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Synthesis of Functionalized Metal-Organic Framework MIL-101 for CO_2 Capture from Natural Gas of Iraq's Siba Gas Field

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Abstract

Post-synthetic modification of MIL 101(Cr)-NH_2 frameworks was performed with a series of amines at different loadings and applied for the CO_2 capture. At first, structural and morphological properties of MOFs were studied by Fourier transform spectroscopy (FTIR), scanning electron microscopy (SEM), thermal gravimetry analysis (TGA) and X-ray diffraction (XRD). Results confirm the successful synthesis of products. In the next step, CO_2 adsorption of MOFs and potential applications in carbon capture were realized by the Low-pressure gas sorption measurements and CO_2 cycling experiments analyses. Our findings highlighted the significant impact of various factors, such as the choice of amine, loading amount, temperature, and pressure, on the CO_2 adsorption capacity of MOFs. Three distinct types of amines namely polyethyleneimine (PEI), diethylenetriamine (DETA), and ethylenediamine (ED) were employed for the functionalization of MOFs. The results unveiled a distinct hierarchy in the CO_2 adsorption capacities of MOFs modified with these different amines. Specifically, the order of decreasing CO_2 capacity for PSM materials was observed as follows: PEI > DETA > ED. This sequence underscores the varying impact of amine types on enhancing the adsorption potential of MOFs, offering valuable insights into optimizing these materials for efficient carbon capture applications.

Keywords: Metal-organic framework, MIL 101, Adsorption, Carbon dioxide, Natural gas.

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Introduction

In the contemporary context, our global community is confronted with a pressing environmental challenge: the escalating levels of atmospheric carbon dioxide, a primary contributor to the critical issues of global warming and climate change [1-4]. The highest amount of greenhouse gas emissions is caused by the combustion of coal, oil and natural gas, which emphasizes the necessity of implementing strategies to curtail CO_2 emissions, particularly in developing nations [5, 6]. As fossil fuels continue to serve as the linchpin of global electricity production, it is imperative to urgently adopt measures that foster a cultural shift and transform energy distribution plants and infrastructures to accommodate innovative technologies capable of significantly reducing CO_2 emissions [7].

The foremost strategy in mitigating CO_2 emissions involves the capture and sequestration of carbon dioxide. The Carbon Capture and Storage (CCS) process emerges as a viable solution to mitigate the environmental impact of CO_2 emissions [8-10]. Diverse methods have been employed for CO_2 capture and separation, which absorption is superior due to high removal capacity, low corrosion to equipment, ease and cost-effectiveness [11-13]. Materials such as activated carbons, molecular sieves, zeolites, ionic liquids, metal oxides, membranes fluorinated solvents, metal-organic frameworks (MOFs), and covalent organic frameworks have been developed for this purpose [14-16]. The selective adsorption of CO_2 from the feed gas occurs in the initial step, with other components passing through the adsorbent bed. Once saturated with CO_2, the bed undergoes desorption back into the gas phase, involving physical sorption (Van der Waals and electrostatic forces) and chemical sorption (formation of a covalent bond) [17, 18].

Over the last 15 years, Metal-Organic Frameworks (MOFs) with expansive surface areas have demonstrated efficacy in CO_2 capture, separation, concentration, storage, transport, and conversion [19]. MOFs, comprising metal ions or clusters connected by organic linkers, boast a highly ordered and crystalline structure, offering large surface areas and tunable pore sizes [20-23]. These unique properties render MOFs versatile materials with applications in various fields such as sensing, catalysis, separation, drug delivery, gas storage, and environmental remediation [24-26]. Despite their promise in carbon capture processes, challenges persist, including issues related to MOF stability, synthesis scalability, and cost-effectiveness for large-scale applications. Researchers are actively addressing these challenges while exploring new MOF materials to enhance their performance for specific applications [27, 28].

A crucial nexus of energy demands and environmental impact is exemplified by Iraq's Siba Gas Field, situated in the Basra Governorate with abundant hydrocarbon reserves. The natural gas extraction and utilization processes at Siba Gas Field release substantial amounts of CO_2 into the

atmosphere, necessitating a comprehensive approach to address climate change concerns. As the field plays a pivotal role in meeting domestic energy needs and explores the potential for exporting natural gas, there is an increasing emphasis on adopting sustainable practices and carbon capture technologies to mitigate environmental impacts.

This research endeavors to synthesize and explore the application of MOFs in capturing CO_2 from Iraq's Siba Gas Field natural gas stream. The study seeks to assess the efficiency, capacity, and stability of various MOF materials for CO_2 adsorption, with a specific focus on their potential for industrial-scale application. The goal is to identify promising MOF materials with high CO_2 adsorption capacity and selectivity, paving the way for potential deployment in capturing CO_2 from Iraq's Siba Gas Field. The research aims to provide valuable insights into the feasibility of integrating MOF-based carbon capture systems into existing gas processing facilities.

