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Harnessing solvent effect to integrate alkylamine into metal-organic frameworks for exceptionally high CO_2 uptake

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Humanity's heavy dependence on fossil fuels causes the release of large amounts of carbon dixoide (CO_2) into the air. To avoid an irreversible disturbance of the atmosphere and global climate, considerable research efforts have been devoted to reducing CO_2 emissions. Employing metal-organic frameworks (MOFs) as solid adsorbents for CO_2 is deemed as a promising means to alleviate the problem. Among the MOF family, MIL-101(Cr) is a member with ultrahigh porosity, large window openings, and excellent stability, which is anticipated to display very high CO_2 capture capacities if functionalized with alkylamine. However, the reported alkylamine modified MIL-101(Cr) materials have not shown impressively high CO_2 uptakes as other alkylamine functionalized MOFs whose pristine frameworks have comparably high porosities and large window or channel sizes as MIL-101(Cr). The rare existence of an excellent MIL-101(Cr) based CO_2 adsorbent drives us to investigate the alkylamine tethering process to further unleash the potential of modified MIL-101(Cr) as CO_2 adsorbent. Herein, we report incorporating alkylamine into MIL-101(Cr) using a solvent (cyclohexane) with vanishingly small polarity as the dispersion medium. The resulting modified MOF displays an enhanced amine loading amount and a significantly increased CO_2 capture capacity compared with that prepared in a more polar solvent. The improvement is mainly attributed to the weaker interaction between alkylamine and solvent and the concomitant higher chemical potential of the dispersed alkylamine molecules. This drives more alkylamine molecules into the framework from the solution, and leads to MOFs with higher alkylamine loading amounts and higher CO_2 uptakes. The generated tris(2-aminoethyl)amine (TAEA) modified MIL-101(Cr) exhibits exceptionally high CO_2 uptakes of 4.21 mmol/g at 150 mbar and 25 °C, and 4.06 mmol/g at 150 mbar and 40 °C in gas sorption measurements. Apart from this, the material also displays remarkably different breakthrough time for CO_2 and N_2, and is capable to capture 4.35 mmol/g CO_2 at 25 °C or 4.22 mmol/g CO_2 at 40 °C in the dynamic breakthrough experiments with a gas mixture of 15:85 CO_2/N_2 (v/v). This performance reveals the promise of our material to be practically applied as an effective CO_2 capture adsorbent.

Introduction

Human society continues to rely heavily upon fossil fuels as the main energy source for development. The combustion of fossil fuels inevitably generates carbon dioxide (CO_2) and increases the CO_2 concentration in air due to uncontrolled release.[1] To prevent irreversible disturbance of the atmospheric balance and pursue sustainable living, research efforts have been directed to studying how to mitigate CO_2 emissions.[2] Since 60% of the total CO_2 emission worldwide comes from electricity generation,[3] employing effective measures to remove CO_2 from gas mixtures of power plants would significantly reduce the emission amount. Current technologies entail the use of aqueous amine absorbents to capture CO_2, but they consume excessive energy for regeneration and incur severe corrosion to the infrastructure.[4] Thus, it is pressing to explore new materials to remove combustion-generated CO_2 efficiently.

Metal-organic frameworks (MOFs) are an emerging class of crystalline porous materials built from metal ions/clusters and organic ligands.[5] Their unique high porosities and high surface areas enable a wide range of applications, such as gas storage,[6] separation,[7] catalysis,[8] chemical sensing,[9] drug delivery,[10] etc.[11] When employed as adsorbents to capture CO_2, the solid nature of MOFs helps them circumvent the high regeneration energy and equipment corrosion issue as associated with the traditional methods. Moreover, the high porosities, controllable pore sizes and modifiable functionalities of MOFs facilitate the chemically altering of their interior for the achievement of desired CO_2 capture performance.[12]

