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

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TÓM TẮT

Nồng độ khí CO_2 đang tăng rất nhanh đe dọa sự nóng lên toàn cầu, cảnh báo đến môi trường và sức khỏe của 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 kỷ gần đây, việc ứng dụng các vật liệu có độ xốp cao như vật liệu khung hữu cơ kim loại (MOF) để hấp phụ và tách lọc khí CO_2 đang rất thu hút. Trong nhóm MOF, vật liệu MIL, điển hình là MIL-53(Cr) rất được chú ý với khả năng hấp phụ và tách lọc cao nhờ vào tính ổn định nhiệt, diện tích bề mặt riêng rất lớn và chứa các vị trí kim loại mở, v.v. Do vậy, nghiên cứu này sử dụng chính phương pháp mô phỏng Monte Carlo chính tắc lớn, một phương pháp mô phỏng phân tử cổ điển, để tính lượng khí hấp phụ trong MIL-53(Cr) và làm sáng tỏ khả năng hấp phụ CO_2 và tách lọc CO_2/H_2 ở nhiệt độ phòng và áp suất dưới 50 bar. Kết quả chỉ ra khả năng hấp phụ CO_2 và tách lọc CO_2/H_2 của MIL-53(Cr) được đánh giá cao. Cụ thể, lượng khí hấp phụ CO_2 tinh khiết trong MIL-53(Cr) đạt đến 9,18 mmol/g ở 298 K và 50 bar. Độ tách lọc CO_2/H_2 lớn nhất, $S_{CO_2/H_2(max)}$ của MIL-53(Cr) đạt 116 ở 298 K. Nghiên cứu cũng chỉ ra tỷ lệ mol CO_2:H_2 gần như không làm thay đổi giá trị $S_{CO_2/H_2(max)}$ mà chỉ làm thay đổi áp suất đạt $S_{CO_2/H_2(max)}$ đó. Hơn nữa, việc giảm nhiệt độ cũng làm tăng đáng kể khả năng tách lọc khí CO_2/H_2, 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.*

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

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ABSTRACT

Carbon dioxide (CO_2) concentrations are increasing, threatening global warming limits and 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 separation based on the adsorption of highly porous materials, especially metal-organic framework (MOF) materials have become an issue of great interest. Among MOFs, MIL material, notably MIL-53(Cr), has been a top concern for its noteworthy adsorption and separation capacity due to its thermal stability, ultra-high specific surface, open metal sites, and more. Therefore, this work mainly uses grand canonical Monte Carlo simulation, a classical molecular simulation method, to calculate the amount of gas adsorbed in MIL-53(Cr) and study CO_2 adsorption and CO_2/H_2 separation capacity in the mixture of hydrogen (H_2) and CO_2 at room temperatures and low pressures below 50 bar via adsorption isotherms. This research explored the high CO_2 adsorption capacity and the impressive CO_2/H_2 selectivity of MIL-53(Cr). 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, the CO_2/H_2 mole fraction has almost no effect on the value of the maximum SO_2/H_2 separation, $S_{CO_2/H_2(max)}$, but leads to the change of pressure reaching $S_{CO_2/H_2(max)}$. Furthermore, reducing the temperature significantly increases the separation capacity of CO_2/H_2; specifically, $S_{CO_2/H_2(max)} = 245$ 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, and more, and causes severe 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 demands for clean energy production, gas separation, and efficient storage have grown dramatically. Tremendous advances have been achieved in both theory and experiments thanks to the outstanding properties of porous materials.[4–6]

Metal-organic framework (MOF), a new type of inorganic-organic hybrid porous material with a periodic network, appears as a potential technology.[6–9] Since the early 1990s, MOFs have

gained increasing attention, leading to more MOFs that 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, and more.[12–15] In 2002, the first MIL, published 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 molecules 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 to calculate the gravimetric amount of gases (CO_2 and H_2) adsorbed in a solid porous material, MIL-53(Cr),[25] at room temperature and pressure up to 50 bar. The GCMC simulations run up to 3.0 x 10^5 cycles after an initial equilibration of 1.5 x 10^4 steps.

