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Modeling and simulation of adsorption of methane, ethane, hydrogen sulfide and water from natural gas in (FP)YEu Metal–Organic Framework.

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Abstract. Metal Organic Frameworks (MOFs) are novel type of hybrid porous materials that have been proposed for natural gas separation and purification due to the possibility of tailoring their capabilities by changing the organic linkers, tuning the length of the organic linker and changing or mixing the metal ion. Molecular simulation helps to understand experimental results by providing a detailed picture on the molecular scale that is not easily accessible from experimental and can be used to study the applicability of classical force fields.

In this work, FPYEu MOF [1] [2] was carefully chosen as an example of a model MOF for studying applicability of force fields, cutoff radius besides the effect of different distributions of metal ions in FPYEu MOF on adsorption of CH_4, C_2H_6, H_2S as well as H_2O.

Grand Canonical Monte Carlo (GCMC) simulations were used to perform gases adsorption on FPYEu MOF cells containing different distributions of Yttrium and Europium. All simulations in this work have been carried out using Towhee code [3].

The applicability of different force fields available in the literature was tested and some of them were applicable like H_2S, where good agreement was found with experimental results, while others were not applicable, like CH_4, C_2H_6 and H_2O, where the calculated isotherms "over or under" estimated the experimental ones. In addition, eight different configurations having Eu atoms arbitrarily located in the system were explored to evaluate the sensitivity of distribution of metal ions.

1. Introduction

Adsorption is one of the most promising and widely used for natural gas separation and purification [4] [5] [6][7]. Different types of adsorbents have been reported for adsorption of gas such as activated carbons, metal oxides, zeolites and metal–organic frameworks (MOFs) [8] [9] [10] [11] [12] [13] [14] [15] [16] [17] [16] [18] [19] [20] [21] [1] [2] [22]. The advantages of MOFs over other porous materials are that MOFs have attractive properties such as, large internal surface areas, synthetic advantages, organic-inorganic hybrid nature, and versatile applications in gas separations, sensors, gas storage and gas purification.

MOFs are a special type of hybrid porous materials constructed by the assembly of organic linking units with metal clusters [23] Figure 1. The numbers of linkers that can be connected to a metallic centre depend on the coordination of the metal and its oxidation state, which result in three-dimensional structures with different topology [23].

The (FP)YEu MOF, with molecular formula of $[(Y_{1.9},Eu_{0.1}) (phen)_2(fdc)_3 \cdot 2(H_2O)]$ as reported by Shi *et al*. in 2014 [1], is an example of a photoluminescent MOF with luminescent properties, 3-dimensional structure and the capability to withstand high temperatures up to 350−400 °C in air, displaying both porosity and selectivity, with the potential to be used as a hydrogen sulfide sensor at low pressure [1] [2].
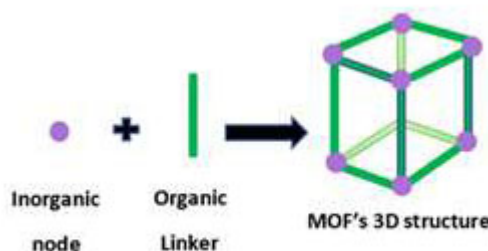
Figure 1. Diagram illustrations the construction of MOFs.

Molecular simulation helps to understand experimental adsorption results by providing a detailed picture on the molecular level that is not possible from experimental methods [24] [25] [26]. Molecular simulation is quicker than experiment and reducing the time and capital investment on experimental work [27] [24] [25] [26]. One of the most popular simulation methods is Monte Carlo (MC) simulation which is widely used to calculate adsorption isotherms of a given MOF by quick study of the impact of molecular scale properties such as surface area, pore size or pore shape on the adsorption performance for specific applications [22] [26] [28] [26] [29].

