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A theoretical study of noxious gases storage using covalent organic frameworks (COFs)

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Abstract. Using covalent organic frameworks (COFs) to capture noxious gas has become an increasing research interest, especially for the purpose of environmental protection. A theoretical study on the interactions of carbon monoxide (CO), sulfur dioxide (SO₂) and nitric oxide (NO), respectively with COF-300 has been proposed, based on the theory of the continuum approximation using Lennard-Jones potential. We discover that COF-300 can store more SO₂ in comparison to CO and NO under an increasing pressure at 77K. The present methodology is computationally efficient and can be employed in other types of gases and nano-porous materials without conceptual difficulties.

1. Introduction

Air pollution has become a serious global problem and triggered enormous worldwide attention. Most of the developed countries and increasing number of the developing ones are overwhelmed by poor air qualities. Particulate matter of radius being less than 2.5 μm , or PM2.5 can penetrate through the doors, windows, vents and other ventilation systems into buildings thus worsen the indoor air quality (IAQ). PM2.5 can be accumulated in human lungs leading to severe respiratory decreases and even lung cancer [1], and also leading to high health risk explored by indoor occupants. Most PM2.5 are form in the atmosphere as a result of complex reactions for noxious gases such as sulfur dioxide and nitrogen oxides, which are pollutants emitted from power plants, industries and automobiles.

To mitigate the environmental damage caused by PM2.5, one of the best methods is to remove its sources gas before the formation of PM2.5. Due to the superior physical and chemical properties, and huge surface area to volume (STV) ratio of nanomaterials, nanomaterials themselves or embedded into a membrane system can provide an effective medium to store gases. In particular, certain materials such as metal-organic frameworks (MOFs) and Covalent Organic Frameworks (COFs) could alter their topology to accommodate more gasses [2].

As a matter of fact, MOFs have emerged as promising H₂ storage materials. MOFs can be redesigned due to their flexibility and their structural diversity causing ultrahigh porosity and exceptional hydrogen uptake capacities. Recently, covalent organic frameworks (COFs) have been synthesized and structurally characterized and it was found that the organic building units were held together by strong covalent bonds such as C-C, C-O, B-O, and Si-C rather than metal ions so as to produce materials with high porosity, for example 3472 m²/g for COF-102 and 4210 m²/g for COF-103, and low crystal density for example 0.17 g/cm³ for COF-108 [3]. Due to its thermal stability up to



490°C and exceptionally high permanent porosity with a surface area of $1360 \text{ m}^2\text{g}^{-1}$ [4]. These characteristics make COFs excellent candidates for gas storage.

As consequence, COFs have been largely used for gas storage as reported in literatures. Mendoza-Cortes et al [5] studied the adsorption of CH_4 using 14 new covalent organic frameworks (COFs) near ambient temperatures using Grand Canonical Monte Carlo (GCMC) simulations. Dorcheh et al. [6] investigated noble gas storage using three classes of microporous frameworks (MFs) including COFs. Srepusharawoot et al. [7] dealt with the investigation of H_2 adsorption energies of the lithium (Li) functionalized COF-366 by using the density functional theory method. Furukawa et al. [8] experimentally investigated storage of H_2 and CH_4 near 35 bar, at 77 K for H_2 and 298 K for CH_4 , respectively using different COFs. On the other hand, it was found that the performance of CH_4 adsorption in COFs is not good as H_2 adsorption because of the weak interactions between the adsorbent and adsorbates. One also conducted a systematic computational investigation on the dispersion behaviors of ionic liquids (ILs) in COFs and MOFs, for studying the separation performance of the composites of CO_2/CH_4 and CO/N_2 .

In terms of the methodology, all these above researches on gas adsorption using COFs can be divided into two categories, which are experiments and simulations [9]. Among these simulation works, most of them are molecular dynamic (MD) simulations, which require large computational space and time.

In this paper, the effort is placed in studying the storage of noxious gases in COF-300, using a novel but much simpler simulation method compared to conventional MD simulations. Besides, COF-300 is chosen due to its highest surface area of all other types of COFs, which is crucial for gas storage.

2. Characteristics of COF-300 and the mathematical model development characteristics of COF-300

COF-300 is the first crystalline 3-D framework material constructed solely from C-C and C-N covalent linkages. Its preparation and characterization was studied and its permanent porosity was also demonstrated by Uribe-Romo et al. [4]. It had been concluded that COF-300 has good thermal and chemical stability. Therefore, its ability of storing noxious gases was investigated in this study. Figure 1 shows a schematic diagram of molecule structure for COF-300.

