Nghiên cứu khả năng hấp phụ và tách lọc carbon dioxide của vật liệu MIL-53(Cr) bằng phương pháp mô phỏng cổ điển

TÓM TẮT

Các nguồn năng lượng dựa trên nhiên liệu hóa thạch ngày càng cạn kiệt và lượng khí thải độc hại, đặc biệt là carbon dioxide (CO_2), đang tăng rất nhanh và báo động đến môi trường và sức khỏe con người. Do đó, việc làm giảm hoặc chuyển đổi CO_2 thành các hợp chất có giá trị là hết sức cấp thiết. Trong những thập niên gần đây, việc ứng dụng các vật liệu có độ xốp cao như nhóm vật liệu khung kim loại hữu cơ (MOF) để hấp phụ CO_2 và tách lọc khí CO_2/H_2 đang rất thu hút. Trong các vật liệu MOF, MIL, đặc biệt là MIL-53 rất được chú ý với khả năng hấp phụ và tách lọc cao nhờ vào tính ổn định nhiệt, diện tích bề mặt riêng lớn và chứa các vị trí kim loại mở, v.v. Do vậy, công trình này muốn làm sáng tỏ khả năng hấp phụ và tách lọc CO_2 ở nhiệt độ phòng và áp suất thấp dưới 50 bar bằng phương pháp mô phỏng Monte Carlo chính tắc lớn. Kết quả chỉ ra MIL-53 có khả năng hấp phụ CO_2 cao kể cả khi có và không có mặt H_2 và độ tách lọc CO_2/H_2 cũng rất đáng chú ý. Lượng khí CO_2 (tinh khiết) hấp phụ trong MIL-53(Cr) đạt được là 9,18 mmol/g ở 298 K và 50 bar. Ở 298 K, độ tách lọc CO_2/H_2 cực đại của MIL-53(Cr) là $S_{CO_2/H_2(max)} = 116$. Kết quả đáng chú ý đó là $S_{CO_2/H_2(max)}$ gần như không phụ thuộc vào tỉ lệ mol CO_2:H_2 mà chỉ làm thay đổi áp suất đạt được $S_{CO_2/H_2(max)}$ đó, nhưng lại phụ thuộc rất mạnh vào nhiệt độ, cụ thể $S_{CO_2/H_2(max)}$ = 245 khi giảm nhiệt độ đến 273 K.

Từ khóa: *Hấp phụ CO_2, Bắt giữ CO_2, Tách lọc CO_2/H_2, Vật liệu MIL-53, Mô phỏng cổ điển.*

A classical simulation study for carbon dioxide adsorption and separation capacity of MIL-53(Cr)

ABSTRACT

In addition to the escalating depletion of fossil fuel-based energy sources, toxic emissions, particularly carbon dioxide (CO_2), are rapidly increasing, leading to an alarming impact on the environment and human health. Therefore, reducing or converting CO_2 into high-value chemicals is necessary. In recent decades, CO_2 capture and CO_2/H_2 separation based on the adsorption of highly porous materials, especially metal-organic frameworks (MOFs), has become very attractive. Among MOFs, MIL, notably MIL-53, has been a top concern for its noteworthy adsorption and separation capacity due to its thermal stability, ultra-high specific surface, open metal sites, etc. Therefore, this work mainly uses grand canonical Monte Carlo simulations to study CO_2 adsorption and separation with and without H_2 at room temperatures and low pressures below 50 bar. The high CO_2 adsorption capacity with and without hydrogen and remarkable CO_2/H_2 selectivity of MIL-53(Cr) are explored. For pure CO_2, the absolute CO_2 uptake in MIL-53(Cr) is 9.18 mmol/g at 298 K and 50 bar. Besides, the maximum CO_2/H_2 selectivity of MIL-53(Cr) is $S_{CO_2/H_2(max)} = 116$ at 298 K. Remarkably, this value of $S_{CO_2/H_2(max)}$ is almost independent on the CO_2/H_2 mole fraction, which only changes pressure corresponding to that $S_{CO_2/H_2(max)}$, but dramatically dependent on temperature, reaching $S_{CO_2/H_2(max)} = 245$ when the temperature drops to 273 K.

