TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Nghiên cứu khả năng bắt giữ khí thải của vật liệu khung hữu cơ kim loại $Ni(BDC)(TED)_{0,5}$ bằng phương pháp mô phỏng cổ điển

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TÓM TẮT

Sự phát thải các khí độc hại tác động tiêu cực ồ ạt đến môi trường và sức khỏe của con người như CO_2 và SO_2 do sự tăng nhanh dân số toàn cầu và việc đốt ngày càng nhiều nhiên liệu hóa thạch để đáp ứng nhu cầu năng lượng. Song song với việc tìm ra nguồn năng lượng thay thế nhiên liệu hóa thạch, việc tìm ra một biện pháp để bắt giữ, giảm tải và xử lý khí thải độc hại ra môi trường, gây hiệu ứng nhà kính cũng hết sức quan trọng và cấp bách nhằm ngăn chặn sự biến đổi khí hậu ngày càng trầm trọng hơn. Vật liệu khung hữu cơ kim loại $Ni(BDC)(TED)_{0,5}$ được đánh giá là vật liệu xốp có khả năng hấp phụ mạnh CO_2 và SO_2. Bằng phương pháp mô phỏng Monte Carlo chính tắc lớn, chúng tôi đã đánh giá được khả năng bắt giữ hai loại khí này của $Ni(BDC)(TED)_{0,5}$ với lượng hấp phụ SO_2 mạnh hơn CO_2 ở vùng áp suất thấp dưới 25 bar; trong khi đó, ở vùng áp suất cao, lượng hấp phụ CO_2 có khuynh hướng tăng (đạt 14,4 mmol/g ở 50 bar) nhưng hấp phụ SO_2 thì sớm bão hòa ở áp suất 5 bar với 13,6 mmol/g. Sự hấp phụ mạnh hơn của SO_2 so với CO_2 trong vùng áp suất thấp cũng được làm sáng tỏ qua nhiệt hấp phụ của SO_2 (32,7 kJ/mol) lớn hơn nhiều so với CO_2 (17,3 kJ/mol) trong $Ni(BDC)(TED)_{0,5}$.

Từ khóa: *$Ni(BDC)(TED)_{0,5}$, mô phỏng Monte Carlo chính tắc lớn, bắt giữ CO_2, bắt giữ SO_2, hấp phụ đẳng nhiệt.*

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Research on the capture of flue gases of the metal-organic framework Ni(BDC)(TED)$_{0.5}$ by the classical simulation method

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ABSTRACT

The emission of toxic gases has massive negative impacts on the environment and human health such as CO_2 and SO_2 because of the rapid increase of the global population and the burning of more and more fossil fuels to meet energy needs. Together with seeking alternative clean energy sources, finding methods to capture, reduce and treat harmful gases in the environment is urgent to prevent climate change and global warming. The metal-organic framework Ni(BDC) (TED)$_{0.5}$ was evaluated as a porous material with strong adsorption of CO_2 and SO_2. By grand canonical Monte Carlo simulation, we quantitatively evaluated the capture capacities of CO_2 and SO_2 in Ni(BDC) (TED)$_{0.5}$ based on the adsorption mechanism. Our results indicated the adsorption of SO_2 was higher than that of CO_2 in the pressures below 25 bar. Meanwhile, in the high-pressure range, the CO_2 adsorption in Ni(BDC) (TED)$_{0.5}$ was still in increase, reaching 14.40 mmol/g at 50 bar, but SO_2 adsorption was soon saturated at the pressure of 5 bar with 13.6 mmol/g. The stronger adsorption of SO_2 compared with CO_2 in the low-pressure range was also elucidated by the isosteric heat of adsorption that was Q_{st} of SO_2 (32.7 kJ/mol), which was much greater than that of CO_2 (17.3 kJ/mol) on Ni(BDC) (TED)$_{0.5}$.