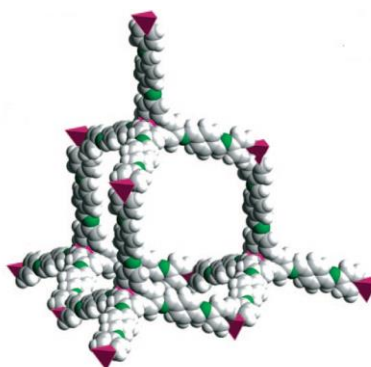


Figure 1. A schematic for a COF.

A multi-scale mathematical model was set up based on the structure of COF-300 to investigate the absorption of gas inside the COF-300 crystal model as shown in Figure 1. As the shape of a single unit in COF-300 crystal model is a regular polyhedron, leading to a fact that the distances between each atom in the units and unit centre are approximately the same; hence COF-300 can be approximated by an envisaged spherical structure for our mathematical model development.

Figure 1 also shows the cross-sectional 2D diagram of the spherical structure. The radius of sphere is the distance between unit cells in a repeated crystal unit. Hence, the gas molecules inside the sphere would interact with the atoms arising from the crystal unit.

2.1. Mathematics model development

In our mathematical model, two different types of molecular interactions were considered. The first type would be the molecular interactions between gas molecule and atoms in COF-300 and they were evaluated by the Lennard-Jones potential [10], where the later interaction could be obtained using a mean field theory. The second type would be the interactions between different gas molecules such as between NO and SO₂.

For the first type interaction, Lennard-Jones potential is calculated using [11-13]

$$E_1 = \eta \oint_{\text{Sphere surface}} \left(-\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) ds, \quad (1)$$

where E_1 is the Lennard-Jones potential related to the first type interaction, η the number density of atoms of COF-300, A and B the attractive and repulsive constants respectively, and ρ the distance between the COF-300 atom and the gas molecule.

Based on the spherical model shown in Figure 1, and the geometrical relation as shown in Equation (2)

$$\rho^2 = r^2 + R^2 - 2rR \cos \theta. \quad (2)$$

We can obtain

$$E_1 = A\eta \int_0^\pi \int_0^{2\pi} \frac{R^2 \sin \theta}{(r^2 + R^2 - 2rR \cos \theta)^3} d\varphi d\theta - B\eta \int_0^\pi \int_0^{2\pi} \frac{R^2 \sin \theta}{(r^2 + R^2 - 2rR \cos \theta)^6} d\varphi d\theta, \quad (3)$$

where R is the radius of the spherical surface, r the distance between the spherical centre and the gas molecular, and φ and θ the standard coordinates in spherical coordinates systems.

The integrations in Equation (3) give

$$E_1 = A\eta \frac{\pi R}{2r} \left[\frac{1}{(R+r)^4} - \frac{1}{(R-r)^4} \right] - B\eta \frac{\pi R}{5r} \left[\frac{1}{(R+r)^{10}} - \frac{1}{(R-r)^{10}} \right], \quad (4)$$

where the attractive and repulsive constants, A and B respectively, were calculated by using the following equations.

$$A = 4\varepsilon\sigma^6, \quad (5)$$

$$B = 4\varepsilon\sigma^{12}, \quad (6)$$

where ε and σ denote the electrical energy and radius of gas molecule, i.e., van der Waals radius.

For the interaction potential between gases, E_2 , using the same method for determining E_1 to yield

$$E_2 = -4\eta e^{r-R}. \quad (7)$$

The total interaction potential E_{total} is hence

$$E_{\text{total}} = E_1 + E_2 = \frac{2\eta\varepsilon\sigma^6\pi R}{r} \left[\frac{1}{(R+r)^4} - \frac{1}{(R-r)^4} \right] - \frac{4\varepsilon\sigma^{12}\pi R}{5r} \left[\frac{1}{(R+r)^{10}} - \frac{1}{(R-r)^{10}} \right] - 4\eta e^{r-R}. \quad (8)$$

In COF-300, the cavity inside sphere comprises the bulk and adsorption regions of which the volume is V_{bulk} and $V_{\text{adsorption}}$, respectively. Boltzmann's distribution gives

$$V_{\text{bulk}} = \int_{\text{Sphere volume}} \exp\left(\frac{|E_{\text{total}}|}{kT}\right) dV, \quad (9)$$

$$V_{\text{adsorption}} = \int_{\text{Sphere volume}} \left[1 - \exp\left(\frac{|E_{\text{total}}|}{kT}\right)\right] dV, \quad (10)$$

where T is temperature and k the Boltzmann's constant.

