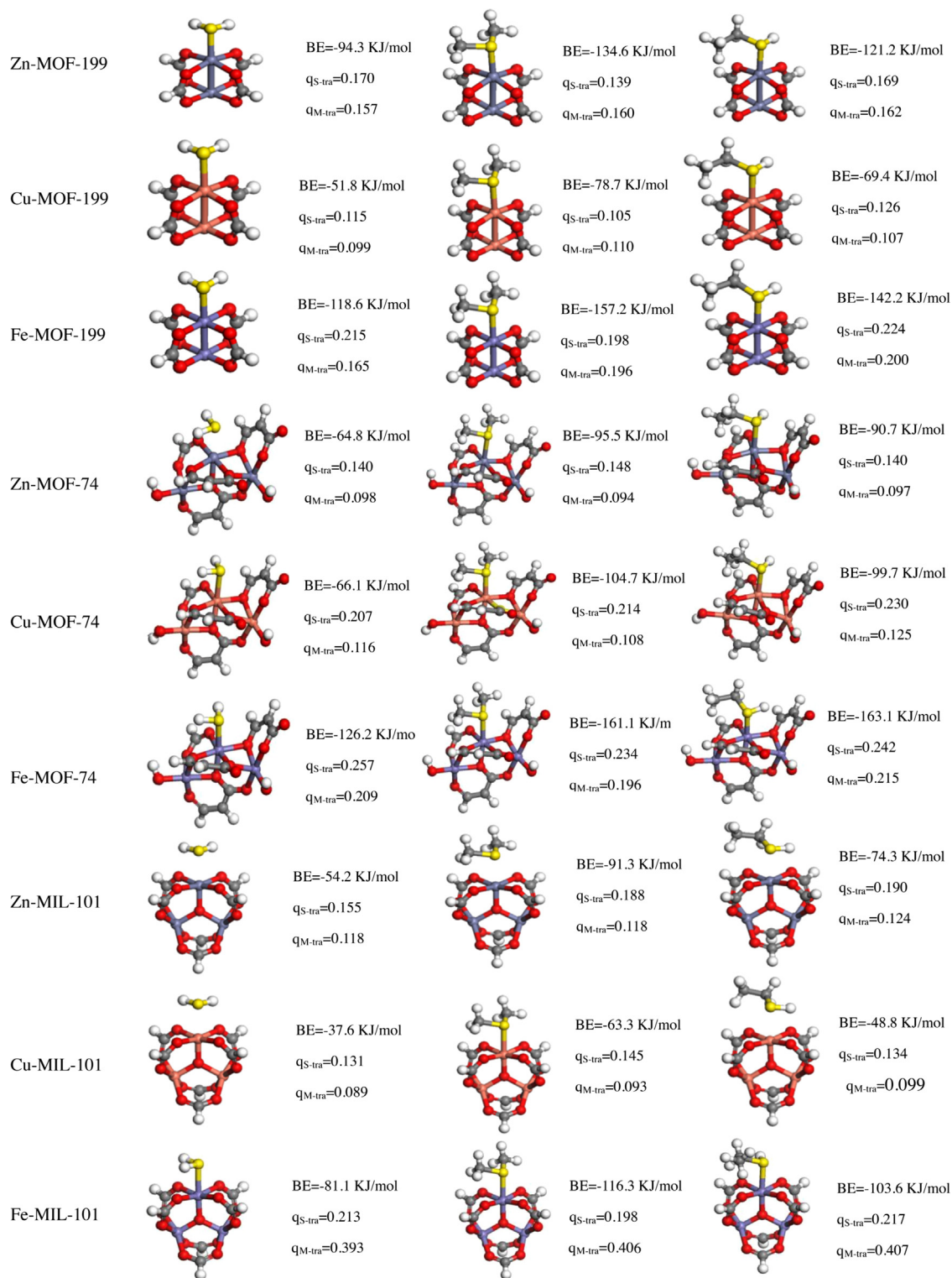


Fig. 6. Adsorption energy and Mulliken charge transfer value of the most stable structures for adsorbing S-compounds over CUS.

than -27.1 kJ/mol. Combined with results in Table 2 and Fig. 6, it can be seen that the adsorption of sulfur compounds on organic ligands except NH_2 -BDC are all weaker than that on metal centers, regardless of the existence of open metal sites. Meanwhile, it was also found that, metal centers with CUS have distinct advantage over that without CUS in adsorbing sulfur compounds. For example, H_2S adsorption on the metal site (Cu-Cu) of Cu-MOF-199 has a binding energy of -51.8 kJ/mol, whereas that on Zn_4O of IRMOF

is -27.1 kJ/mol. In summary, MOFs with unsaturated metal center was found have the strongest adsorption strength, NH_2 -BDC comes second, followed by saturated metal center, and the organic ligands without substituent group show the weakest adsorption strength. These results indicate that sulfur adsorption capacity is primarily contributed by the unsaturated metal center in MOFs. Thus, it is expected that when sulfur compounds contact with MOFs, they are preferentially adsorbed on open metal sites.