In order to obtain the simulation box for GCMC, a unit cell of MIL-53 (including 20 hydrogen, 32 carbon, 20 oxygen, and 4 chromium) was optimized 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).
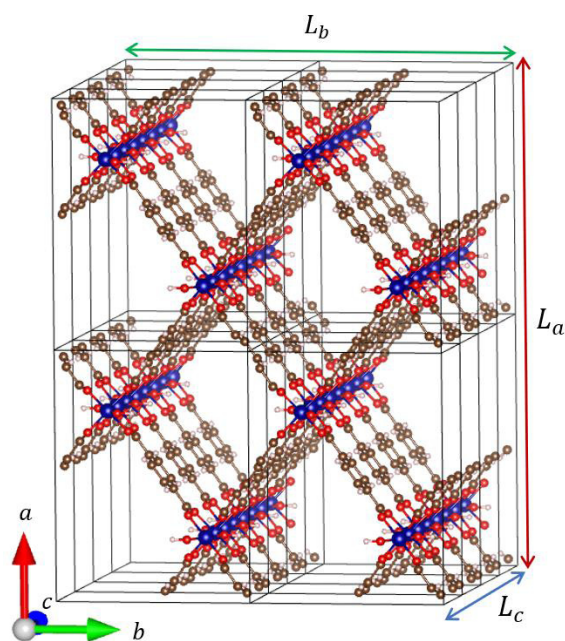

Figure 1. The simulation box of MIL-53(Cr). Each rectangular cube represents a unit cell.

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 presented 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 (Table 1).

The adsorption separation or selectivity of CO_2 over H_2 (CO_2/H_2) in their mixture is calculated via the formula[13]

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

where q_{CO_2} and q_{H_2} are the amount of adsorbed CO_2 and H_2 (mol/g) in MIL-53, respectively; n_{CO_2} and n_{H_2} are mole fractions of the CO_2 and H_2 components 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.
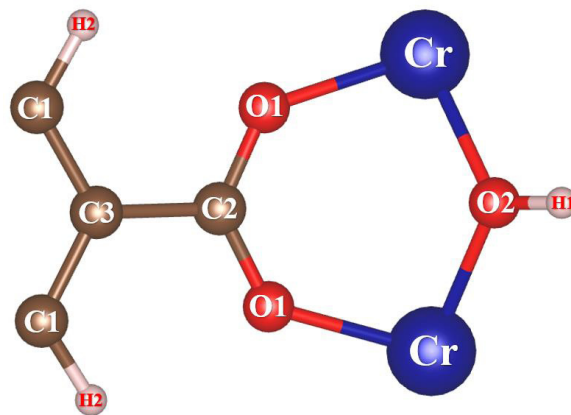

Figure 2. The labeled atoms of MIL-53(Cr), where hydrogen (H), carbon (C), oxygen (O), and chromium (Cr) atoms are displayed by soft pink, brown, red, and blue balls, successively.

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)	Partial point 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 determined 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 the maximum pressure of 50 bar (blue solid line). However, the maximum excess CO_2 uptake is 8.02 ± 0.02 mmol/g or 387.23 ± 0.93 mg/g at the saturated pressure of 30 bar (red dashed line). 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] Moreover, 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 absolute CO_2 adsorption isotherm obtained from molecular simulations (blue line with solid circles) also agrees well with that of the Schneemann group (back open circles for experimental data) (Figure 3).[31] These agreements between simulation and experimental measures indicate the reliability of the GCMC simulations.

At room temperature, MIL-53(Cr) is not able to capture CO_2 as strongly as the most highly evaluated MOFs available today, such as MOF-200 (2400 mg/g at 50 bar), MOF-210 (2396 mg/g at 50 bar), MOF-117 (33.5 mmol/g), MIL-100(Cr) (18 mmol/g), and more;[14] however, these results are comparable to the MIL-88 series (4.0 – 12.1 mmol/g), relatively well recorded for CO_2 uptake with the isosteric heat of adsorption of the MIL-88 series (31.8 – 34.9 kJ/mol).[14]
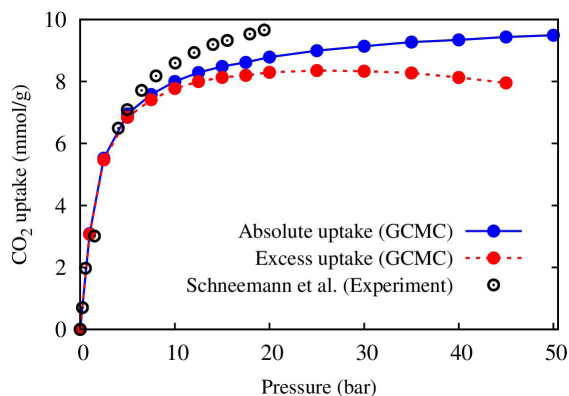