In the bulk region, the adsorption properties are described by the conventional van der Waals equation of states. In the adsorption region, however, the heat of adsorption Q should be calculated by using

$$Q = |E_{\text{total}}| + kT/2. \quad (11)$$

The volumes of bulk and adsorption regions in the multi-scale model can be calculated by using

$$P \frac{V_{\text{bulk}}}{n_{\text{bulk}}} = R_b T, \quad (12)$$

$$P \frac{V_{\text{adsorption}}}{n_{\text{adsorption}}} = R_b T \exp\left(-\frac{Q}{RT}\right), \quad (13)$$

where P is the external pressure, n_{bulk} and $n_{\text{adsorption}}$ the number density of gas molecules stored in the bulk and adsorption regions, respectively. Therefore the total number density n_{total} of gas molecules stored in COF-300 can be determined by using the following equation.

$$n_{\text{total}} = n_{\text{bulk}} + n_{\text{adsorption}} = \frac{PV_{\text{bulk}}}{R_b T} + \frac{PV_{\text{adsorption}}}{R_b T \exp\left(-\frac{Q}{RT}\right)}. \quad (14)$$

We comment that the present methodology matched well with other experimental and simulation results, especially the storage of hydrogen in graphene sheets and MOFs [14], which boosts our confidence on using such methodology for the current topic.

3. Results of the mathematical model development

For determining the total number density of gas molecules storage, n_{total} , with the aforementioned mathematical model, the attractive and repulsive constants, A and B respectively, should be firstly determined. The calculations of A and B were based on the electrical energy of two interactions (COF-300 and gas molecules). It was also based on Van der Waals radius of each gas molecule.

Atoms C, N, and H are contained in COF-300 ($C_{41}H_{28}N_4$). For each of the gas molecules (CO, SO_2 , or NO), there are three attractive and repulsive constants, which correspond to C, H, and N, respectively. The values of ϵ and σ are given in Table 1. Interaction energy was calculated according to the parameters shown in Table 1. The results of the attractive and repulsive constants, A and B, are shown in Table 2, where the molecular masses for CO, NO and SO_2 are also illustrated.

Table 1. Parameters of electrical energy ϵ and Van der Waals radius σ (Å) [15].

	ϵ (eV)	σ (Å)
CO	0.009134	3.676
SO ₂	0.02172	4.290
NO	0.01025	3.470
C	0.00455	3.431
H	0.0019	2.571
N	0.007889	3.681

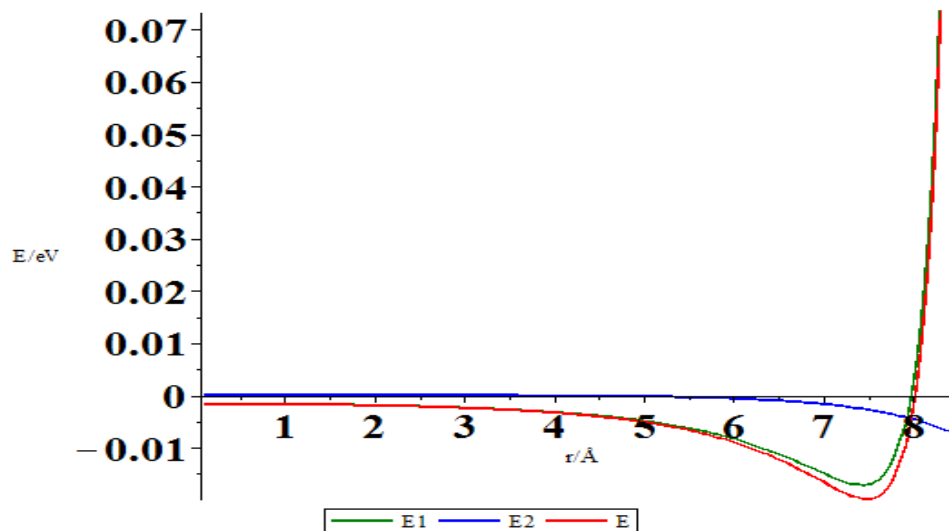
Table 2. The attractive and repulsive constants, A and B.