Keywords: *Ni(BDC)(TED)$_{0.5}$, grand canonical Monte Carlo, CO_2 capture, SO_2 capture, adsorption isotherms.*

1. INTRODUCTION

Flue gas emissions such as CO_2 and SO_2 have seriously affected the environment and human health. It is always the hot problem at conferences, workshops, and seminars due to the urgent need to find solutions to capture, treat and convert exhaust gases. Several studies have been performed on separating and capturing toxic gases from the gas mixture so far. Over the past few decades, adsorption-based gas capture and storage in porous materials have been noticed due to their extraordinary features such as high surface area, high pore, extra-high porosity up to 90% free volume, adjustable internal surface properties, and tunable pore size.[1] Many adsorbents have been investigated, such as activated carbon (AC), zeolite, silica gel (SG), and especially metal-organic frameworks (MOFs).[2,3] Among porous materials, MOFs seem to be the most encouraging.

More than 90,000 MOFs have been synthesized, and more than 500,000 structures

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have been predicted up to now.[4] Nevertheless, very few MOFs have been evaluated and analyzed for storage, capture, separation, and other applications. Among MOFs, Ni(BDC)$(TED)_{0.5}$ structure, in which the metal component is Ni^{2+} (nickel ion), and the organic linkers are H_2BDC = 1,4-benzene-dicarboxylate (C_4H_6-1,4-$(CO_2H)_2$, TED = triethylenediamine ($C_6H_{12}N_2$), has been noted for CO_2 and SO_2 captures. By both experiment and computation, K. Tan et al. showed that Ni(BDC)$(TED)_{0.5}$ had higher SO_2 adsorption than M(BDC)$(TED)_{0.5}$ (M = Zn, Mg) and many other MOF structures.[5] However, this research was only performed in the pressure range below 2 bar. For CO_2, Arstad and co-workers also showed, at the room temperature, Ni(BDC)$(TED)_{0.5}$ adsorbed 14 wt% at the atmosphere pressure and up to at 25 atm.[6]

For comparing the experiment data and extending the uptake in the pressure range up to 50 bar, we performed grand canonical Monte Carlo (GCMC) simulations. The obtained results evaluate and explain the capture of CO_2 and SO_2 in Ni(BDC)$(TED)_{0.5}$ at 298 K and the pressures under 50 bar in detail.

2. GRAND CANONICAL MONTE CARLO METHOD

GCMC method[7] was employed to quantitatively assess CO_2 and SO_2 uptakes on the surface of the Ni(BDC)$(TED)_{0.5}$ MOF. The interactions between gases (CO_2, SO_2) and the MOF are the pairing interaction between the atoms *i* and *j* at a distance r_{ij}, described by:

$$U(r_{ij}) = k\frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad (1)$$

In Formula (1), the first term describes the electrostatic (Coulomb) interactions between the pairs of atoms *i* and *j*, where $k = \frac{1}{4\pi\varepsilon_0}$ is the Coulomb constant (ε_0 is the electric constant), q_i is the i^{th} atomic charge in Ni(BDC)$(TED)_{0.5}$, including nickel (Ni), nitrogen (N), oxygen (O), carbon (C), and hydrogen (H). These partial charge parameters were calculated using DDEC (Density Derived Electrostatic and Chemical) algorithm to set the force field for electrostatic interactions. Besides, these interactions were handled using the Ewald summation technique[8] with the cut-off radius of 12 Å. The remaining term in Formula (1) describes the van der Waals interactions with an Lennard-Jones (LJ) potential, 6-12 potential. Here, ε_{ij}, σ_{ij} correspond to the depth and diameter of the potential well for each pair of atoms *i* and *j*, handled using Lorentz–Berthelot rule:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j};\ \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad (2)$$

where σ_i, ε_i (*i* represents Ni, N, O, C, H of Ni(BDC)$(TED)_{0.5}$) were taken from general force fields for MOF in RASPA sofware[7] (Table 1). A cut-off radius of 14 Å was utilized for the LJ interactions. This factor affects calculation results, therefore it was checked carefully and showed in the results and discussion section. The calculation used the TraPPE force field for CO_2 molecule[9] with a linear three-point model with bonding length d_{C-O} = 1.16 Å ; whereas, SO_2 was modeled as the three-point model[10] with $d_{S-O} = 1.43$ Å, $\angle_{O-S-O} = 119.5°$. The force field parameters of CO_2 and SO_2 are also listed in Table 1.