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Among the rich library of MOFs, MIL-101(Cr) is an ultraporous framework with two types of mesopores (2.9 nm and 3.4 nm in diameter, respectively) and large windows (1.2 nm and 1.6 nm in diameter, respectively).[13] These structural advantages allow the network to readily accommodate functional moieties as well as the gas species to be adsorbed. Additionally, MIL-101(Cr) is extraordinarily stable and can survive in harsh chemical conditions including highly basic alkylamine solutions.[14] Thus, functionalizing MIL-101(Cr) with alkylamine has been proposed to not only enhance the CO_2 affinity in the MOF but also maintain its advantages as a porous solid adsorbent to selectively adsorb CO_2 from gas mixtures.[14a, 15] Precedent examples are reported with alkylamine modified MIL-101(Cr) showing apparently higher CO_2 adsorption amounts than the pristine MOF.[14a, 15-16] However, these reported values are much lower than other MOFs functionalized by alkylamine whose pristine frameworks have similarly high porosities and comparably large window or channel sizes, such as Mg_2(dobpdc).[7e, 12d, 12n, 17] We believe the CO_2 capture potential of alkylamine modified MIL-101(Cr) has not been completely realized yet. The idea encourages us to inquire into the alkylamine tethering process and develop an approach to unleashing the potential of alkylamine modified MIL-101(Cr) in CO_2 capture.

Herein, we report incorporating alkylamine into MIL-101(Cr) using a solvent species (cyclohexane) with vanishingly small polarity as the dispersion medium. The generated amine modified MOF has CO_2 uptakes of 4.21 mmol/g at 150 mbar and 25 °C, and 4.06 mmol/g at 150 mbar and 40 °C on the basis of pure gas sorption measurements. The adsorbent also exhibits comparably high CO_2 adsorption capacities of 4.35 mmol/g at 25 °C and 4.22 mmol/g at 40 °C with successful CO_2/N_2 separation when evaluated in dynamic breakthrough experiments using a gas mixture of 15% CO_2 and 85% N_2. The excellent CO_2 capture performance of the material is mainly ascribed to the weaker interaction between the less polar solvent and alkylamine molecules, and the concomitant higher chemical potential of the dispersed alkylamine than those in more polar solvents. The higher chemical potential drives more alkylamine molecules into the framework, and leads to MOFs with higher alkylamine loading amounts, higher CO_2 affinity and enhanced CO_2 capture abilities.

Experimental

Preparation of alkylamine modified MIL-101(Cr)

Method A. Activated MIL-101(Cr) powder (100 mg, 0.146 mmol) was added to an alkylamine solution prepared by dispersing 1.11 mmol of diethylenetriamine (DETA, 0.120 mL; **Figure 1** left) or tris(2-aminoethyl)amine (TAEA, 0.166 mL; **Figure 1** right) in 8 mL of anhydrous dichloromethane (DCM). The suspensions were stirred at room temperature (RT) for 24 h. The resulting solids (denoted as Sample 1 and Sample 2, respectively) were washed with anhydrous DCM for three times, desiccated under vacuum with a Schlenk line, and activated under vacuum at 60 °C before gas sorption measurements. Note that the quantities of MOF powder, DETA and DCM were maintained to be the same as reported.[14a] The amount of TAEA was calculated by making its number of moles the same as DETA.

Method B. Activated MIL-101(Cr) (100 mg, 0.146 mmol) was added to an alkylamine solution prepared by dispersing 1.11 mmol of DETA (0.120 mL) or TAEA (0.166 mL) in 8 mL of anhydrous cyclohexane (CH). The suspensions were stirred at RT for 5 min. The resulting solids (denoted as Sample 3 and Sample 4, respectively) were washed with anhydrous CH for three times, desiccated under vacuum with a Schlenk line, and activated under vacuum at 55 °C before gas sorption measurements. Note that the quantities of MOF powder, alkylamine and solvent were kept to be the same as those in Method A. Only the solvent species was changed from DCM to CH. The amine tethering conditions of the four samples are summarized in **Table 1**.

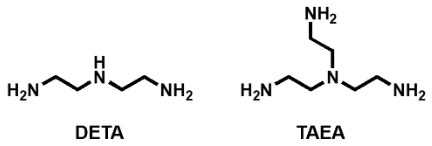

Figure 1. Chemical structures of the alkylamine species utilized to functionalize MIL-101(Cr).