Keywords: *CO_2 adsorption, CO_2 capture, CO_2/H_2 selectivity, MIL-53 material, classical simulations.*

1. INTRODUCTION

Fossil fuels are our primary energy source, and their consumption is increasingly uncontrollable. This problem has a significantly negative impact on the environment and human health due to the increasing amount of emissions such as CO_2, CO, NO_x, etc., and causes serious energy shortage issues. Furthermore, CO_2 capture, H_2 purification, and CO_2 separation over H_2 are significant in combustion plants and refineries.[1–3] To overcome those problems, the demand for clean energy production, gas separation, and efficient storage has been growing dramatically. Tremendous advances have been achieved in both theory and experiments thanks to the outstanding properties of porous materials.[4–6]

A new type of inorganic-organic hybrid porous materials, metal-organic frameworks (MOFs) with a periodic network, appears as a potential technology.[6–9] Since the early 1990s, MOFs have gained increasing attention, leading to more MOFs have been successfully synthesized by experiments and proposed by simulation methods. Researchers have successfully synthesized about 100,000 MOFs through experiments and have predicted over 500,000 structures by simulations or theories, but only nearly 3,500 works related to MOFs have been published.[10,11]

MILs (Material Institute of Lavoisiers), a class of MOFs, have gained recognition as promising adsorbents for H_2 purification and CO_2 capture thanks to unique properties such as extraordinary chemical and thermal properties, water stability, ultra-large specific surface areas, high porosity, coordinately unsaturated or open metal sites, etc.[12–15] In 2002, the first MIL introduced by Ferey and co-workers was the MIL-53 with M = chromium(III) (Cr^{3+}).[16,17] MIL-53, obtained by the hydrothermal method, has many potential applications because of its good thermal stability and flexibility compared to other MOFs.[18,19] Several works have displayed that MIL-53 (Cr or Al) materials have superior CO_2 capture[20–22] and high selective adsorption for binary mixtures such as CO_2/H_2, CO_2/CH_4, and CO_2/N_2.[19,23,24]

Due to the potential of MIL-53, in this work, we use the classical grand canonical Monte Carlo (GCMC) simulation (a suitable approach to simulate the equilibrium of the physisorption of small gases in porous at well-defined pressure and temperature) to study the capacities of CO_2 capture and CO_2/H_2 separation on MIL-53(Cr).

2. COMPUTATIONAL APPROACHES

GCMC simulations are carried out using the RASPA software[25] to calculate the gravimetric amount of gases (CO_2 and H_2) adsorbed in a solid porous material, MIL-53(Cr), at room temperature and pressures up to 50 bar. The simulation cycles are performed up to 3.0×10^5 Monte Carlo (MC) cycles followed by 1.5×10^4 equilibration steps.

In order to obtain the simulation box, a unit cell of MIL-53 (including 20 hydrogen, 32 carbon, 20 oxygen, and 4 chromium) was optimized by using the density functional theory (DFT),[26] and then repeated the unit cell to 2, 2, and 4 times for a, b, and c lengths ($a = 16.73$ Å, $b = 13.04$ Å, $c = 6.81$ Å), leading to $L_a = 33.46$ Å, $L_b = 26.08$ Å, and $L_c = 27.24$ Å, respectively (Figure 1).

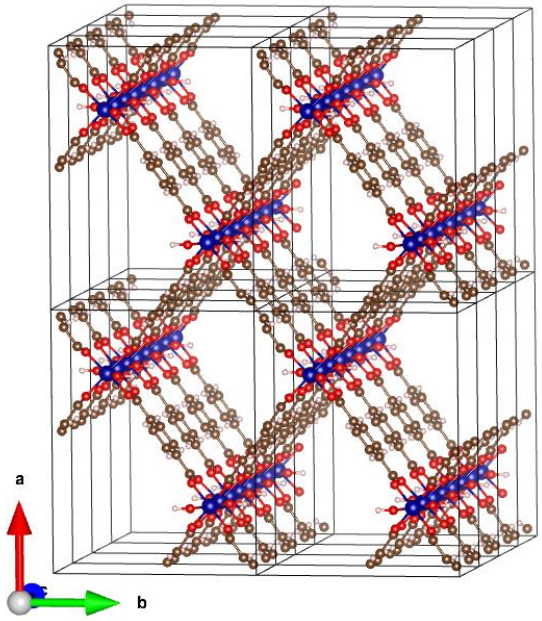

Figure 1. The simulation box of MIL-53(Cr). Each rectangular cubic represents a unit cell.