Our calculations used the μVT set, where volume V, temperature T and chemical potential μ were constant in the simulation process. The room temperature (298 K) and pressures up to 50 bar were selected. The optimized primary unit cell of Ni(BDC)$(TED)_{0.5}$ has 22 C, 20 H, 8 O, 2 N, 2 Ni (54 atoms). In GCMC, the simulation box was kept fixed, while adsorbate molecules were moved randomly to reach equilibrium adsorption. Each calculated point ran 10^4 equilibration cycles and followed by 2×10^5 MC cycles. These parameters were checked carefully for their equilibrium.

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Table 1. LJ parameters of the atoms in $Ni(BDC)(TED)_{0.5}$

Atoms	ε/k_B [K]	σ [Å]	q [e]
Ni (MOF)	7.55	2.52	0.660
N (MOF)	38.95	3.26	-0.118
O (MOF)	48.16	3.03	-0.528
C (on BDC)	47.86	3.47	-0.067
C (BDC-TED)			-0.079
C (on TED)			-0.025
C (bonded with O)			0.636
H (on BDC)	7.65	2.85	0.093
H (on TED)			0.071
C (CO_2)	27.00	2.80	+0.700
O (CO_2)	79.00	3.05	- 0.350
S (SO_2)	145.90	3.62	0.471
O (SO_2)	57.40	3.01	-0.236

Note that for calculating gas adsorption in MOF, measured experimental data are usually the excess adsorption amount (N_{ex}). Simulations usually calculate the total adsorption amount or the absolute amount of gas adsorbed (N_{ab}). The expression describing the relationship between them is

$$N_{ab} = N_{\text{ex}} + \rho V_{\text{p}}, \quad (3)$$

In which, V_{p} is the pore volume and ρ is the density of gas (CO_2, SO_2) in the bulk phase.

3. RESULTS AND DISCUSSION

3.1. Optimizing and selecting the simulation box for $Ni(BDC)(TED)_{0.5}$

$Ni(BDC)(TED)_{0.5}$ has tetragonal structure symmetry with the lattice constants $a = b$ and the angles $\alpha = \beta = \gamma = 90^o$ (Figure 1). In $Ni(BDC)(TED)_{0.5}$, the metal-oxide-carbon (Ni-O-C) clusters link to BDC and TED ligands. Herein, BDC and TED stand for 1,4-benzene dicarboxylate and triethylenediamine. Stability and high porosity of the paddle-wheel units in the heat are the noticed characteristics to improve the amount of gas adsorbed.[11]

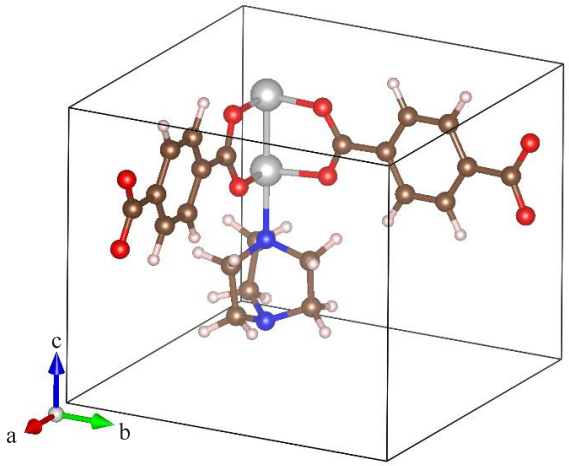

Figure 1. The primary unit cell of $Ni(BDC)(TED)_{0.5}$, herein the atoms Ni, N, O, C, and H correspond to light gray, blue, red, brown, and light pink balls.