Experimental

Materials

Chromium nitrate nonahydrate (Cr $(NO_3)_3 \cdot 9H_2O$), 2-Aminoterephthalic acid ($H_2NC_6H_3$-1,4-$(CO_2H)_2$), 4,4-bipiperidyl-dihydrochloride ($C_{10}H_{20}N_2 \cdot 2HCl$ 99 %), Trimesic acid ($C_6H_3(CO_2H)_3$ 95 %), Sodium bicarbonate ($NaHCO_3 \geq 99.7$ %), Nitric acid (HNO_3), Sodium bicarbonate ($NaHCO_3$), Ethylenediamine ($C_2H_8N_2$), Polyethyleneimine ($(C_2H_5N)_n$, linear form), Ethylenediamine ($C_2H_8N_2$), and DMF (C_3H_7NO), were purchased from Sigma-Aldrich Co. Ethanol ≥ 99.7 %, Methanol ≥ 99.8 %, Phosphorous acid 97 %, and Sulphuric acid 98 %, were obtained from Merk.

Materials and methods

Synthesis of MIL-101(Cr)

Bulk MIL-101(Cr) was synthesized by a procedure reported by Jiang et al. [29]. H_2O (9.6 mL) was added to $Cr(NO_3)_3 \cdot 9H_2O$ (0.8 g, 2.00 mmol) and terephthalic acid (0.33 g, 1.99 mmol), and then the solution was stirred for 10 min at room temperature. The suspension was heated in a Teflon® lined autoclave at 220 °C for 8 h. After cooling the autoclave, terephthalic acid was removed by filtration. The suspension was then centrifuged for 5 min. The obtained green powder was washed three times with ethanol. The solid product was treated with hot ethanol at 80 °C for 4 h.

Synthesis of MIL-101(Cr)-NH_2

To synthesize graphene oxide aerogel MIL-101(Cr)-NH_2, 7 mL water was added to 2-aminobenzene-1,4-dicarboxylic acid (H_2bdc-NH_2) (0.23 g, 1.26 mmol) and Cr $(NO_3)_3 \cdot 9H_2O$ (0.50 g, 1.25 mmol). After stirring for 3 h at room temperature, the suspension was heated in a Teflon-

lined autoclave at 130 °C for 24 h. After cooling to room temperature, the product was centrifuged and the resulting green powder was washed five times with ethanol [30].

PSM of MIL-101(Cr)-NH_2 with DETA and PEI

According to the method that reported by Lin and co-workers, wet impregnation MIL-101(Cr)-NH_2 with polypropyleneimine octamine dendrimer (DAB-AM-8), diethylenetriamine (DETA) and polyethyleneimine (PEI) was conducted.

Prior to the modification, MIL-101(Cr)-NH_2 was activated under vacuum at 110 °C for 24 h. The suitable amount of DETA or PEI (0.3 g) was added to approximately 1 mL of methanol under stirring for 10 min. Dehydrated MOF (0.2 g) was added to the solution and stirred for another 10 min. The mixture was then purged with N2 overnight at room temperature. Finally, modified samples were prepared by activation under vacuum at 110 °C overnight [31].

PSM of MIL-101(Cr)-NH_2 with ED

A suspension of MOF (0.2 g), ethylenediamine (ED) (0.3 g), and toluene (30 mL) was refluxed overnight. The desired product was isolated by centrifuge and washed with H_2O and ethanol. The isolated product was activated under a vacuum overnight at 90°C [32].

Three samples of MIL-101(Cr)-NH_2-PEI with different PEI loadings (75, 100 and 150 wt%) were prepared. MIL-101(Cr)-NH_2 modified with 100 wt% DETA and 150 wt% ED was prepared. The following equation was used to obtain the theoretical loading of the materials.

$$Amine\ Loading = \frac{mass_{amine}}{mass_{MIL\ 101}} \times 100 \qquad (1)$$

The theoretical loading (wt%) and the loading after vacuum activation (wt%) is given in Table 1.

Table 1. Theoretical amine loadings (wt%), the amine loadings after vacuum activation (evac).

Amine	Theoretical loading / wt%	Loading after evac / wt%
PEI	75	68
PEI	100	88
PEI	150	130
ED	150	128
DETA	100	88

Characterization

The X-ray powder diffraction (XRD) (Phaser Bruker Copper Anode), Fourier transform infrared spectrometer (FT-IR) (Agilent Cary 630 Diamond ATR), Scanning electron microscope (SEM) (JEOL EM J1010 microscope) and Thermal gravimetry analysis (TGA) (Setaram TGA 92) were used in this research to analyze and assessment of the structure, morphology, compositions, and surface properties of as-prepared materials.