In this work, MC used to study the effect of the distribution of different metals in the system on the adsorption isotherm. In accordance with the previous work have been studied CH_4, C_2H_6, H_2S and H_2O adsorptions in FPYEu MOF using molecular simulation and the applicability of the force fields focusing on the configuration in which the Europium atoms are close in a model of FPYEu MOF [2]. It was found that force field applicability needs to be treated carefully, as in all cases large deviation with experimental results are obtained [2]. Notably, these force fields were not developed for a specific MOF. In current work, different combinations of force fields were explored to assess their validity [30]. The influence of cutoff radius on adsorbed amounts, nonpolar gases adsorption isotherms were also explored using cutoff radius of 10 Å [30]. In addition, eight different configurations having Europium atoms arbitrarily located in the system were explored to evaluate the sensitivity of distribution of metal ions on adsorption of gases.

The characterisation of FPYEu MOF presented in this work such as the geometric pore volume, crystal density and pore size were computed using Poreblazer package proposed by Sarkisov and Harrison [31]. For the geometric pore volume, the Universal force field (UFF) [32] were used to describe the Lennard-Jones (LJ) interactions of Helium and the framework atoms. The properties of FPYEu MOF are summarized in Table 1. The difference in geometric pore volume between experimental and theoretical is about 10%. This is duo to using different guest molecule to run these experiments and simulations.

Table 1. Theoretical and experimental properties of FPYEu MOF.

| ρ_{cyrst} [a] (g/cm^3)	V_{pore} [a] ($Å^3$)	ρ_{cyrst} [b] (g/cm^3)	V_{pore} [b] ($Å^3$)	Pore limiting [b] (Å)	Max. Pore [b] (Å)
1.573	8808.3	1.516	9833.4	2.61	5.23

[a] From reference [1];

[b] Computed using Poreblazer v3.0.2, proposed by: Lev Sarkisov, 2012 [31];

2. Methodology

2.1 Models

The crystallographic information of the FPYEu MOF atoms were adopted from Shi *et al*. [1]. This study builds on the previous work where 3-unit cells with lattice: 28.96×28.96×30.50 Å, with 48 metal atoms have been used, having 46 Yttrium atoms and 2 Europium atoms Figure.2.

(a)   (b)   (c)
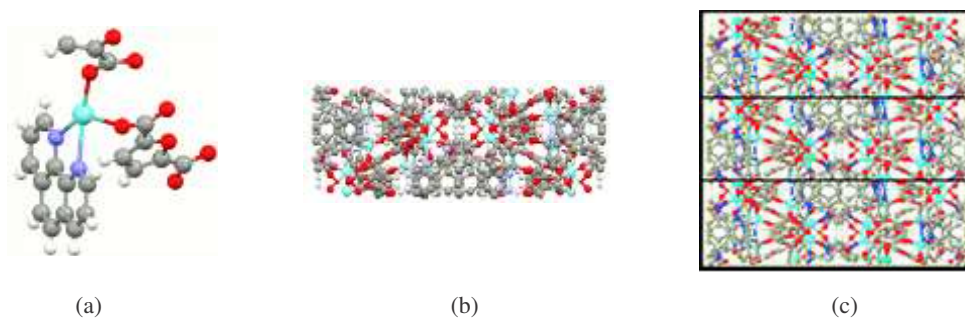
Figure 2. (a) The asymmetric unit cell of FPYEu MOF (yttrium/ europium: light blue, carbon: grey, oxygen: red, hydrogen: white and nitrogen: blue) [1] [2]. (b) FPYEu MOF unit cell with dimensions 28.9603, b = 28.9603 and c = 10.5023 Å [1] [2]. (c) FPYEu MOF simulation box has 3-unit cells with dimensions: 28.9603×28.9603×30.5023 Å [1] [2].