Figure 3. The comparison of the absolute CO_2 adsorption capacity on MIL-53(Cr) at 298 K between GCMC simulation and experimental data.[31]

Next, we study the co-adsorption capacity of MIL-53 for H_2 and CO_2 in the binary 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 below 50 bar (Figure 4 and Table 2). At 298 K, our simulations also exhibit that the uptake of CO_2 is much higher than that of H_2. This conclusion is reasonable because the average adsorption heat of CO_2 (30.04 kJ/mol) is more than two times higher than that of H_2 (12.87 kJ/mol) in the low-pressure range. Indeed, Figure 4 shows that MIL-53(Cr) adsorbs CO_2 ($9.16 \rightarrow 6.26$ mmol/g) superiorly than H_2 ($0.02 \rightarrow 0.55$ mmol/g) when the molar ratio of CO_2:H_2 changes from 1:9 $\rightarrow$ 9:1. The exciting result is that the CO_2 uptake insignificantly changes when the molar ratio of H_2 is less than or equal to 60% in the mixture. For example, the CO_2 uptake decreases from 9.18 mol/g for pure CO_2 adsorption to 8.37 mmol/g for the case of CO_2:H_2 = 4:6 (40% CO_2 and 60% H_2), making an only 8.82% reduction compared to pure CO_2. The presence of a high mole fraction of H_2 in the mixture leads to a significant decrease in CO_2 uptake of MIL-53(Cr). More specifically, compared to pure CO_2 uptake (9.18 mmol/g), the CO_2 uptake decreases by 12.64% to 8.02 mmol/g, 18.52% to 7.48 mmol/g, and 31.81% to 6.26 mmol/g when the molar ratio of H_2 in

the binary mixture occupies 70% (CO_2:H_2 = 3:7), 80% (CO_2:H_2 = 2:8), and 90% (CO_2:H_2 = 1:9) (Table 2), respectively. These impressive results demonstrate that MIL-53(Cr) has stable and good selective adsorption for CO_2 over H_2 in their binary mixture.

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

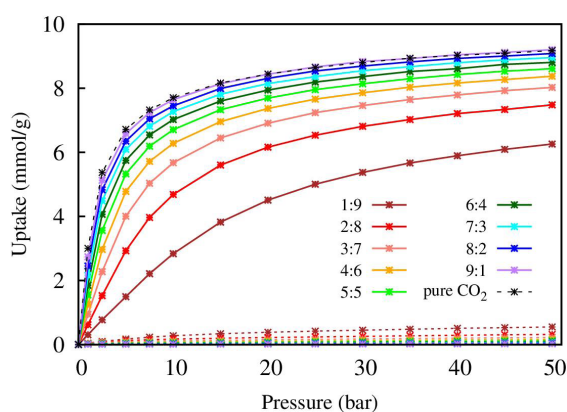**Figure 4.** The CO_2 and H_2 co-adsorption isotherms of MIL-53(Cr) at 298 K with different CO_2:H_2 ratios from 1:9 to 9:1. Solid and dot lines refer to the adsorption amount of CO_2 and H_2 on MIL-53(Cr). The black dashed line represents pure CO_2 adsorption on MIL-53(Cr).

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

From Figure 5a, it is evident that at 298 K, the highest selectivity achieved for each CO_2:H_2 mole-fraction greatly depends on pressure. Specifically, the CO_2/H_2 selectivity sharply increases at low pressure, peaks at the maximum CO_2/H_2 selectivity [$S_{CO_2/H_2(max)}$], and then gradually decreases with pressure to 50 bar. As a result, the maximum CO_2/H_2 selectivity varies for CO_2:H_2 mole ratios, listed in Column 3 of Table 3 (298 K). In addition, the pressure corresponding to the maximum CO_2/H_2 selectivity decreases with an increase in CO_2 mole fraction and a decrease in H_2 mole fraction. More detail, the maximum selectivity $S_{CO_2/H_2(max)}$ = 107.87 at 25 bar for CO_2:H_2 = 1:9, 114.30 at 15 bar for CO_2:H_2 = 2:8, …, and 118.25 at 5 bar for CO_2:H_2 = 9:1 (at 298 K of Table 3). Surprisingly, the maximum CO_2/H_2 selectivity in MIL-53(Cr) remains nearly consistent regardless of the change in the molar ratio between CO_2 and H_2, averaging $S_{CO_2/H_2(max)}$ = 116 at 298 K (pink line in Figure 6). This tendency is similar to the case of MOF-5 and Cu-BTC studied by experiments.[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 than that of many previous MOFs, such as microporous silica (3.5), activated carbon (45.0), zeolites Na-4A (70.7), Cu-BTC (150 at 12.5 bar), MOF-5 (36 at 50 bar)[32] and IR-MOF-*n* with *n* = 9, 10,…, 14 (≤ 100).[33]