CO_2 capture analysis

Sorption measurements

In the following sections, the general process of investigations carried out on MOFs is described. CO_2 adsorption and desorption were measured by combined TGA and differential thermal analysis (DTA). The aim of these experiments is to assess the extent to which the sorbent is capable of adsorbing and releasing CO_2 at one or more specific temperatures. The MOFs activated under Ar at an elevated temperature for 1 h. After cooling the system to the desired temperature for adsorption/desorption, the thermo analyzer was equilibrated for 20 minutes before the sample gas was switched on. CO_2 volume of inlet gas was gradually increased in five steps (2.1, 5.2, 14.7, 29.7, and 49.8 vol%) and then reduced in five steps (29.7, 14.7, 5.2, 2.1, and 0 vol%) by increasing the amount of Ar in the gas stream. The temperature was kept constant for another 20 min after the last stage of desorption. At the end, the MOFs were activated in order to desorb the CO_2 fully.

Low-pressure gas sorption measurements of MOFs

The effect of different PEI loadings and different amines on the gas uptakes and sorption kinetics were investigated by measurement of Low-pressure (0-0.5 bar) natural gas adsorption and desorption isotherms at 25, 45, 75 and 105 °C.

Water stability of MOFs

Intelligent Gravimetric Analyser modified by the addition of a vapor generator used to investigation of H_2O stability of the materials determined by measuring sorption isotherms for CO_2 of natural gas and H_2O vapor at 25 °C. Before the experiment to obtain the isotherms, the MOF sample was degassed overnight at activation temperature. Absolute pressure of the adsorptive gas progressively changed in order to record Adsorption/desorption isotherms. To approach equilibrium, a time interval of 15 to 30 min is allowed however up to 40 min at each pressure point were allowed for H_2O vapour. In order to investigate the H_2O stability of the material, CO_2 isotherm of natural gas was record and H_2O isotherm was measured after that a second CO_2 isotherm was record and

compared with the initial isotherm.

CO_2 cycling experiments

Thermogravimetric analysis was applied to measure the stability and regenerability of the MOFs. Before cycling test, the samples are degassed under vacuum overnight. 10-30 mg of MOF was activated at activation temperature under Ar for 1 h. After that, according to the kinetics observed in the adsorption experiments at low pressure the system was cooled to 25, 45, 75 or 105 °C. The change in partial pressure of sample gas between 0.05 and 0.15 bar led to obtain ten cycles of adsorption/desorption with 20 min equilibration time for each step. For the wet cycling experiments, after activation step, the MOFs are exposed to a stream of humid Ar and saturated with 1vol% H_2O vapour before the test with wet sample gas/Ar mixtures.

Results and discussion

Materials assessments

FT-IR

FT-IR analysis has been performed to description and determine functional groups and bonds on the surface of synthesized materials. The FT-IR spectrum of MIL-101(Cr)-NH_2 samples before and after post-synthetic modification by desired amines are shown in Figure 1. The observed bands between 600 cm^{-1} and 1600 cm^{-1} are attributed to the phenyl groups, which primarily include the C=C stretching vibration at 1508 and the C-H bond deformation bending vibration peak at 1159 cm^{-1}. The peak at 1680 cm^{-1} is corresponding to the water molecule [33]. The antisymmetric peak in 1539 cm^{-1} and the symmetric peak in 1393 cm^{-1} are related to the carboxyl group. The absorption peak at 657 is the N-H bending vibration of the primary amine [34]. The appearance of these peaks indicates that MIL-101(Cr) has been successfully synthesized. The FTIR spectrum of MIL-101(Cr)-NH_2 after modification with PEI shows that the presence of ED, DETA, and PEI did not change the structure of the parent MOF, only the appearance of the peaks became slightly smaller. The introduction of neat amines caused the disappearance of the peak at 1700 cm^{-1} of MIL-101(Cr)-NH_2. By mixing amines, the bands from 2700 cm^{-1} to 3700 cm^{-1} disappeared [35]. The band at 1100 cm^{-1} is attributed to the C-N stretching vibration of aliphatic amines, which appears after PSM modification [36]. As can be seen in the figure a shift in the position of absorption bands corresponding to the asymmetric (3480 cm-1) and symmetric (3372 cm-1) stretch of the amine moieties towards the asymmetric (3335 cm-1) and symmetric (3260 cm-1) stretch of the neat amines shows the incorporation of amine into MIL-101(Cr)-NH_2. Moreover, the presence of

asymmetric (2930 cm-1) and symmetric (2800 cm-1) CH2 stretch vibrations further confirmed the successful modification.