Table 1. Summary of the solvent, alkylamine species, and reaction time (the time the suspension is stirred after pristine MOF is added to the alkylamine solution) for Sample 1-4.

Sample No.	Solvent	Alkylamine	Reaction time
1	DCM	DETA	24 h
2	DCM	TAEA	24 h
3	CH	DETA	5 min
4	CH	TAEA	5 min

Recyclability test

The recyclability of the sample was performed on a thermogravimetric analysis (TGA) instrument. About 13 mg of sample was loaded into the aluminium pan. In the preparation step, the sample was maintained in a He flow at 40 °C for 10 min before being heated to 70 °C to remove the remaining solvent or moisture. After 10 min, the temperature was reduced back to 40 °C and was held at 40 °C for 10 min before the recyclability test. In each cycle, the adsorption condition was 40 °C with a gas flow of 15% CO_2 and 85% He, while the desorption condition was 90 °C with a pure He flow. The adsorption and desorption periods were set to be 30 min and 10 min, respectively. After each cycle, the sample was maintained in a He flow at 40 °C for 10 min before the next cycle.

Breakthrough experiments

Dynamic column breakthrough experiments were carried out using a home-built setup coupled with a mass spectrometer (Hiden QGA) (**ESI, Figure S25**).[18] Dry MOF powders (0.2-0.4 g) were packed into a stainless steel column (7 cm in length and 0.46 cm in inner diameter) in a glovebox. Before experiments, the packed column was purged under a constant He flow (8 ± 0.5 mL min^{-1}). A (15 ± 1)/(85 ± 1) CO_2/N_2

(v/v) binary gas mixture with a flow rate of 9.5 ± 0.5 mL min^{-1} was introduced to the bypass line with a resistance (controlled by a needle valve) comparable to the pressure drop (0-0.2 bar) in the adsorbent column to calibrate the dead volume of the system. A He flow (8 ± 0.5 mL min^{-1}) was introduced to clean the whole system afterwards. Breakthrough experiments were initiated by switching from the purging He gas to the (15 ± 1)/(85 ± 1) CO_2/N_2 (v/v) binary gas mixture (stabilized for 30 min in advance). An Ar flow was kept at 5 mL min^{-1} during the experiments as an internal reference gas to calibrate the flow rate of the exit gas. The upstream and downstream pressures were recorded by pressure gauges. The original breakthrough curves were obtained as a relative $CO_2/N_2/Ar$ composition versus elapsed time. The data were converted to molar fraction ratio versus CO_2 injection amount subsequently.

Results and discussion

In our previous investigation of alkylamine tethering in a MIL-101(Cr) based MOF bearing sulfonic acid groups, four different solvents (methanol, tetrahydrofuran, DCM and CH) were utilized to disperse the alkylamine, while all the other experimental factors were maintained to be the same to perform control experiments.[19] It was unveiled that the amine modified MOF prepared in CH had evidently more alkylamine incorporated and displayed a higher CO_2 uptake, which was ascribed to the very small polarity of CH. So we propose that such experience can be taken advantage of to prepare an excellent alkylamine modified MIL-101(Cr) sample for CO_2 capture by substituting the commonly used more polar solvents with the much less polar CH as the dispersion medium. Through this approach, we would be able to incorporate sufficiently large amount of alkylamine molecules into MIL-101(Cr) so that a framework with strong CO_2 affinity as well as adequate space to allow easy access to the amine groups for CO_2 molecules can be achieved to better realize the CO_2 capture potential of alkylamine modified MIL-101(Cr).

The precedent adsorbent based on which we set up our control experiments is a DETA modified MIL-101(Cr) material prepared in DCM, which has a moderately high CO_2 uptake.[14a] Four samples were prepared following different procedures. Sample 1 was synthesized exactly as previously reported.[14a] Sample 2 was fabricated by only replacing the alkylamine species DETA in the reported procedure with TAEA, which has more amine groups in a single molecule and is likely to improve the CO_2 uptake of the generated sample. Sample 3 was prepared by merely substituting the solvent species DCM in the reported procedure with CH. As for Sample 4, both the alkylamine and solvent were changed with TAEA and CH, respectively (**Table 1**).[19] To investigate whether these adjustments can give rise to adsorbents with better performance in CO_2 capture and also clarify which of the two experimental factors affects the CO_2 capture ability of the resulting material more significantly, the gas sorption properties of the four samples were examined and carefully analyzed.