After designing and optimizing the unit cell, all the atomic positions in the structure were relaxed to meet the equilibrium state based on the density functional theory with van der Waals (vdW-DF) correction.[12] The obtained results are $a = b = 11.98$ Å and $c = 9.38$ Å, leading to the volume of the unit cell is 1131 Å.[3] The simulated results are entirely close to the experiment data of Tan's group,[5] $a = b = 11.15$ Å and $c = 9.53$ Å. The lengths of the simulation box were repeated three times (≥ 28 Å) to perform GCMC simulations with high accuracy, as shown in Figure 2.

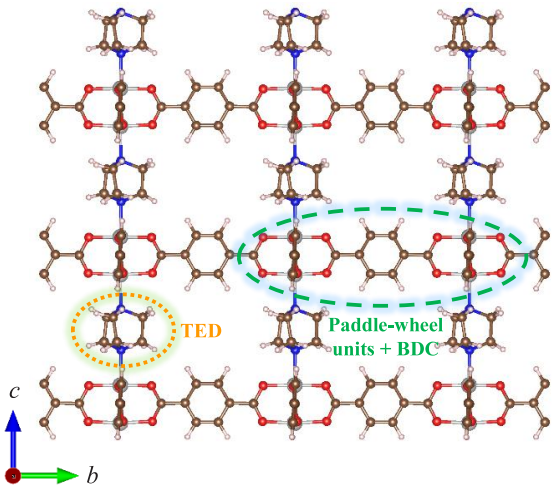

Figure 2. The 2D box of GCMC simulation (viewed along a axis). Two paddle-wheel units and one BDC ligand are in the blue curve; the TED unit is in the orange curve.

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3.2. The cut-off radius for Lennard–Jones interactions

The cut-off radius for electrostatic interactions was taken by default as 12 Å in the code because it has little impact on the amount of gas adsorbed to the MOF. In this section, the cut-off radius for the LJ interactions was regarded.

Based on the amount of gas adsorption in the MOF versus the LJ cut-off radius (r_c) at 1 bar, 5 bar and 10 bar (Figure 3), the value 14 Å was determined. Increasing r_c can improve accuracy, but it is insignificant and takes a long time for calculations. Therefore, we selected the value of approximately 14 Å with the unit cell repeating up 3 x 3 x 3 (*i.e.* 27 times) the unit cell in Figure 2. Furthermore, we also carefully checked the convergence of equilibration and MC cycles. The results achieved 10^4 equilibration cycles and 2 x 10^5 MC cycles.

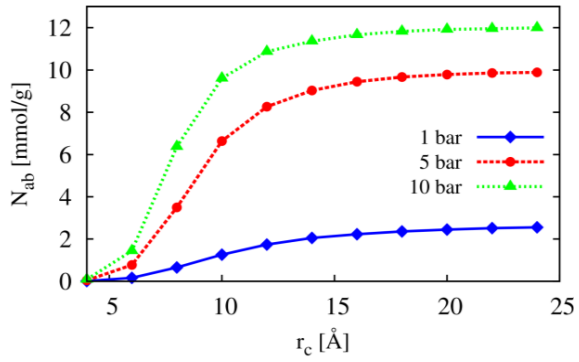

Figure 3. The selected LJ cut-off radius based on CO_2 adsorption in Ni(BDC)(TED)$_{0.5}$.