	CO	NO	SO ₂
Attractive constant for H atom	15.5	13.4	41.9
Repulsive constant for H atom	14400	10200	68300
Attractive constant for C atom	51.9	46.1	132
Repulsive constant for C atom	105000	77800	436000
Attractive constant for N atom	84.1	75.2	210
Repulsive constant for N atom	208000	157000	841000
Molecular mass	4.45e-26	4.983e-26	1.06e-25

3.1. Variation of interaction potential energy in different location

With the given values of A and B, further numerical results can be calculated based on the present mathematical model, i.e. equations (4) to (14). We found that at different locations, the interaction potential energy is different. The molecular interactions of CO, SO₂ and NO in the COF-300 multi-scale sphere model with radius of 11 Å was calculated and are presented in Figure 2, 3 and 4 respectively.

It can be seen from the Figure 2 that the CO is densely occupied around $r=7.5$ Å, where E_1 reaches its peak due to the keenest molecular interactions arising from COF-300. This also induces relatively higher CO-CO interactions as the intensity of CO-CO interaction fades towards the cavity centre as shown in the Figure 2. The same trends are also observed in Figure 3 and 4, where the minimum interaction potential energy for CO, SO₂ and NO is given by -0.018 eV, -0.018 eV and -0.022eV, respectively.

**Figure 2.** Interaction of carbon monoxide (CO) in COF-300 E versus the radius r.

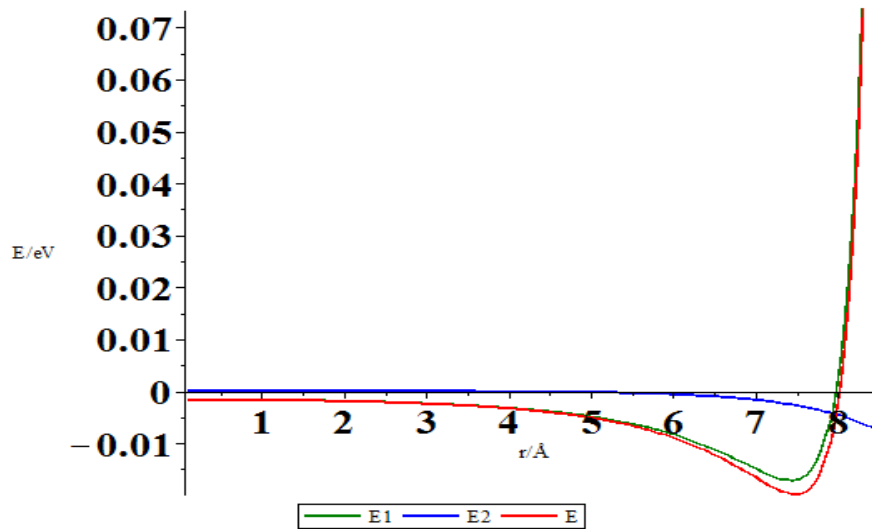


Figure 3. Interaction of sulfur dioxides (SO_2) in COF-300 versus radius r .

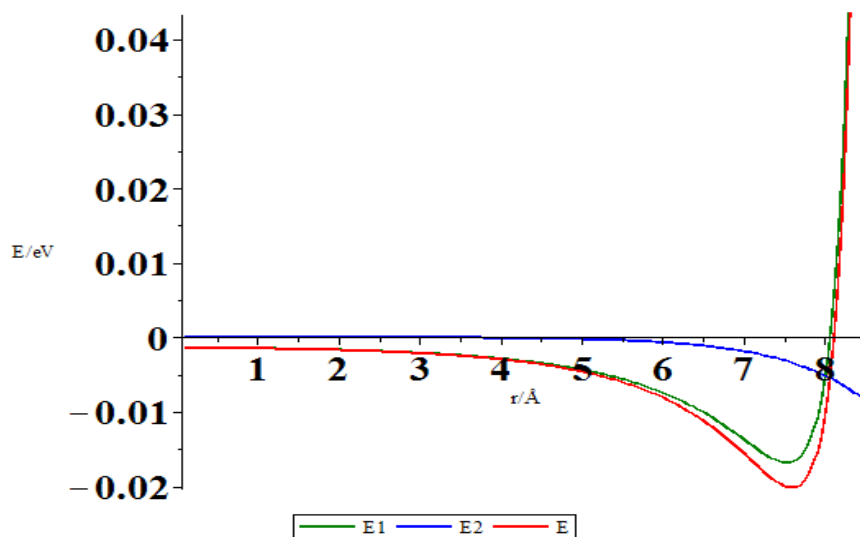


Figure 4. Interaction of nitric oxide (NO) in COF-300 versus radius r .