Furthermore, our study delves into the influence of temperature on the selectivity of CO_2/H_2 in MIL-53(Cr). To accomplish this, we perform further investigation at temperatures of 273 K, 323 K, and 348 K surrounding 298 K, visualized in Figures 5 b, c, and d, respectively. Our results show the pressure with the maximal value of S_{CO_2/H_2} decreases with the lowering temperature (Figure 5 and Table 3). For instance, at 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 for CO_2/H_2 separation broaden as the temperature increases (Figure 5). The maximum CO_2/H_2 selectivity and the pressure corresponding to different mole ratios at four temperatures are listed in Table 3.

Similar to the case of 298 K discussed above, the maximum S_{CO_2/H_2} values in MIL-53(Cr) also remain constant with changes in the molar ratio between CO_2 and H_2 at 273 K, 323 K, and 348 K. The average maximum selectivities are 245, 116, 64, and 39 at 273 K, 298 K, 323 K, and 348 K, respectively (Figure 6). These results indicate that decreasing temperature significantly increases CO_2/H_2 separation. 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. Specifically, the maximum CO_2/H_2 selectivity increases 25, 53, and 128 when the temperature drops from 348 K to 323 K, 323 K to 298 K, and 298 K to 273 K, successively. As reported in the literature, the gas adsorption

capacity at different temperatures strongly depends on the gas-MOF interactions.[34] At higher temperatures, the reduction in CO_2/H_2 selectivity is attributed to the weaker interaction between CO_2 and MIL-53, causing a remarkable decrease in the CO_2 adsorption of MIL-53. Conversely, the H_2 adsorption in MIL-53 is minimal, so it remains largely unaffected by changes in temperature compared to CO_2.[1] Therefore, the CO_2/H_2 separation capacity strongly depends on the temperatures. It should also be noted that in order to gain insight into the interactions between H_2, CO_2 and MIL-53(Cr), first-principles calculations are essential, and it takes a long time to implement; therefore, we will explore this issue further in future studies.

It can be concluded that to significantly boost the CO_2 selective adsorption in the mixture of CO_2 and H_2, lowering the temperature is able to achieve the desired CO_2/H_2 separation at appropriate pressures based on the determined CO_2:H_2 mole fraction.
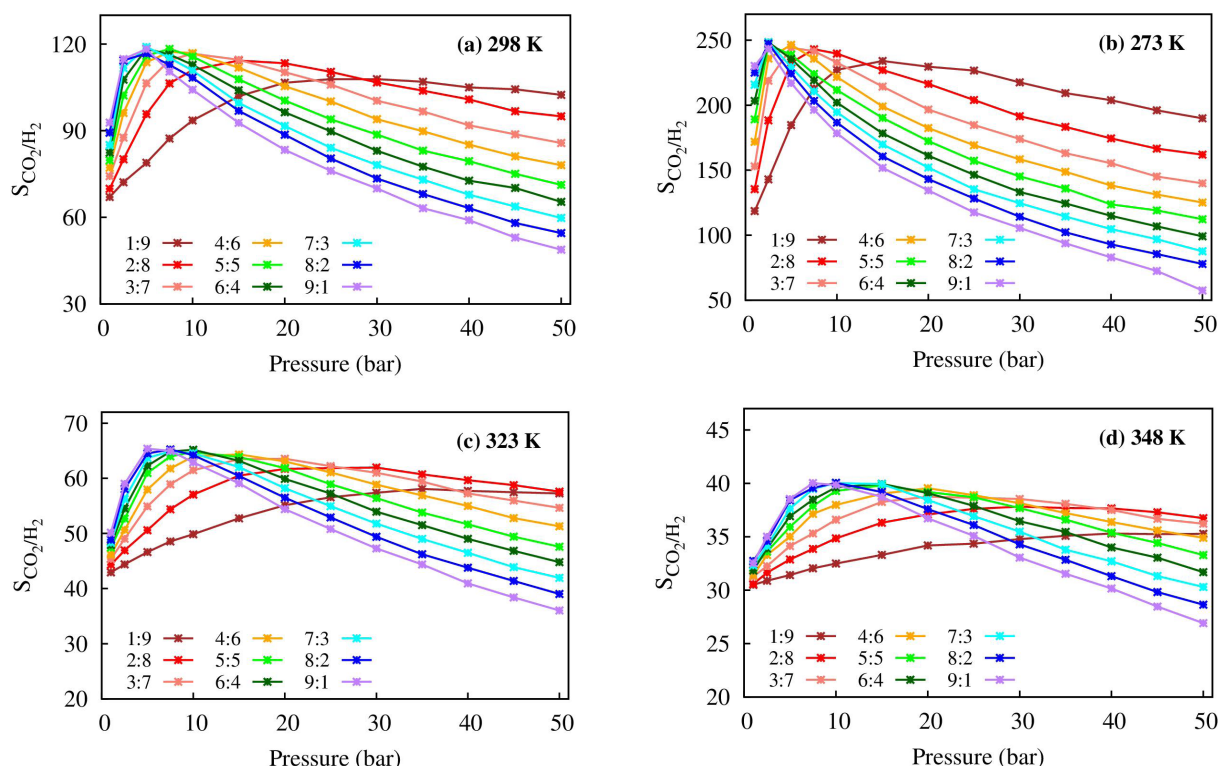