3.3. Investigation of structural features of Ni(BDC)(TED)$_{0.5}$

After relaxing the ions in the structure and selecting suitable parameters, we also calculated the specific surface area (SSA) and pore volume (V_p) of Ni(BDC)(TED)$_{0.5}$, essential features of porous crystalline frameworks affecting gas capture. The parameters SSA and V_p were determined by calculating the adsorption amount of nitrogen (N_2) at 77 K. This calculation proved to be relatively consistent with the Brunauer-Emmett-Teller (BET) method.[13]

The simulation results are and SSA = 1686 m^2/g and V_p = 0.76 cm^3/g, in good agreement with previous measurement results of experimental groups with specific surface areas corresponding to 1763 m^2/g[11] and 1698 m^2/g.[14] The achievements also show that although the SSA is smaller than the experimental data of X. Fan with 1905 m^2/g for Ni(BDC)(TED)$_{0.5}$, it closely resembles the remaining structural series M(BDC)(TED)$_{0.5}$ (M = Zn, Co, Cu).[15] Besides, the computed results also show that the pore volume of the MOF (0.76 cm^3/g) is entirely suitable with the obtained experimental data of 0.757 cm^3/g.[15] Again, it is proved that our calculations are very reliable.

3.4. Evaluation of the gas capture capacities

Firstly, we selected and tested the force field models before performing the calculations. The amount of gas adsorption corresponding to two force field models for CO_2 molecules, TraPPE[9] and EMP2,[16] are similar at 298 K and under 1 bar (Figure 4). The obtained results are N_{ab} = 2.30 mmol/g (*i.e.* 10.13 wt%) and N_{ex} = 2.27 mmol/g (10 wt%) at room temperature and standard atmospheric pressure. These values are also relatively close to the experimental data of Arstad et al. with 14 wt% under the same conditions.[6]

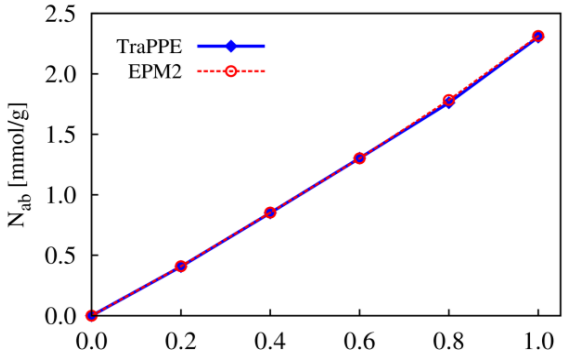

Figure 4. The CO_2 adsorption of Ni(BDC)(TED)$_{0.5}$ using TraPPE and EMP2 force fields.

Two force field models give the same results, so we use the TraPPE model for CO_2 in this work. The gas sorption amounts in Ni(BDC)(TED)$_{0.5}$ with various pressure points up to 50 bar were calculated, and then we plotted the adsorption isotherms for CO_2 and SO_2 at 298 K (Figure 5). At this temperature, CO_2 uptake in

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$Ni(BDC)(TED)_{0.5}$ results in N_{ab} = 13.53 mmol/g (59.53 wt%) and N_{ex} = 12.63 mmol/g (59.56 wt%) at 25 bar. Under the conditions above, Arstad et al.[6] experimentally measured N_{ex} = 60 wt%). Furthermore, at 30 bar, our evaluated excess uptake is approximately 12.7 mmol/g. In this same condition, Chen and coworkers computed N_{ex} = 13.6 mmol/g (*i.e.* 600 mg/g or 60 wt%) for $Zn(BDC)(TED)_{0.5}$,[17] listed in Table 2. In this publication, the highest amount of CO_2 capture in $Ni(BDC)(TED)_{0.5}$ was achieved at the value of 14.40 mmol/g (63,37 wt%) at 50 bar. This value is also remarkable compared to other MOFs evaluated for CO_2 adsorption.[18]

For SO_2, Figure 5 determines that adsorption-based SO_2 capture in $Ni(BDC)(TED)_{0.5}$ rapidly increases at low pressures under 5 bar. The adsorbed gas amount saturate at about 5 bar corresponding to N_{ab} = 13.6 mmol/g. Greater than 5 bar, the adsorbed amount insignificantly increase with increasing pressure to 50 bar (only 0.1 mmol/g achieved in this pressure range). At about 1 bar, our simulation indicated that the amount of gas adsorbed is 12 mmol/g, slightly higher than that of the K. Tan group with 10 mmol/g.[5]

Table 2. Absolute (total) and excess uptakes of CO_2 in $Ni(BDC)(TED)_{0.5}$, compared to other MOFs.