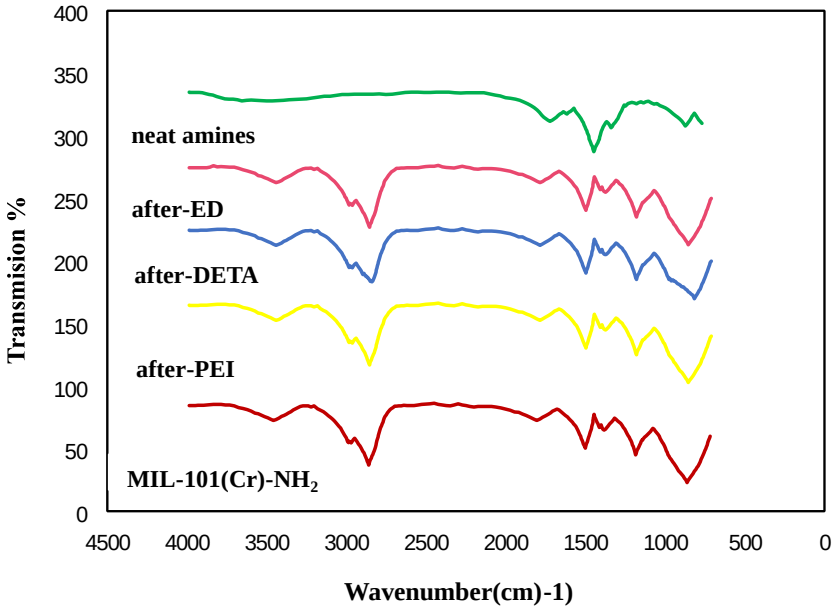

Figure 1. FTIR spectrum of MIL-101(Cr)-NH_2 before and after the PSM.

XRD

The XRD test is a precise and simple method used to confirm the presence of a crystal structure and the crystalline properties of samples. This analysis contains electromagnetic radiation with a short wavelength, in which X-rays depend on the Molecular weight and density of the material. This evaluation employs electromagnetic radiation with a very short wavelength, with the dependence of X-rays on the material's molecular weight and density. Figure 2 displays the results of the XRD analysis conducted in this study. The results show that MIL101(Cr) is successfully synthesized and has a complete crystalline form. After post-synthesis modification, the intensity of the peak decreases. The peak of the characteristics of the material at 2θ=9.2 and 11.5 becomes weaker with the mixing of the amount of amine. This could be because the post-synthetic modification by amine causes pore-occupancy, which reduces the crystallinity of MIL 101(Cr).

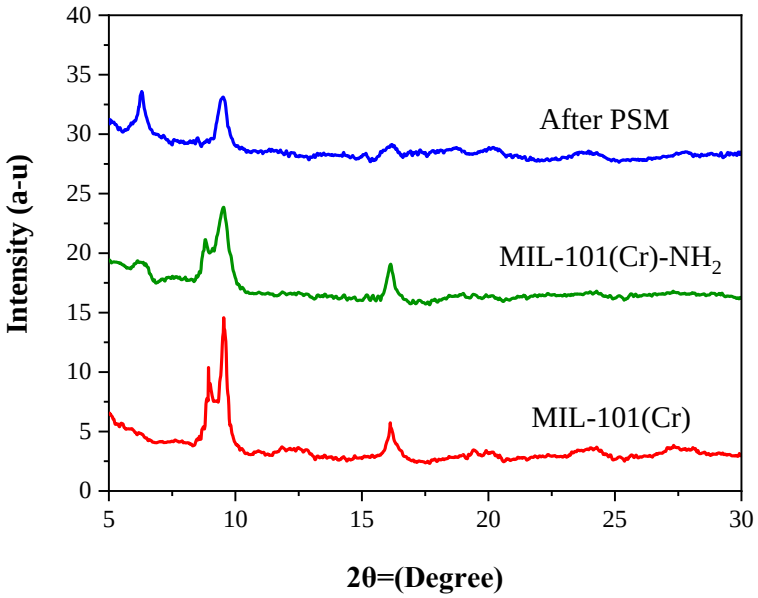

Figure 2. XRD spectrum of MIL-101(Cr), MIL-101(Cr)-NH_2 and MIL-101(Cr)-NH_2 after PSM.

SEM analysis

The SEM analysis is one of the methods of investigating the uniformity of morphology and structure, and physical attributes of the material surface. SEM images of MIL-101(Cr)-NH_2, MIL-101(Cr)-NH_2-DETA-88, MIL-101(Cr)-NH_2-PEI-68 are shown in Figure 3. As can be seen in the Fig. (3a), the mother MOF crystal is consistent with past research. After modification by polyethylenimine, it retains its crystal structure, but the crystal order and integrity are slightly reduced. From the comparison of images b and c, it can be seen that the introduction of DETA has a greater effect than PEI, which causes the MOF pores to be covered. PEI only roughened the MOF surface morphology, which seems more favorable for carbon dioxide adsorption based on previous studies.