The interactions between gases (CO_2, H_2) and MIL-53(Cr) include (*i*) van der Waals (vdW) interactions using the Lennard-Jones (LJ) model and (*ii*) electrostatic interactions.

First, the LJ 12-6 repulsive and attractive interactions between pairs of atoms of gases and MIL-53 are described by

$$V_{ij}^{LJ} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], \qquad (1)$$

Herein, ε_{ij} and σ_{ij} are pair LJ parameters, calculated using the pair combining rule of Lorentz and Berthelot,[25] in which σ_i and ε_i are taken from the force fields for MOFs with universal force field for metal (Cr) and DREIDING for other elements of MIL-53 (H, C, O),[27] listed in Table 1. The cut-off radius used for the vdW interaction is 16 Å, tested for reliability.

Second, electrostatic or Coulomb interactions between pairs of atoms are as follows:

$$V_{ij}^{elec} = k_c \frac{q_i q_j}{r_{ij}}, \qquad (2)$$

where k_c is the Coulomb constant and q_i is the partial point charge of atom *i*, calculated by the DFT-based density-derived electrostatic and chemical charges (Table 1 with the labeled atoms as in Figure 2).[28] Additionally, TraPPE force fields are used for CO_2 and H_2, listed in Table 1.

The adsorption separation or selectivity of CO_2 over H_2 in a mixture of H_2 and CO_2 is calculated via the formula[13]

$$S_{CO_2/H_2} = \frac{q_{CO_2}}{q_{H_2}} \Big/ \frac{n_{CO_2}}{n_{H_2}}, \qquad (3)$$

where q_{CO_2}, q_{H_2} are the amount of adsorbed CO_2 and H_2 (mol/g) in MIL-53 and n_{CO_2}, n_{H_2} are mole fraction of the CO_2 and H_2 component in the mixture, respectively. The investigated molar fractions of CO_2:H_2 includes 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1.

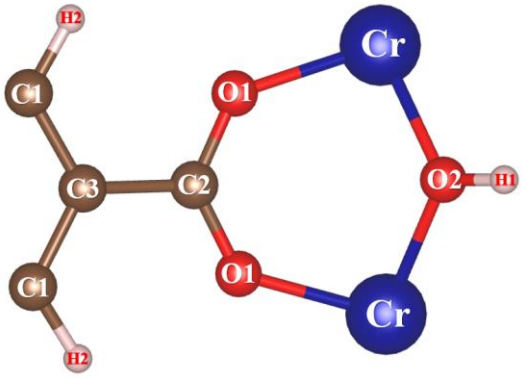

Figure 2. The labeled atoms of MIL-53(Cr), where hydrogen (H), carbon (C), oxygen (O), and chromium (Cr) atoms are displayed by soft pink, brown, red, and blue balls, successively.

Table 1. LJ parameters and partial atomic charges of MIL-53 and gases (H_2 and CO_2).

Atoms	ε/k_B (K)	σ (nm)	Atomic charges (*e*)
Cr	7.548	0.269	+1.581
H1	7.649	0.285	+0.414
H2			+0.100
C1	47.856	0.347	-0.077
C2			+0.636
C3			-0.033
O1	48.158	0.303	-0.589

O2			-0.938
C $[CO_2]$[29]	27.000	0.280	+0.700
O $[CO_2]$[29]	79.000	0.305	-0.350
H_{COM} $[H_2]$[30]	36.700	0.296	-0.936
H $[H_2]$[30]	-	-	+0.468