Moreover, the focus was on close configuration in the previous work Figure 3 [2]. In this study, eight different configurations having Europium atoms arbitrarily located in the simulation box Figure 4 were explored to evaluate the sensitivity of distribution of metal ions on adsorption of gases. Noteworthy, the locations of Europium atoms have been randomly chosen in configurations.
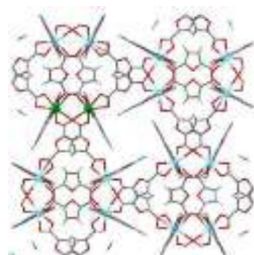

Figure 3. Close configuration, FPYEu with two close europium atoms [2].
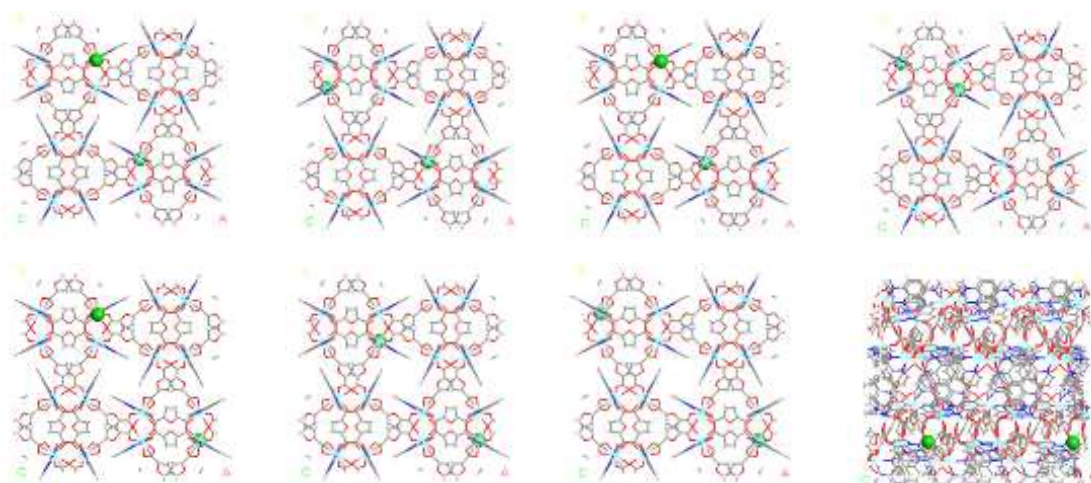
Figure 4. Eight different random configurations, FPYEu with two europium atoms randomly placed, (yttrium: light blue, europium: green, carbon: grey, hydrogen: white, nitrogen: blue and oxygen: red).

Table 2. The partial charges for FPYEu MOF obtained from Qeq method adopted from our previous work [2]. Atom locations can be identified in Figure.5 [2].

atom	Y	Eu	N1	N2	O1	O2	O4	O5	O6	C18	C20
q	0.910	1.088	-0.235	-0.219	-0.444	-0.437	-0.456	-0.481	-0.424	0.067	0.072
atom	O7	C1	C2	C3	H3	C4	H4	C5	C6	H18	C21
q	-0.441	0.068	0.085	0.085	0.068	0.068	0.061	0.053	0.059	0.078	0.082
atom	C7	C8	C9	H9	C10	H10	C11	H11	C12	C19	O3
q	0.066	0.068	0.090	0.079	0.068	0.051	0.068	0.065	0.055	0.076	0.072
atom	H12	C13	C14	H14	C15	H15	C16	C17	H17	H19	O8
q	0.048	0.055	0.060	0.061	0.090	0.075	0.074	0.069	0.077	0.061	-0.109
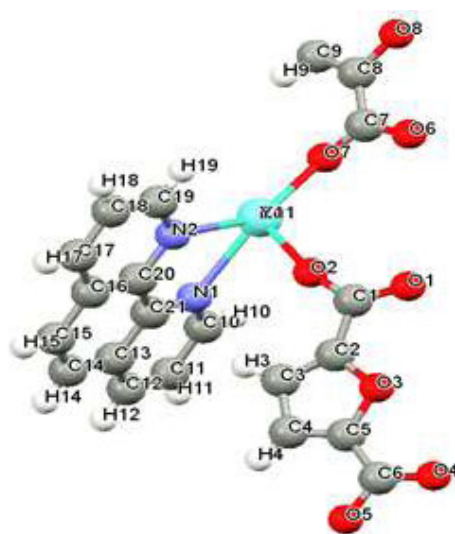
Figure 5. A symmetric unit cell displays atoms labels used to recognise partial charges in table 2 [2].