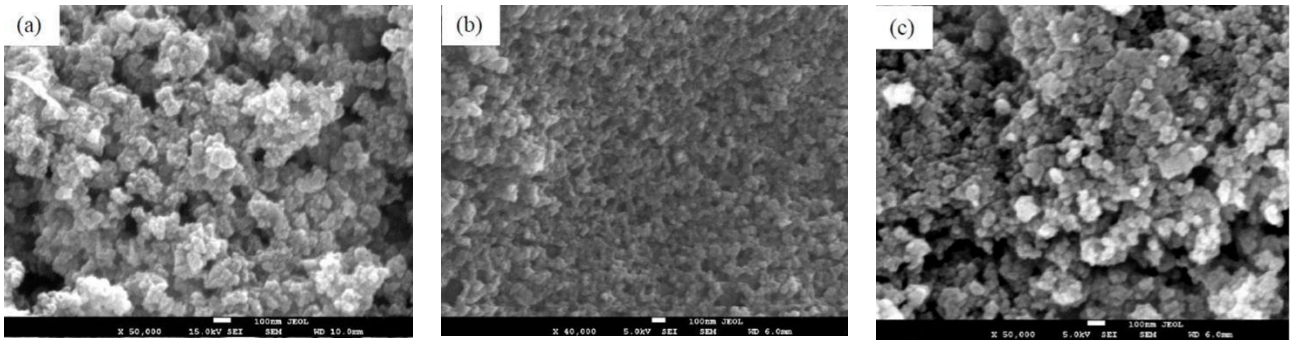

Figure 3. SEM analysis of (a) MIL-101(Cr)-NH_2, (b) MIL-101(Cr)-NH_2-DETA-88, (c) MIL-101(Cr)-NH_2-PEI-68.

TGA

The thermal gravimetric analysis (TGA) was performed on functionalized MOF after post-synthetic modification and is shown in Figure 4. The thermogram between 40 and 110 °C of MIL-101 (Cr)-NH_2 shows the decrease in initial mass due to the removal of water and volatile substances. At temperatures between 110 and 360 °C, H_2O molecules coordinated to chromium trimers were removed (4–5 wt%). The first weight loss was significantly reduced after PSM MIL-101 (Cr)-NH_2, probably due to the reduction of pore volume and vacuum activation of the modified materials during their preparation. Incorporation of amines appeared to decrease thermal stability, as starting at approximately 200–240 °C (depending on the amine present), there was a gradual weight loss for all PSM materials consistent with loss of amines. However, the temperature corresponding to the complete decomposition of the framework increased somewhat.

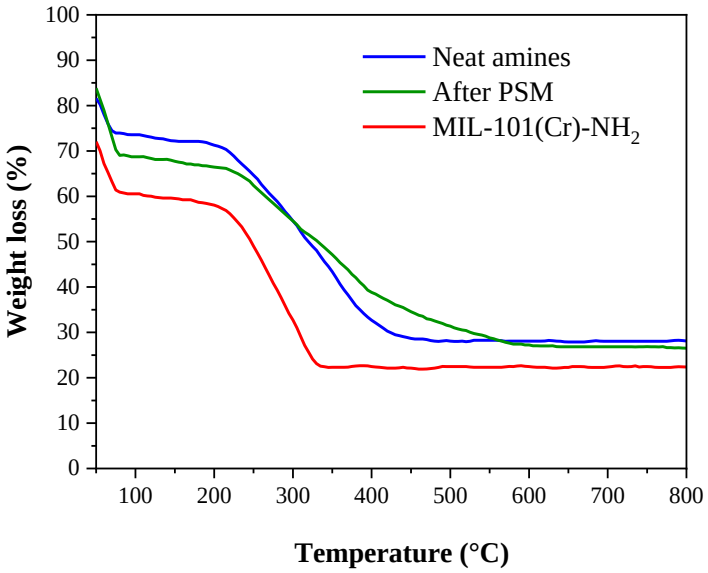

Figure 4. TGA on MIL-101-NH_2, After PSM and neat amines.

Carbon capture analysis

After analyzing the identification tests and confirming the methods of fabrication and formation of materials, in this section, adsorption studies including low-pressure gas sorption measurements and adsorption kinetics study have been discussed. The investigation examined how different PEI loadings and various amines influence gas absorption and sorption kinetics. This was accomplished by analyzing the isotherms of natural gas adsorption and desorption at low pressure (0-0.5 bar) across temperatures ranging from 25 to 105 °C.