Uptakes	Pressure [bar]		
	1	25	30
N_{ab} (N_{ex}) [mmol/g]	2.30 (2.27)	13.53 (12.63)	13.81 (12.68)
N_{ab} (N_{ex}) [wt%]	10.14 (10.00)	59.53 (55.56)	60.76 (55.80)
$Ni(BDC)(TED)_{0.5}$[6] [wt%]	14	60	
$Zn(BDC)(TED)_{0.5}$[17] [mmol/g]			13.6

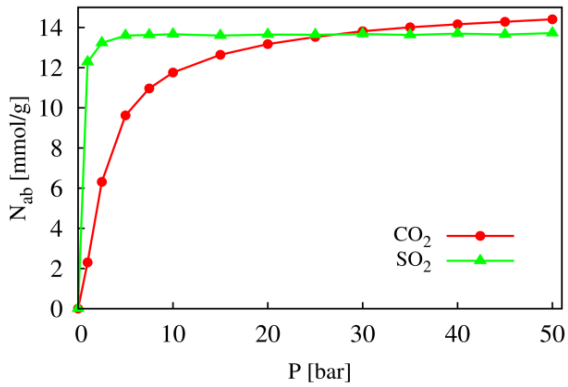

Figure 5. The CO_2 and SO_2 adsorption isotherms in $Ni(BDC)(TED)_{0.5}$ at T = 298 K and P ≤ 50 bar.

Our results also show that SO_2 adsorbs much more powerfully than CO_2 in the low-pressure region below 25 bar. Remarkably, the amount of SO_2 saturates while the CO_2 adsorption continues to increase at higher pressures. Therefore, at 50 bar, it results in N_{ab} CO_2 = 14.4 mmol/g, slightly larger than that of SO_2 with 14.4 mmol/g.

The gas adsorption (the linear 3-atom model) and SO_2 (the 3-atom model with the 119.5^o angle) were also visualized via Figure 6 and Figure 7, respectively. Visualization of gases shows that there is slightly more SO_2 than CO_2 in $Ni(BDC)(TED)_{0.5}$ at identical conditions. Significantly, the amount of SO_2 enormously increases compared to CO_2 according to the pressure up to 5 bar.

We also know the isosteric heat of adsorption (Q_{st}) is also an important parameter relating to gas adsorption. The results, calculated at low-pressures up to 1000 Pa (Figure 8), exhibit the average adsorption heats of SO_2 and CO_2 on $Ni(BDC)(TED)_{0.5}$ with respect to 32.7 kJ/mol and 17.3 kJ/mol. These values also elucidate that this MOF captures SO_2 more highly than CO_2 in the low-pressure region. This tendency is also consistent with the results of D. N. Son et al. with the prediction of adsorption capacities of CO_2 and SO_2 by adsorption energy based on density functional theory.[19] Herein, their work showed that, when studying the simultaneous adsorption of two gases, $Ni(BDC)(TED)_{0.5}$ strongly adsorbs

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SO_2 than CO_2 due to the primary interactions between the *d*-orbitals of Ni metal with the states (*2n, 3n, 4n*) of the SO_2 molecule but barely interacting with those of the CO_2 molecule.