Pore volumes and CO_2 uptakes of the alkylamine modified MIL-101(Cr)

The crystallinities of the MOFs are maintained well after the incorporation of alkylamine, because their PXRD patterns remain unchanged compared with that of the pristine MIL-101(Cr) (**Figure S7**), eliminating the possibility of structural collapse or phase change. The pore size distributions of Sample 1-4 (determined from their N_2 adsorption isotherms at 77 K, **Figure 2a**) also indicate the maintenance of sufficient pores in the frameworks after the incorporation of alkylamine.

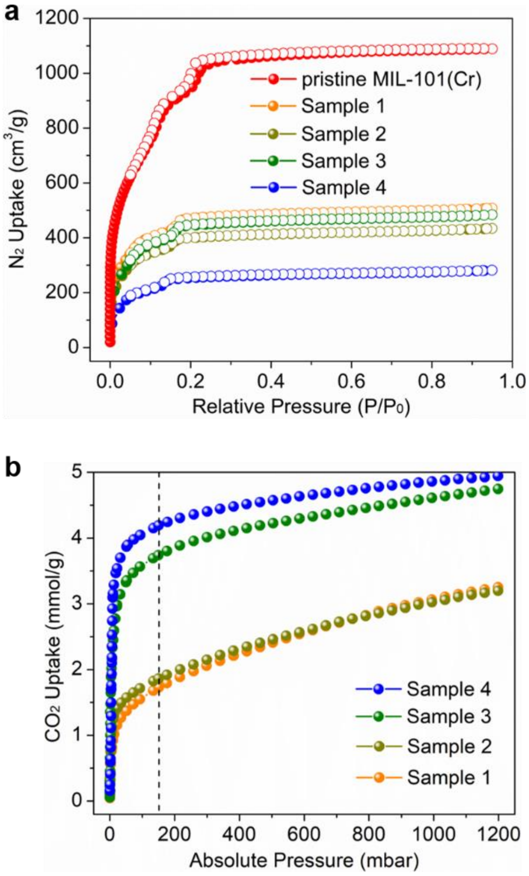

Figure 2. (a) N_2 uptakes at 77 K of Sample 1-4; (b) CO_2 uptakes at 25 °C of Sample 1-4. The dashed line represents an absolute pressure of 150 mbar.

The CO_2 adsorption isotherms of Sample 1-4 are collected at 25 °C (**Figure 2b and ESI Section 15**). Both the CO_2 and N_2 isotherms of Sample 1 closely resemble those of the reported material,[14a] suggesting our successful repetition of the material. Comparing the samples prepared in the same solvent, the CO_2 uptake of the TAEA-modified MIL-101(Cr) at 150 mbar is approximately 10% higher than that of the DETA counterpart. By contrast, MOFs modified with the same alkylamine but in different solvents display remarkably different CO_2 adsorption isotherms. The CO_2 uptakes of Sample 3 (3.75 mmol/g) and Sample 4 (4.21 mmol/g) at 150 mbar are more than twice as much as those of Sample 1 (1.70 mmol/g) and Sample 2 (1.88 mmol/g), respectively. These outcomes strongly indicate that solvent species during sample preparation is a more crucial experimental factor in determining the CO_2 capture performance of the alkylamine modified MOFs in this system.

Thermodynamic equilibria reached in alkylamine incorporation

To investigate why solvent species is so influential to the CO_2 adsorption performance of the generated samples, it is important to discern whether the question should be approached from a thermodynamic or kinetic perspective.