Effect of PEI loading

CO_2 adsorption/desorption in natural gas pseudo-isotherms of MIL-101(Cr)-NH_2 before and after PSM with PEI are shown in Figure 5. Initially, for MIL-101(Cr)NH_2, no discernible CO_2 saturation was evident within the examined pressure range. However, following the introduction of PEI, a notable increase in CO_2 adsorption capacities occurred, particularly at pressures surpassing approximately 0.15 bar.

An intriguing observation emerged concerning the suitability of PEI-modified materials for high-pressure separations. Contrary to expectations, CO_2 saturation was noted at lower pressures, implying limitations for high-pressure applications. The impact of temperature on CO_2 adsorption capacities across all MOFs was investigated, revealing a consistent decrease as temperatures rose. This aligns with classical adsorption behavior, where heightened kinetic energies at elevated temperatures diminish the equilibrium concentration of adsorbed species. Notably, the CO_2 adsorption behavior of MIL-101(Cr)-NH_2-PEI-130 exhibited a departure from the typical trend. In this instance, CO_2 adsorption remained comparable at 25 and 45°C, showing an increase with temperature up to 75°C. The unique aspect of MIL-101(Cr)-NH_2-PEI-130 lies in its complete internal porosity occupied by PEI, resulting in a slow penetration of CO_2 during the experiment, preventing the achievement of equilibrium adsorption. At 105°C, the increased mobility of PEI facilitated quicker and more efficient CO_2 penetration, yet the higher temperature simultaneously reduced the equilibrium concentration of adsorbed species. The hysteresis observed between adsorption and desorption in unmodified MIL-101(Cr)-NH_2 is attributed to strong interactions between CO_2 and coordinatively unsaturated sites (CUS) in the framework structure. For PEI-modified materials, the hysteresis between adsorption and desorption signals apparent irreversibility in CO_2 adsorption at lower temperatures, likely due to the experiment's timescale (20 min equilibration time). This implies that CO_2 diffusion into the pores is constrained at lower temperatures. Examining the CO_2 adsorption capacity of PEI-modified MIL-101(Cr)NH_2, a clear hierarchy emerged: MIL-101(Cr)-NH_2-PEI-130 < MIL-101(Cr)-NH_2-PEI-68 < MIL-101(Cr)-NH_2-PEI-88. The diminished CO_2 capacity of MIL-101(Cr)-NH_2-PEI-68 can be rationalized by the lower concentration of amine groups. Despite exhibiting the smallest capacity at low temperatures, MIL-101(Cr)-NH_2-PEI-130 demonstrated the highest adsorption capacity at 75°C. This phenomenon is attributed to the increased mobility of PEI at higher temperatures, facilitating access to previously inaccessible pores and allowing efficient CO_2 diffusion.