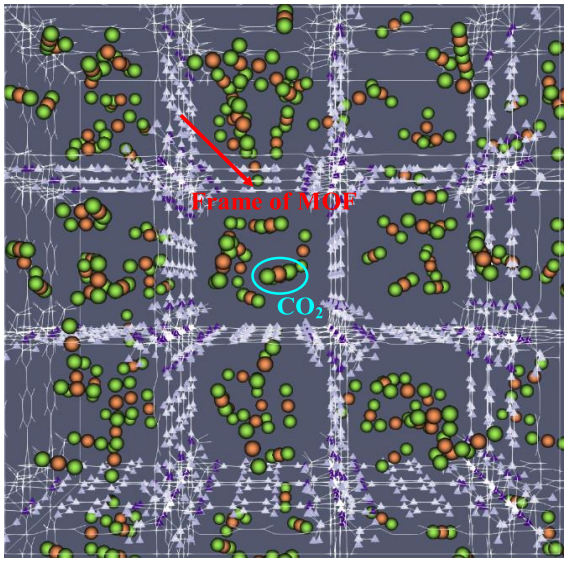

Figure 6. Visualization of CO_2 adsorption in Ni(BDC)$(TED)_{0.5}$ at 0.1 bar and 298 K, herein C and O atoms of CO_2 correspond to dark-orange and light-green balls.

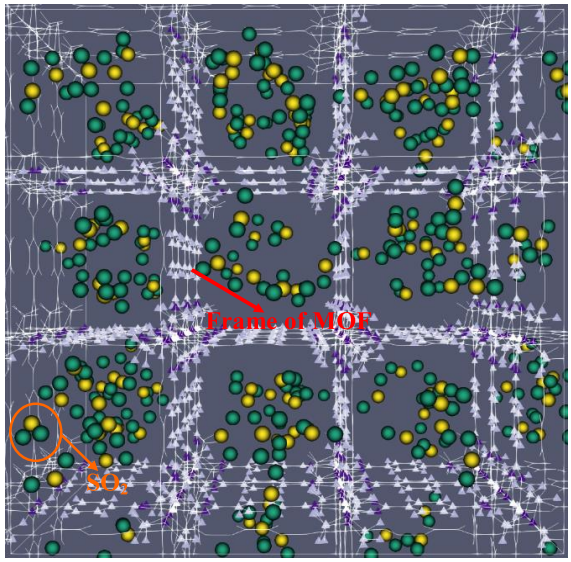

Figure 7. Visualization of SO_2 adsorption in Ni(BDC)$(TED)_{0.5}$ at 0.1 bar and 298 K, in which S and O atoms of SO_2 correspond to yellow and green balls.

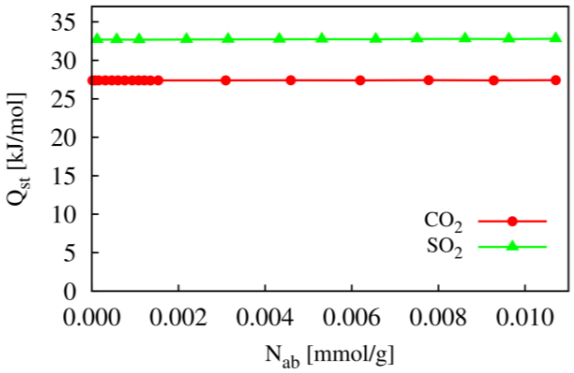

Figure 8. Heat of adsorption (Q_{st}) for CO_2 and SO_2 on Ni(BDC)$(TED)_{0.5}$ at 298 K.

4. CONCLUSIONS

In our research, the cut-off radius for the LJ potential with 14 Å is suitable for GCMC simulations to evaluate CO_2 and SO_2 capture capacities in Ni(BDC)$(TED)_{0.5}$. This value is an important parameter affecting the gas amount adsorbed in the Ni(BDC)$(TED)_{0.5}$ MOF.

Our calculations show that, at low pressures below 25 bar, the capture capacity of SO_2 is more robust than that of CO_2 in Ni(BDC)$(TED)_{0.5}$. Until the pressure exceeds 25 bar, only CO_2 uptake increases slightly while SO_2 uptake saturates. The calculated results are significant with 14.4 mmol/g for CO_2 capture at 50 bar and 13.6 mmol/g for SO_2 at 5 bar.

The heat of gas adsorption on Ni(BDC)$(TED)_{0.5}$ corresponding to the values 32.7 kJ/mol and 17.3 kJ/mol for SO_2 and CO_2 also shows that the SO_2 adsorbs more strongly than CO_2 in the MOF above in the low-pressure range.

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