In Method A, the reaction time is 24 h, which is sufficiently long to assume that the amine tethering system has reached its equilibrium. However, in Method B, the reaction time is merely 5 min, which is comparatively inadequate to arrive at the same conclusion. To clarify this point, control experiments were conducted by extending the reaction time in Method B to 30 min while keeping the other experimental factors unchanged to obtain Sample 5 (modified by DETA) and Sample 6 (modified by TAEA). It turns out that both CO_2 and N_2 sorption isotherms of Sample 5 almost overlap those of Sample 3, with a slight difference at high pressures in the CO_2 isotherms. This might have come from the different disposition of the alkylamine molecules within the framework that made the approachable space for CO_2 molecules slightly varied in different samples (**Figure S9**). Such phenomena were also observed for Sample 6 and Sample 4. These results indicate that regardless of the alkylamine species, increasing the reaction time in Method B cannot produce a sample with appreciably different gas sorption properties compared with the one prepared in just 5 min. This implies that equilibrium has also been achieved in the alkylamine tethering system in Method B. As a result, the effect of solvent should be rationalized from a thermodynamic perspective.

Influence from solvent polarity in alkylamine incorporation

We propose that the essential property in solvent that affects the CO_2 uptakes of the modified MOFs is the polarity of solvent. Specifically, CH (0.006) is a far less polar solvent compared with DCM (0.309), as indicated by their relative polarity values.[20] Accordingly, it has relatively weaker interaction with the alkylamine molecules dispersed in it. This leads to a higher chemical potential of the alkylamine in CH than that in DCM. The higher chemical potential of alkylamine in CH would act as a stronger driving force to propel more alkylamine molecules into the framework from the solution (**ESI Section 14**). Consistently, as the initial alkylamine loaded MOFs were washed by the corresponding solvent, more alkylamine would be retained in the framework in the case of CH. This is also owing to the weaker interaction between alkylamine and CH and its less potency in the competition against MOF for the bound alkylamine molecules. So the less polar CH is beneficial for more alkylamine to be incorporated in both the alkylamine loading step and subsequent washing step, which gives rise to a modified MOF with a higher alkylamine loading amount and consequently a higher CO_2 uptake.

Our explanation is well supported by the experimental data. Firstly, the amine group density in a MOF is quantified by elemental analysis (EA) and energy dispersive X-ray spectroscopy (EDX), which characterize the N/F and F/Cr ratios, respectively (**ESI Section 8**). The N/Cr ratio is obtained by multiplying the N/F and F/Cr ratios (**Table 2**). With the same alkylamine species, the sample prepared in CH has an apparently higher N/Cr value than the counterpart prepared in DCM, suggesting that a larger quantity of alkylamine has been incorporated into the framework. Thus, a less polar solvent contributes to a higher alkylamine loading amount in MOFs, substantiating the rationalization mentioned before. Secondly, the pore volume remaining in the framework after modification also serves as an indirect evidence to indicate the amount of alkylamine integrated in the MOF in that more alkylamine molecules would occupy more internal space and leave less pore volume for the subsequent gas sorption. Accordingly, a sample prepared in less polar CH is expected to have lower pore volumes, which is also corroborated by the experimental results (**Table 2**), and justifies our reasoning as well. Thus, solvents with smaller polarities are found to be more favorable for the inclusion of alkylamine into MOFs and contribute to modified MIL-101(Cr) with higher amine loading amounts and CO_2 capacities (**Figure 3**). The same trend was also observed in the MIL-101(Cr) based MOF bearing sulfonic acid groups,[19] with alkylamine loading amount rising with decreasing solvent polarity. This suggests the conducive effect of a less polar solvent to generating a modified MOF with high CO_2 uptakes is not exclusive to one MOF but can be extended to various MOFs as well.

Table 2. Summary of solvent polarities, alkylamine species, relative alkylamine amounts and pore volumes of Sample 1-4.

Sample No.	Solvent polarity[a]	Alkylamine	n(N)/ n(Cr)	Pore volume (cm^3/g)[b]
1	0.309(DCM)	DETA	2.52	0.68
2	0.309(DCM)	TAEA	3.49	0.58
3	0.006(CH)	DETA	3.96	0.64
4	0.006(CH)	TAEA	5.29	0.36

[a] Relative polarities of the solvents are summarized from ref. 20. Abbreviations of solvent species are included in parentheses for clarity. [b] Pore volumes are determined from N_2 isotherms by Density Functional Theory (DFT).