Figure 5. CO_2/H_2 selectivity of MIL-53(Cr) with different CO_2/H_2 mole fractions at temperatures: (a) 298 K, (b) 273 K, (c) 323 K, and (d) 348 K.

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.

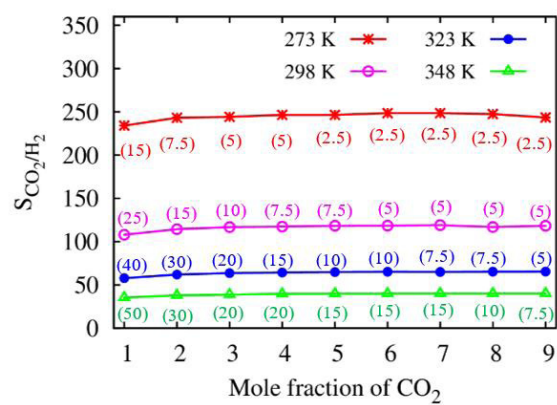| $CO_2:H_2$	273 K	298 K	323 K	348 K
1:9	233.97 (15.0 bar)	107.87 (25.0 bar)	57.73 (40.0 bar)	35.27 (50.0 bar)
2:8	243.04 (7.5 bar)	114.30 (15.0 bar)	61.95 (30.0 bar)	37.82 (30.0 bar)
3:7	244.17 (5.0 bar)	116.68 (10.0 bar)	63.55 (20.0 bar)	38.75 (20.0 bar)
4:6	246.44 (5.0 bar)	117.30 (7.5 bar)	64.33 (15.0 bar)	39.54 (20.0 bar)
5:5	246.43 (2.5 bar)	118.31 (7.5 bar)	64.74 (10.0 bar)	39.81 (15.0 bar)
6:4	248.46 (2.5 bar)	118.34 (5.0 bar)	65.17 (10.0 bar)	39.95 (15.0 bar)
7:3	248.44 (2.5 bar)	118.96 (5.0 bar)	64.89 (7.5 bar)	40.02 (10.0 bar)
8:2	247.38 (2.5 bar)	116.78 (5.0 bar)	65.23 (7.5 bar)	40.04 (10.0 bar)
9:1	243.44 (2.5 bar)	118.25 (5.0 bar)	65.37 (5.0 bar)	40.02 (7.5 bar)

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 corresponding to the maximum CO_2/H_2 selectivity for each $CO_2:H_2$ mole fraction.

4. CONCLUSIONS

This study obtained significant results:

- The CO_2 uptakes in MIL-53(Cr) are high with the absence and presence of H_2. 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 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 separation capacity of CO_2 over H_2. Specifically, the maximum CO_2/H_2 selectivity decreases from 116 to 245 with the decreasing temperature from 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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