3. RESULTS AND DISCUSSION

3.1. CO_2 adsorption of MIL-53(Cr)

Firstly, the absolute CO_2 adsorption capacity or uptake is computed and compared with available experimental data. The results (Figure 3) show that the CO_2 uptake increases rapidly in the pressure region below 5 bar, then increases slightly with increasing pressure. The absolute CO_2 uptake is 9.18 ± 0.02 mmol/g or 403.70 ± 0.88 mg/g at 50 bar (the maximum excess CO_2 uptake is 8.02 ± 0.02 mmol/g or 387.23 ± 0.93 mg/g at 30 bar). Our findings show that the absolute amount of CO_2 adsorption on MIL-53(Cr) is consistent with the available data of Bourrelly et al., about 10 mmol/g at 30 bar and 304 K.[20] Otherwise, the obtained CO_2 adsorption heat of MIL-53(Cr) is 30.04 kJ/mol, consistent with data of Bourrelly and co-workers (about 32 kJ/mol).[20] We also find that, at 298 K, the CO_2 adsorption isotherm obtained from molecular simulations also agrees well with the experimental results of the Schneemann group (Figure 3).[31] These agreements between simulation and experimental measures indicate the reliability of the GCMC simulations.

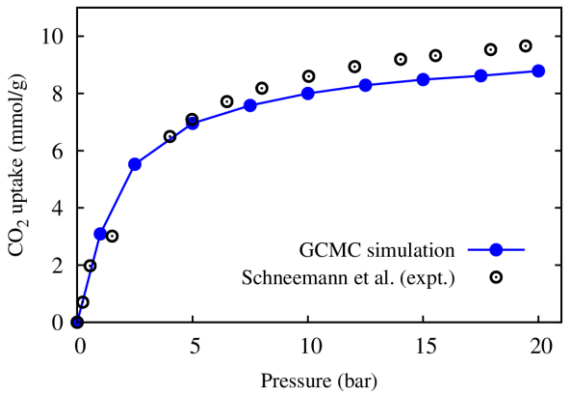

Figure 3. The comparison of the absolute CO_2 adsorption capacity on MIL-53(Cr) at 298 K between GCMC simulation and experimental (expt.) data.[31]

MIL-53(Cr) does not capture CO_2 as strongly as the most highly evaluated MOFs available today; however, these results are comparable to the MIL-88 series (4.0 – 12.1 mmol/g), highly evaluated for CO_2 uptakes[14] with the isosteric heat of adsorption of the MIL-88 series (31.8 – 34.9 kJ/mol).

Next, we study the co-adsorption capacity of MIL-53 for H_2 and CO_2 in their mixture at many different mole fractions (CO_2:H_2 = 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1) at 298 K and pressures $p \leq 50$ bar. Our simulations also exhibit that the CO_2 adsorption is much higher than H_2 because of its high isosteric heat of adsorption (30.04 kJ/mol) compared to H_2 (12.87 kJ/mol) at 298 K and in the low-pressure range. Indeed, Figure 4 shows that MIL-53(Cr) adsorbs CO_2 (9.16 → 6.26 mmol/g) superiorly than H_2 (0.02 → 0.55 mmol/g) when the molar ratio of CO_2:H_2 changes from 1:9 to 9:1. Indeed, the CO_2 uptake insignificantly decreases when the molar ratio of H_2 increases, less than 70% in the mixture, *i.e.* decreasing from 9.18 mol/g (pure CO_2) to 8.37 mmol/g with 8.82% at CO_2:H_2 = 4:6. When the mole fraction of H_2 occupies a large portion of the mixture, the CO_2 uptake decreases significantly. More specifically, the CO_2 uptake in MIL-53(Cr) decreases by 12.64% (9.18 → 8.02 mmol/g), 18.52% (9.18 → 7.48 mmol/g), and 31.81% (9.18 → 6.26 mmol/g) when the molar ratio of H_2 is 70% (CO_2:H_2 = 3:7), 80% (CO_2:H_2 = 2:8), and 90% (CO_2:H_2 = 1:9) compared with pure CO_2 uptake (Table 2). These data demonstrate that MIL-53(Cr) has good selective adsorption of separation for CO_2 over H_2 in the binary mixture of CO_2 and H_2.

Table 2. The absolute CO_2 and H_2 uptakes of MIL-53(Cr) with the different mole fractions of CO_2:H_2, compared to pure CO_2 uptake at room temperature.