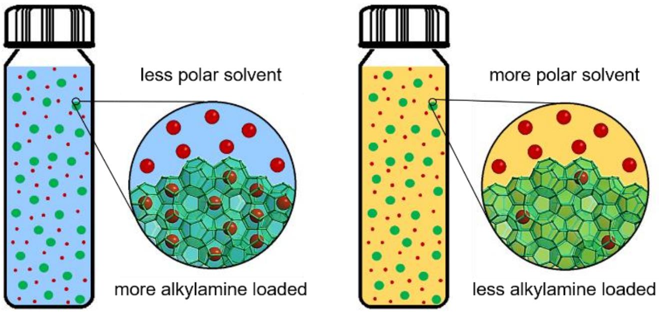

Figure 3. Illustration of the different alkylamine loading amounts in the MOF samples prepared in CH (left) and DCM (right). The enlarged circles show the interface between alkylamine solution and MOF. MIL-101(Cr) is represented with green balls and green networks. Red balls represent alkylamine. Blue and yellow liquids stand for CH and DCM, respectively.

The fact that the quantity of the integrated alkylamine holds a positive relationship with the CO_2 uptakes of Sample 1-4 is based upon an important premise that pore volumes are still adequate in these samples after the modification with alkylamine. As revealed in our previous research, a modest quantity of alkylamine is crucial to achieve a high CO_2 uptake in the modified MOF, because a balance needs to be stricken between high amine group density and adequate pore space to guarantee easy access to these amine groups for the CO_2 molecules to be adsorbed.[19] Such balance was well realized in Sample 4, because sufficiently large amount of alkylamine (indicated by N/Cr molar ratio) was incorporated and adequate pore volume (indicated by N_2 uptake at 77 K) was also retained. Both these factors contribute the high CO_2 uptakes at low pressures achieved in Sample 4.

Thermal stability characterized by thermogravimetric analysis coupled with mass spectrometry

It is worth noting that Sample 4, whose CO_2 capture ability is the best among the four, has a n(alkylamine)/n(Cr) ratio higher than 1 (**Table S19**). This unusual value is further confirmed by NMR result (**ESI Section 9**), implying that besides the coordination bonds formed between Cr open metal sites (OMSs) and amine groups, some alkylamine molecules are bound by intermolecular interactions, such as hydrogen bonds and van der Waals interactions. Intermolecular interactions are usually considered weak and might incur alkylamine leaching problem in modified MOFs during regeneration. To clarify whether there is alkylamine leaching from Sample 4 when regenerated, its thermal stability was evaluated by TGA-MS. The results show that no apparent characteristic mass peaks of TAEA are detected before the temperature reaches 150 °C (**Figure S23**), which is higher than the usual CO_2 desorption temperature. It suggests that intermolecular interactions are strong enough to fixate the alkylamines anchored in MIL-101(Cr) and there will be no leaching of alkylamine during recovery of the material.

Recyclability test and isosteric heat of CO_2 adsorption

The recyclability of Sample 4 was also evaluated using the TGA instrument. During the adsorption stage, the material was exposed to a gas flow of 15:85 CO_2/He (v/v) at 1 bar and 40 °C for 30 min. While in the desorption step, the sample was activated at 90 °C under pure He flow for 10 min. No appreciable decrease was observed in the CO_2 uptake (converted from the mass change) after five cycles (**Figure 4a**), suggesting that the material is regenerable and can be applied as a reusable CO_2 adsorbent. Moreover, comparing the CO_2 uptake (4.06 mmol/g at 40 °C and 150 mbar) read from the adsorption isotherm and that in the recyclability test, it is easy to notice that Sample 4 can achieve most of its CO_2 adsorption amount at equilibrium within 30 min, further suggesting the strong CO_2 capture ability of this material.