Table 4

Binding energies of sulfur compounds over saturated metal center in IRMOF and organic ligands of MOF-199, MOF-74 and MIL-101.

Adsorption site	BE(kJ/mol)		
	H ₂ S	CH ₃ CH ₂ SH	CH ₃ SCH ₃
Zn ₄ O	−27.1	−27.43	−33.93
DHTP ^a (MOF-74)	−11.2	−18.34	−17.78
BTC ^a (MOF-199)	−8.52	−22.51	−19.98
BDC(MIL-101)	−13.62	−15.98	−19.81

^a DHTP (2,5-dihydroxyterephthalate) and BTC (benzene-1,3,5-tricarboxylate) is the ligand of MOF-74 and MOF-199, respectively.

Table 5

Breakthrough sulfur capacity of MOFs adsorbing CH₃SCH₃, CH₃CH₂SH and H₂S at 303 K.

S-compounds	IRMOF-3	IRMOF-8	MOF-74(Zn)	MOF-199 (Cu)
CH ₃ SCH ₃	0.580%	0.46%	1.33%	8.48%
C ₂ H ₅ SH	0.592%	0.48%	1.14%	6.35%
H ₂ S	1.061%	0.37%	1.05%	4.07%

4.4. Correlation with experimental results

The adsorption of H₂S, CH₃CH₂SH and CH₃SCH₃ over MOFs in a fixed-bed reactor was investigated in our previous studies [37,38]. Table 5 presented the sulfur capacities of the MOFs obtained at 303 K. It can be seen that desulfurization performance of MOF-199 and MOF-74 with open metal site is superior to the other MOFs without CUS. This is consistent with the DFT calculation results. That is CUS have a significant influence on adsorption of sulfur compounds. The experimental study (Table 5) also shows that, IRMOF-3 with amino group possesses the highest sulfur capacity, followed by IRMOF-8. This trend is also consistent with the DFT predictions. However, it was found that although the calculated sulfur compounds binding energies over CUS in Zn-MOF-74 is stronger than that in Cu-MOF-199, and the density of CUS sites in Zn-MOF-74 (6.16×10^{-3} mol/g) is also higher than that in Cu-MOF-199 (4.96×10^{-3} mol/g), Zn-MOF-74 do not exhibit a better sulfur removal performance than Cu-MOF-199 as expected.

It should be noted that the work in this paper focus on studying the contribution of each fragment (metal center and ligand) of MOFs to sulfur adsorption. These fragments are represented by cluster models in an unlimited opening space when doing DFT calculation. That is to say the effect of the space or pores formed by these fragments of MOFs was not considered in this work. As revealed in many literatures, pore size and geometry have dramatic effect on adsorption of guest molecule. Smaller pores allow the gas molecules to interact with multiple portions of the framework rather than just one secondary building unit or organic linker. There exhibits an enhanced van der Waals potential pockets which can lead to an increase of adsorption capacity, when the kinetic diameter of adsorbate is very close to the pore size of MOFs [39,40]. For example, as for H₂ whose kinetic diameter is 2.8 Å, the ideal pore size of MOFs seems to be approximately 2.8–3.3 Å, or 4.5–5 Å for hydrogen storage [41].

In this study, the pore diameter of Cu-MOF-199 is 5 Å and 9 Å, whereas that of Zn-MOF-74 is 12 Å. Obviously the former is more close to the kinetic diameter of adsorbate H₂S (3.6 Å), CH₃CH₂SH (4.97 Å) and CH₃SCH₃ (4.98 Å). This indicates a stronger attraction of sulfur compound in Cu-MOF-199, as revealed by experiment results.

5. Conclusions

The adsorptions of sulfur compounds over organic ligands, NH₂-BDC, BDC, and NDC, are physical adsorption. Among the

three organic ligands, NH₂-BDC possesses the strongest adsorption strength due to the functional amino-group. This amino-group increases the polarity in the ligand and thus enhanced its interaction with sulfur.

Strong adsorption strength was observed for metal centers with structure M and M-M in MOF-74 and MOF-199. Their weakest binding energy is −51.8 kJ/mol, indicating sulfur compounds adsorption on MOF-74 and MOF-199 all are chemical interaction. Meanwhile, the results show that MOFs containing Fe exhibits the stronger adsorption than that with cations Zn and Cu. In summary, in all studied adsorptive sites, MOFs with unsaturated metal center have the strongest adsorption strength, NH₂-BDC comes second, followed by saturated metal center, and the organic ligands without substituent group show the weakest adsorption strength. The correlation of calculated binding energy with experimental sulfur capacity indicated that pore is another important factor which can strongly impact the sulfur capacity of MOFs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2016.06.078>.

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