CO_2:H_2 mole-fraction	**CO_2 uptake** (50 bar)	**Decrease in comparison to pure CO_2 (%)**	**H_2 uptake** (50 bar)
Pure CO_2	9.18		-
	10 (30 bar)[20]		-
9:1	9.16	0.22	0.02
8:2	9.08	1.09	0.04
7:3	8.95	2.51	0.06
6:4	8.80	4.14	0.09
5:5	8.61	6.21	0.12
4:6	8.37	8.82	0.16
3:7	8.02	12.64	0.22
2:8	7.48	18.52	0.32
1:9	6.26	31.81	0.55

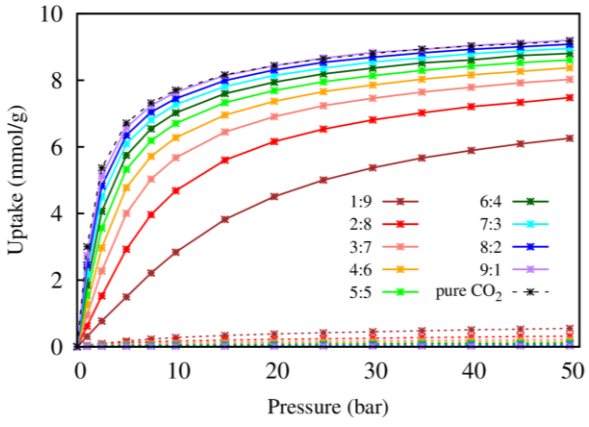

Figure 4. The CO_2 and H_2 co-adsorption isotherms of MIL-53(Cr) at 298 K with different CO_2:H_2 ratios from 1:9 to 9:1. Solid and dot lines refer to the adsorption amount of CO_2 and H_2 on MIL-53(Cr). The black dashed line represents pure CO_2 adsorption on MIL-53(Cr).

3.2. CO_2/H_2 separation of MIL-53(Cr)

From Figure 5b, it can be seen that, at 298 K, the highest selectivity achieved for each CO_2:H_2 mole-fraction greatly depends on pressure. Specifically, they sharply increase at low pressure, reach a peak with the maximum selectivity of CO_2/H_2, and then gradually decrease with pressure to 50 bar. As a result, the maximum CO_2/H_2 selectivity is different for mole ratios of the gas mixture, listed in Column 3 of Table 3 (298 K). When the CO_2 mole-fraction increases, the selectivity reaches its maximum at low pressure (5 – 25 bar). More detail, the maximum selectivity $S_{CO_2/H_2(max)} = 107.87$ at 25 bar for CO_2:H_2 = 1:9, …, and $S_{CO_2/H_2(max)} = 118.25$ at 5 bar for CO_2:H_2 = 9:1 (Table 3). Nevertheless, the maximum selectivity does almost not change with the change of the mole ratio between CO_2 and H_2, $S_{CO_2/H_2} = 116$ (pink line in Figure 6). This trend is similar to the case of MOF5 and Cu-BTC studied previously.[32,33] Remarkably, our data also shows that the CO_2/H_2 selectivity, S_{CO_2/H_2} of MIL-53(Cr) is higher to that of many previous MOFs such as microporous silica (3.5), activated carbon (45.0), zeolites Na-4A (70.7), Cu-BTC ($S_{CO_2/H_2(max)} \approx 150$ at 12.5 bar), MOF-5 ($S_{CO_2/H_2(max)} \approx 36$ at 50 bar)[32] and IR-MOF-*n* with $n = 9, 10, \cdots, 14$ ($S_{CO_2/H_2(max)} \leq 100$).[33]

Furthermore, in this study, we also clarify the effect of temperature on the selectivity of CO_2/H_2 in MIL-53(Cr). Therefore, we performed further research at temperatures of 273 K, 323 K, and 348 K surrounding 298 K. The obtained results, visualized in Figure 5, indicate that the selectivity sharply increases as the temperature decreases. Besides, the pressure at which S_{CO_2/H_2} is maximal decreases with the lowering temperature (Figure 5 and Table 3). For instance, with CO_2:H_2 = 5:5, the maximum selectivities are $S_{CO_2/H_2(max)} = 39.81$ at 15 bar (348 K), 65.17 at 10 bar (323 K), 118.31 at 7.5 bar (298 K), and 246.43 at 2.5 bar (273 K). Figure 5 also shows that the peaks representing the maximum CO_2/H_2 selectivity also reduce as the temperature increases. The maximum CO_2/H_2 selectivity and the pressure corresponding to different mole ratios at four temperatures are listed in Table 3.