To quantitatively evaluate the CO_2 affinity of Sample 4, the isosteric heat of CO_2 adsorption of the material, $-Q_{st}$, was calculated based on its CO_2 adsorption isotherms collected at different temperatures (**Figure 4b**) with Virial equation (**ESI Section 11**). Since the CO_2 uptake had a steep rise at a very low pressure in each isotherm, the pressure in this region was difficult to be measured accurately to give a smooth curve for Virial fitting. The fitting and subsequent calculation of $-Q_{st}$ were thus conducted at a higher starting pressure. Consequently, the $-Q_{st}$ was determined to be 112 kJ/mol when the CO_2 uptake is 3.36 mmol/g (**Figure 4c**), which is still indicative of the impressively strong CO_2 affinity of the material.

Breakthrough experiments

To assess the CO_2/N_2 separation ability of the material in mixed gas scenarios, dynamic column breakthrough experiments were conducted on Sample 4 with a binary gas mixture of 15:85 CO_2/N_2 (v/v) at 25 °C or 40 °C. The breakthrough curves indicate that CO_2 would not be detected as the outlet of the column until the CO_2 injection amounts are 4.96 mmol/g at 25 °C and 4.54 mmol/g at 40 °C. By contrast, N_2 would break through at much earlier stages when the CO_2 injection amounts are merely 0.45 mmol/g at 25 °C and 0.35 mmol/g at 40 °C (**Figure 5**). This suggests the feasibility to separate the two species in the real cases of gas mixtures. The CO_2/N_2 selectivities are determined to be 75 at 25 °C and 78 at 40 °C from the breakthrough data, further revealing the highly selective adsorption ability of CO_2 over N_2 in Sample 4 (**ESI Section 13**). Moreover, the CO_2 capture capacities of Sample 4 are 4.35 mmol/g at 25 °C and 4.22 mmol/g at 40 °C based on the breakthrough experiments, which are comparable to the results attained in its CO_2 isotherms (**Figure 4b**). These values are among the highest CO_2 uptakes achieved in MOFs at the same conditions,[7e, 12k, 12n, 21] which suggests the excellent CO_2 capture performance of our material and the conducive role of the far less polar CH solvent in generating a better alkylamine modified MOF.

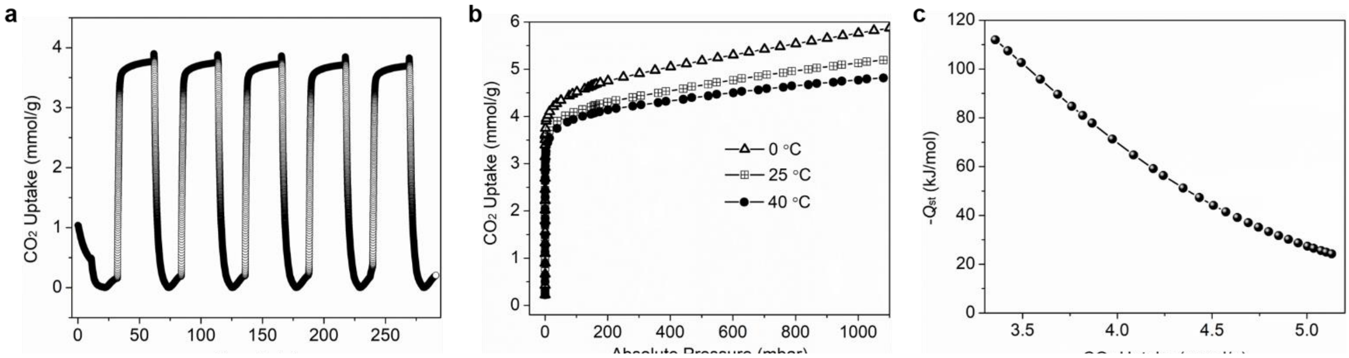

Figure 4. (a) Recycling test of Sample 4 with adsorption and desorption conditions set as a 15:85 CO_2/He (v/v) flow at 40 °C and 1 bar, and a pure He flow at 90 °C and 1 bar, respectively; (b) CO_2 adsorption isotherms of Sample 4 at 0°C, 25 °C and 40 °C; (c) Isosteric heat of CO_2 adsorption of Sample 4.