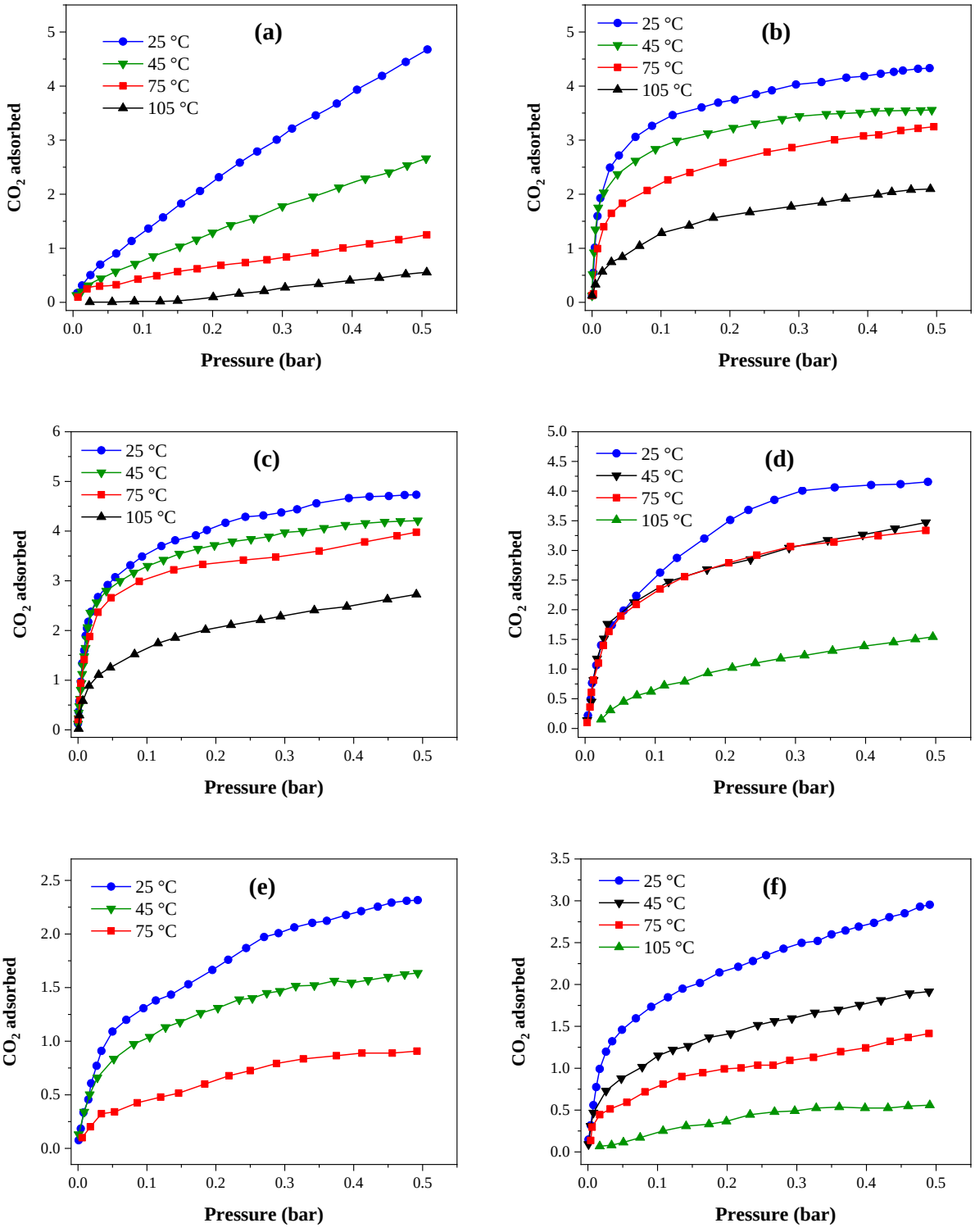

Figure 5. CO_2 adsorption pseudo-isotherms of MOFs at various temperatures a) MIL-101(Cr)-NH_2 b) MIL-101(Cr)-NH_2 PEI-68 c) MIL-101(Cr)-NH_2 PEI-88 d) MIL-101(Cr)-NH_2 PEI-130 e) MIL-101(Cr)-NH_2 ED-128 f) MIL-101(Cr)-NH_2 DETA-88.

The CO_2 isotherms of MIL-101(Cr)-NH_2 before and after PSM with DETA and ED are presented in Figure (5e) and Fig. (5f). The sorption isotherms for MIL-101(Cr)-NH_2-ED-128, owing to its low CO_2 uptakes and the higher volatility of ED, were measured only up to 75 °C. The graphical

representation illustrates that elevating CO_2 pressure correlates with increased CO_2 adsorption capacities, with the PSM materials exhibiting a descending order of capacities: PEI > DETA > ED. Notably, MIL-101(Cr)-NH_2-DETA-88 and MIL-101(Cr)-NH_2-ED-128 neared saturation with CO2, displaying only marginal enhancements in adsorption capacities, particularly evident at 75°C. These improvements were, however, negligible when compared to the outcomes following PSM with polyethyleneimine (PEI). In alignment with observations for PEI-modified materials, the adsorption/desorption isotherms subsequent to PSM with DETA and ED exhibited hysteresis, indicative of the chemical adsorption of CO_2 onto the amines.

Kinetics study

CO_2 adsorption/desorption of MIL-101(Cr)-NH_2 before and after PSM with PEI at temperatures of 25, 45 and 75 °C are shown in Fig. 6, respectively. The adsorption/desorption experiments were performed in a stepwise manner and the CO_2 pressure was changed from 0.1 to 0.5 in each step. The CO_2 adsorption on the PEI-68 and PEI-88 modified samples increased with each pressure step at 25 and 45 °C. On the other hand, PEI-130 showed a slow continuous uptake of CO_2 at low temperatures. Equilibrium in the adsorption/desorption process was not completely achieved within the 20 min timeframe allowed for each adsorption/desorption step at these temperatures. At lower temperatures, the adsorption/desorption rate decreased with higher PEI loadings in the order MIL-101(Cr)-NH_2-PEI-68< MIL-101(Cr)-NH_2-PEI-88 < MIL-101(Cr)-NH_2-PEI-130. As can be seen, at temperature of 25°C, the highest mass change was obtained by the PEI-68, while at 75°C, the highest mass change was obtained by the PEI-130. Enhancement of temperature led to an increase in PEI mobility at higher temperatures, which allowed the CO_2 diffusion into pores that were not available at lower temperatures. This upward shift in the optimal operating temperature may be useful for a vacuum swing adsorption process for CO_2 separation from flue natural gas, which could potentially reduce the required cost for the capture process.