3.2. Gravimetric uptake

To illustrate the effect of storage of CO, SO_2 and NO in COF-300 specifically, the gravimetric uptake for the gases inside COF-300 were determined using the present model, without considering the molecular effect of heat generation, i.e., $Q=0$ in Equation (13), and the gravimetric uptake was calculated as a ratio of the total mass of gas molecules and the mass of COF-300.

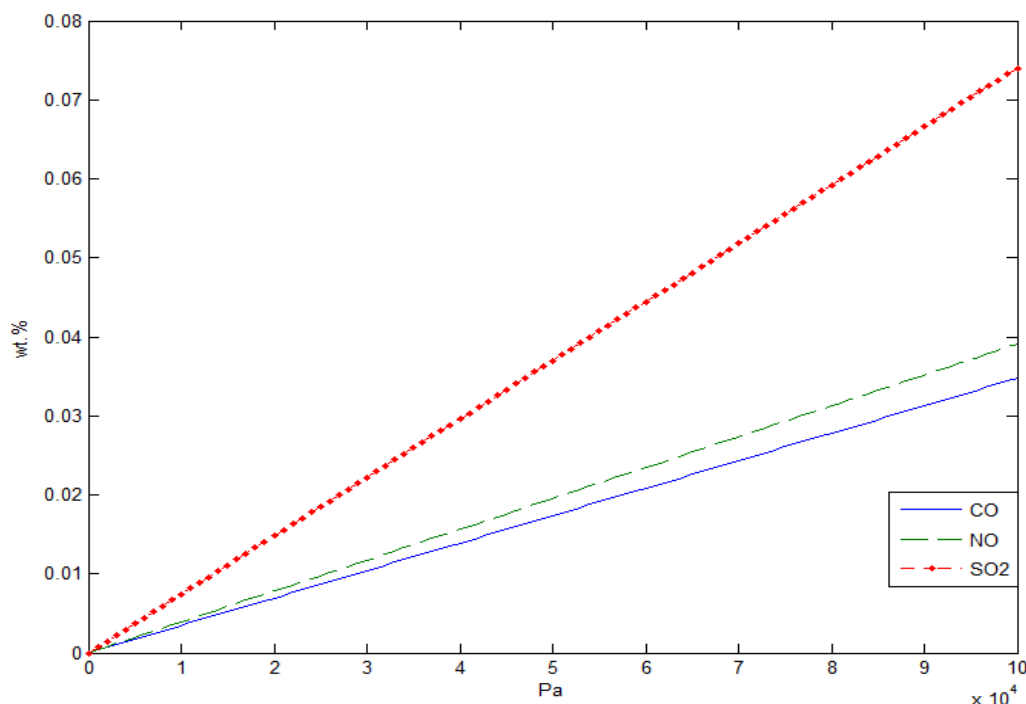


Figure 5. Gravimetric uptake for CO, NO and SO₂ inside COF-300 at T=77K with the pressure range from 0 to 105 Pa.

The gravimetric uptake is then numerically calculated by using Matlab, where n and M denote the total mass of gas molecule and COF-300, respectively, which is shown in Figure 5. It is worthy to note that the present numerical results are obtained in few minutes mincing rapid computational time. However, in practice, most gas filling process is performed under room temperature. To investigate the temperature effect, temperature 77K is changed into 300K, which could also be done easily under the current mathematical frameworks. Due to the higher temperature effect, the higher pressure is needed to squeeze hydrogen into the system in comparison to that at the lower temperature.

4. Conclusions

Here, we conclude the successful use of the Lennard-Jones potential in conjunction with the continuum approximation and the thermal statistics to investigate the encapsulation of various gases in COF-300. We find that COF-300 captures more SO₂ than other proposed gases at 77K. The present methodology is robust and can be employed into other gases and nano-porous materials without any conceptual difficulty.

Acknowledgement

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