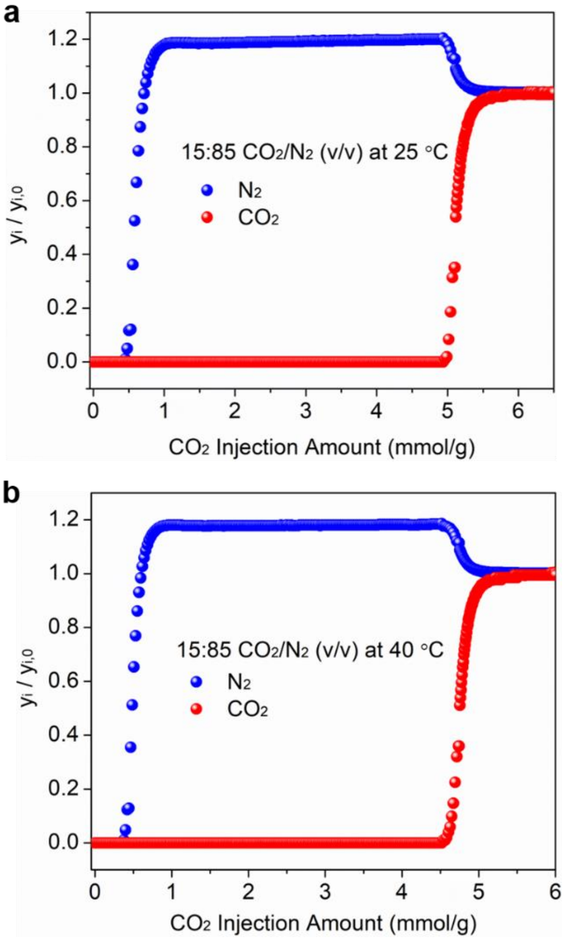

Figure 5. Breakthrough curves of a column packed with Sample 4. The gas flow is a 15:85 CO_2/N_2 (v/v) flow at 25 °C (a) or 40 °C (b) with an inlet pressure of 1.2 bar and an outlet pressure of 1 bar. y_i and $y_{i,0}$ are the molar fractions of a gas species at the inlet and outlet, respectively.

Conclusions

We successfully improve the CO_2 capture performance of alkylamine modified MIL-101(Cr) by conducting the amine tethering process in a solvent with vanishingly small polarity. The results demonstrate that nonpolar or less polar solvents are more favorable for the incorporation of alkylamine into MOFs than more polar ones. This point is rationalized by the higher chemical potential of the alkylamine molecules dispersed in less polar solvents, which drives more alkylamine to be integrated into the framework and leads to the formation of a modified MOF with substantially enhanced CO_2 uptakes. The material prepared by the revised method displays CO_2 uptakes as high as 4.21 mmol/g at 25 °C and 150 mbar, and 4.06 mmol/g at 40 °C and 150 mbar in gas sorption measurements. Its CO_2/N_2 separating ability is also assessed by dynamic column breakthrough experiments with a gas mixture of 15:85 CO_2/N_2 (v/v). The remarkably different breakthrough times of the two species suggests that the material is capable to effectively separate CO_2 from N_2 in the simulated flue gas.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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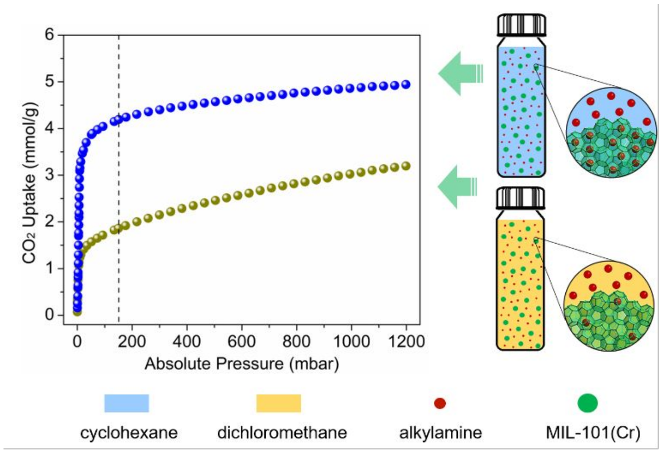

Alkylamine modified MOF prepared in the less polar solvent (cyclohexane) has a higher alkylamine loading amount and higher CO_2 uptake.