Surprisingly, the obtained maximum S_{CO_2/H_2} values are nearly constant when the CO_2 mole-fraction changes from 1/10 to 9/10 of the binary mixture. We determine the average maximum selectivities, $S_{CO_2/H_2} = 245$, 116, 64, and 39 at 273 K, 298 K, 323 K, and 348 K, respectively (Figure 6). This work also shows that the CO_2/H_2 separation significantly increases with decreasing temperature. More importantly, for the maximum S_{CO_2/H_2}, when the temperature drops from 348 K to 273 K, the variation of CO_2/H_2 separation dramatically increases with $\Delta S_{CO_2/H_2} = 25$ (348 K to 323 K), 53 (323 K to 298 K), 128 (298 K to 273 K). Therefore, in order to effectively increase the CO_2 selective adsorption in the mixture (CO_2 and H_2), the temperature can be reduced to achieve the desired separation at suitable pressures for the determined CO_2/H_2 mole-fraction.

Table 3. Maximum CO_2/H_2 selectivity versus mole ratios of CO_2/H_2 at 273 K, 298 K, 323 K, and 348 K.

CO_2:H_2	273 K	298 K	323 K	348 K
1:9	233.97 (15 bar)	107.87 (25 bar)	57.73 (40 bar)	35.27 (50 bar)
2:8	243.04 (7.5 bar)	114.30 (15 bar)	61.95 (30 bar)	37.82 (30 bar)
3:7	244.17 (5 bar)	116.68 (10 bar)	63.55 (20 bar)	38.75 (20 bar)
4:6	246.44 (5 bar)	117.30 (7.5 bar)	64.33 (15 bar)	39.54 (20 bar)
5:5	246.43 (2.5 bar)	118.31 (7.5 bar)	64.74 (10 bar)	39.81 (15 bar)
6:4	248.46 (2.5 bar)	118.34 (5 bar)	65.17 (10 bar)	39.95 (15 bar)
7:3	248.44 (2.5 bar)	118.96 (5 bar)	64.89 (7.5 bar)	40.02 (10 bar)
8:2	247.38 (2.5 bar)	116.78 (5 bar)	65.23 (7.5 bar)	40.04 (10 bar)
9:1	243.44 (2.5 bar)	118.25 (5 bar)	65.37 (5 bar)	40.02 (7.5 bar)