Several sets of LJ parameters have been derived for methane which are used to describe the methane interactions in all materials, of which DREIDING, TraPPE-UA and Goodbody *et al* are most commonly applied in studies of adsorption [37] [30] [38] [39] [34] [36] [22]. Methane in these force fields is represented by a united-atom model with one site. The different between these force fields is only in epsilon Ɛ, for DREIDING is 149 K and for TraPPE-UA or Goodbody *et al* is 148 K.

In this work, TraPPE-UA force field [40] was used to represent methane and the results were compared with previous work [2] where was used DREIDING [33] model for methane.

TraPPE-UA force field [40] was also used to model ethane and the results were also compared with our previous work [2] where we used DREIDING [33] model for ethane. The different between these force fields for ethane is also only in epsilon Ɛ, for DREIDING is 125.8 K and for TraPPE-UA is 98 K.

Kamath *et al*.[41] was used to represent hydrogen sulphide. Such a model has been successfully used to reproduce the experimental vapor−liquid phase equilibrium data and has been validated in previous studies [34] [22]. Simulations were also performed with the OPLS-UA force field [42] to compare with our previous work [2].

TIP4P-Ew force field [43] was used to model water molecules. Simulations were also carried out with the SPC/E force field [44]. The parameters for framework and the adsorbate or gas molecules are listed in Table 3 and Table 4.

Table 3. LJ potential parameters for the atoms of FPYEu MOF.

Atom type	Force field	σ (Å)	Ɛ (K)
Y	UFF [45]	2.980	36.231
Eu	UFF [45]	3.111	4.025
N	DREIDING [33]	3.262	38.948
C	DREIDING [33]	3.473	47.859
O	DREIDING [33]	3.033	48.161
H	DREIDING [33]	2.846	7.6490

Table 4. Lennard-Jones parameters and partial charges of the gas molecules.

Molecule	Force field	Atom type	Partial charge	σ (Å)	Ɛ (K)
H_2S	Kamath *et al*.[41]	H	0.190	0.0	0.0
		S	−0.380	3.72	232
	OPLS-UA [42]	H	0.235	0.0	0.0
		S	-0.47	3.7	125.80
H_2O	SPC/E [44]	HW	0.4238	0.	0.
		OW	-0.8476	3.1656	78.197
	TIP4P-Ew [43]	HW	0.52422	0.0	0.0
		OW	0.0	3.1643	81.8994
		M	-1.04844	0.0	0.0
CH_4	DREIDING [33]	CH4	0.0	3.7327	149.92
	TraPPE-UA [40]	CH4	0.0	3.7300	148.00

| C_2H_6 | DREIDING [33] | CH3 | 0.0 | 3.699 | 125.80 |
| | TraPPE-UA [40] | CH3 | 0.0 | 3.750 | 98.00 |

The adsorption equilibrium between the gas phase and the adsorbed phase was modelled with Grand Canonical Monte Carlo (GCMC) simulations using Towhee code [3] [22]. The descriptions of GCMC simulations are available in several references [3] [46] [47] [28]. In the Grand Canonical Monte Carlo (GCMC) ensemble, the chemical potential μ of each component, the temperature T, and the volume V are fixed as in experiments [22]. The adsorption isotherms were calculated at temperature 298.15 K for hydrogen sulphide, methane and ethane using 5 million Monte Carlo steps for equilibration and 4 million Monte Carlo steps for production [1]. Simulations for water were equilibrated at T= 303.15 K, for 50 million Monte Carlo steps for equilibration and 50 million Monte Carlo steps for production [1]. The translation, rotation, and insertion or deletion of simulation moves was 10%, 20%, and 70% respectively [1]. The distribution of moves is motivated by the desire to have good convergence behaviour in the simulation. In other words, how fast the simulation converges to a stationary distribution to achieve fast equilibration times, fast relaxation times and correlation times. The difference in the temperatures for the calculated isotherms was to enable easy comparison with experimental and simulation data published in the literature [1] [2]. Isotherms were calculated in a range of pressures for comparison with the experimental data [1] [2].

The chemical potentials μ required in the GCMC simulation are taken from our previous work [2]. The influence of cutoff radius on adsorbed amounts [30] [39], nonpolar gases adsorption isotherms were explored for Lennard Jones interactions using cutoff radius of 10 Å and 13 Å. The long-range electrostatic interactions were calculated by the Ewald methodology [22] [28] [48].

3. Results and Discussion

3.1 Adsorption of methane and ethane

The calculated isotherms of methane and ethane in FPYEu MOF compared to the previous work [2] are shown in Figure 6. Although using different combinations of force fields, the calculated isotherms for CH_4 and C_2H_6 are still overestimated the experimental ones. Using TraPPE-UA or DREIDING model gives very similar results.

The results also show that using cutoff radius of 10 Å or 13 Å overestimated the experimental results. Nevertheless, the differences with experimental data for both gases (CH_4 and C_2H_6) indicate different non-accessible volumes [2]. The differences with experimental data could be due to the lack of applicability of Lennard-Jones parameters, pore accessibility or accuracy of the experimental isotherms.

The results also show that the simulations boxes with different Eu distributions do not affect the adsorption of different rare earth metals distributions.

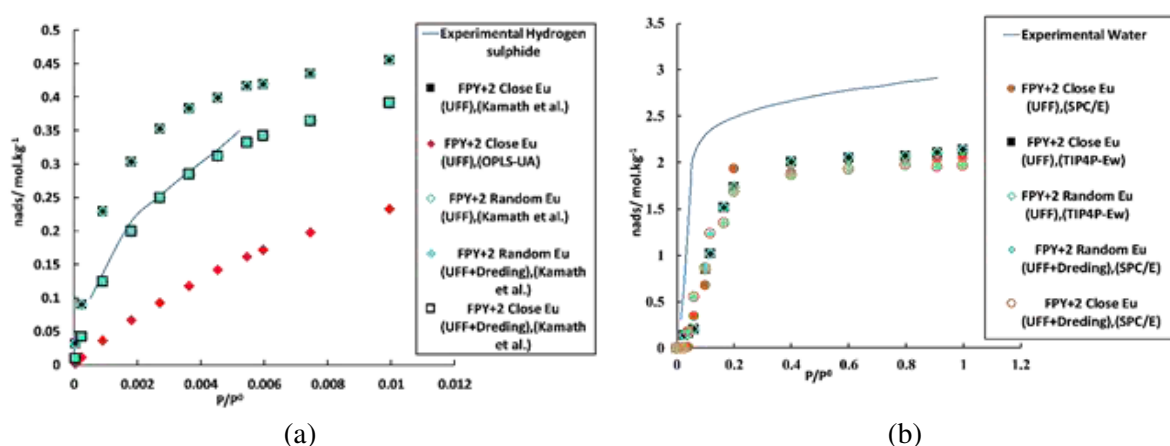(a)   (b)
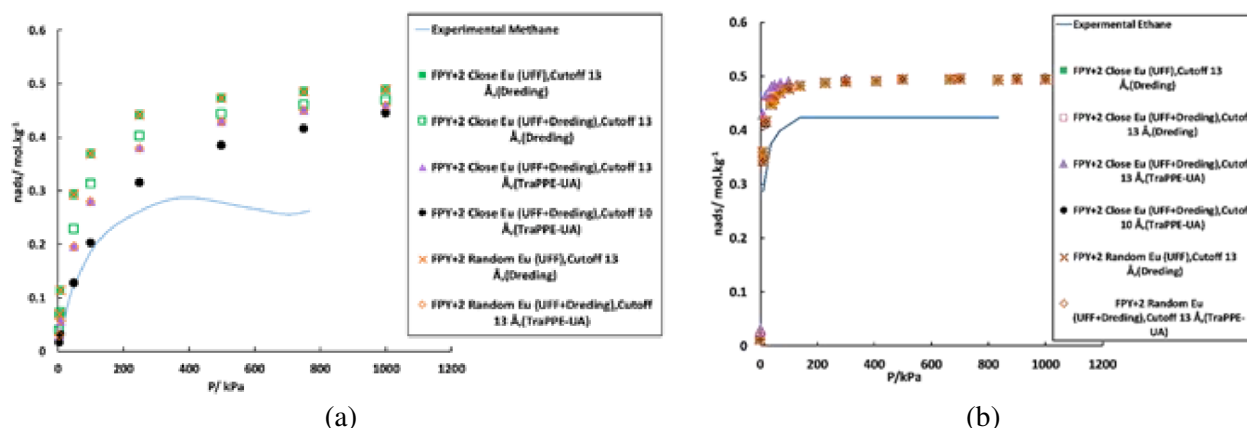
Figure 6. (a) Methane (b) Ethane adsorption isotherms at temperature = 298.15 K on FPYEu with close and random distributions. Results computed by using additional combinations of force fields and cutoff 10 Å. The blue line displays the experimental as reported by Shi *et al*. [1]. The error bars of the calculated loading are smaller than the symbol size.