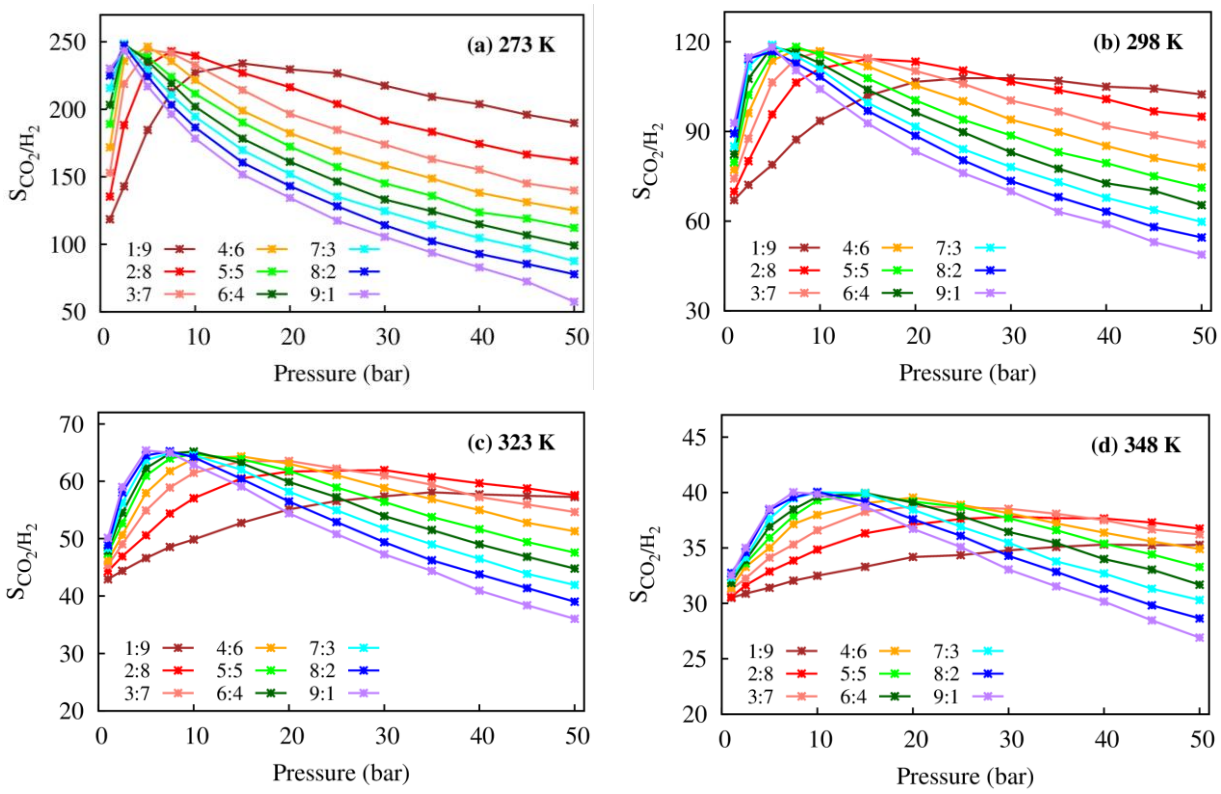

Figure 5. CO_2/H_2 selectivity of MIL-53(Cr) with different CO_2/H_2 mole fractions at temperatures: (a) 273 K, (b) 298 K, (c) 323 K, and (d) 348 K.

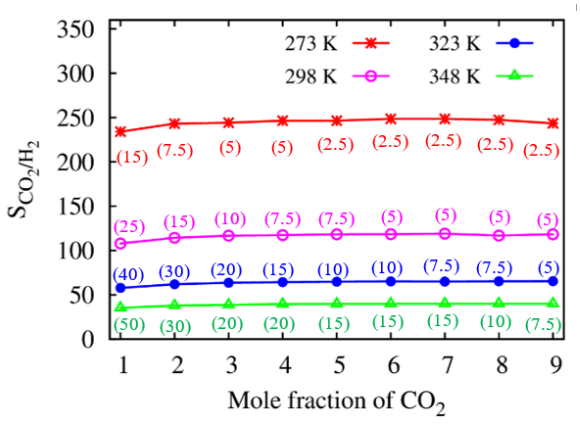

Figure 6. Dependence of maximum CO_2/H_2 selectivity on the mole ratios of CO_2 at 273 K, 298 K, 323 K, and 348 K. The values in parentheses refer to the pressure at which the CO_2/H_2 selectivity is maximum.

4. CONCLUSIONS

This study obtained the important results as follows:

- The CO_2 uptakes in MIL-53(Cr) are high even with the H_2 absence and presence. The CO_2 capture capacity insignificantly decreases when the molar fraction of H_2 increases no more than 60%, *i.e.*, decreasing from 9.18 mmol/g (pure CO_2) to 8.37 mmol/g (CO_2:H_2 = 4:6) with 8.82%.

- The high CO_2/H_2 selectivity is also elucidated at various molar fractions of CO_2:H_2 and at different temperatures (273 K, 298 K, 323 K, and 348 K). The results exhibit that when the CO_2 mole-fraction in the binary mixture increases, the maximum CO_2/H_2 selectivity remains nearly constant, but the pressure corresponding to this maximal selective adsorption remarkably decreases. Moreover, the temperature strongly affects the CO_2 over H_2 separation capacity (116 to 245 for maximum CO_2/H_2 selectivity with decreasing temperature 298 K to 273 K). This work evidences that reducing the temperature can increase the selective adsorption efficiency of CO_2/H_2. Additionally, adjusting the mole fraction between hydrogen and carbon dioxide can help achieve the CO_2/H_2 selectivity at low pressure.

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