3.2 Adsorption of hydrogen sulfide and water

The computed adsorption isotherms for hydrogen sulfide and water with different force fields and sets of charges are shown in Figure 7. It can be observed that the selection of the force field for framework can have a dramatic impact on the simulated data. The agreement between experimental and computed data for hydrogen sulfide is excellent over the whole range of pressure by using DREIDING and UFF for FPYEu and Kamath for hydrogen sulfide, whereas UFF for FPYEu and Kamath for hydrogen sulfide overpredict the experiment data. Nevertheless, using different combinations of force fields for FPYEu has no influence on the simulated data of water. It is possible that modifying the charges of the MOF and/or the force field parameters suggested by Pérez-Peritello [10] and Fairen-Jimenez [49] may satisfactorily address this shortcoming, although it cannot be modified without verifying the pore volume of the MOF.

Interestingly, the calculated adsorption isotherms are not sensitive to the Europium atoms distribution in the system.

(a)   (b)

Figure 7. (a) Adsorption isotherms of hydrogen sulfide at temperature =298.15 K, (b) Adsorption isotherms of water at temperature =303.15 K on FPYEu structures with close and random distributions. Results computed by using additional combinations of force fields. The blue line presents the data of experimental as reported by Shi *et al*. [1]. The error bars of the calculated loading are smaller than the symbol size.

4. Conclusions

The current work has shown that simulation tools can be used to study the applicability of classical force fields and the sensitivity of the calculated adsorption isotherm to the metals atoms distribution in the system. Different force fields available in the literature were used to model the adsorption of gases in FPYEu and some of them were applicable, like H_2S, where good agreement was found with experimental results, while others were not transferable, like CH_4, C_2H_6 and H_2O, where the calculated isotherms "over or under" estimated the experimental ones. While some of the disagreements with experimental data may be due the lack of applicability of Lennard-Jones parameters, pore accessibility, partial charges or accuracy of the experimental isotherms. It is possible that the modifying the charges of the MOF and/or the force field parameters [10] [49] may satisfactorily address this shortcoming, although this was not explored in the present work.

Interestingly, the results also show that the simulations boxes with different Europium atoms distributions do not affect the adsorption of different rare earth metals distributions. The eight different configurations having Europium atoms arbitrarily located in the system give the same results. This also indicates that modelling different ratio of Eu:Y is not necessary.

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