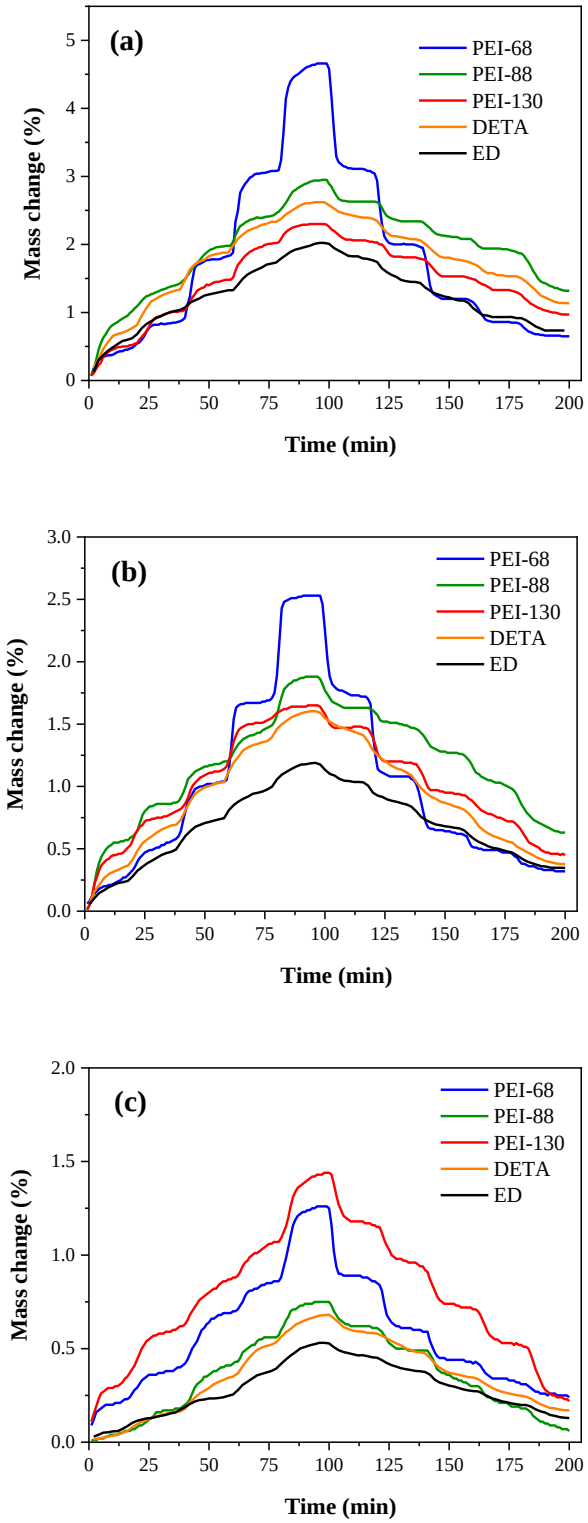

Figure 6. Mass change of MIL-101(Cr)-NH_2 before and after amine modification during stepwise adsorption/desorption test at (a) 25°C (b) 45°C and (c) 75°C.

Cycling experiments on MIL-101(Cr)-NH_2 before and after PSM

The investigation involved assessing the pseudo-equilibrium adsorption uptakes over ten adsorption/desorption cycles, conducted both under dry and wet conditions (1 vol% H_2O). This

rigorous analysis aimed to ascertain the CO_2 adsorption capacity and regenerability of Metal-Organic Frameworks (MOFs), crucial for their viability in industrial applications over multiple cycles, particularly in the presence of water vapor (H_2O). The cycling conditions are comprehensively outlined in Table 2.

Table 2. Summary of cycling conditions and results.

MOF	Cycling temperature (°C)	H_2O uptake (wt%)	Average CO_2 working capacity dry (wt%)	Average CO_2 working capacity wet (wt%)
MIL-101(Cr)-NH_2	25	8.55	0.81	0.85
MIL-101(Cr)-NH_2-PEI-68	75	1.61	0.38	0.35
MIL-101(Cr)-NH_2-PEI-88	75	-	0.47	0.41
MIL-101(Cr)-NH_2-PEI-130	105	-	0.16	0.23
MIL-101(Cr)-NH_2-ED-128	45	5.18	0.27	0.15
MIL-101(Cr)-NH_2-DETA-88	45	1.76	0.25	0.28

As discussed earlier, it is imperative to conduct cycling experiments on Pseudo-Steady-State MOF (PSM) materials at elevated temperatures. This strategic approach accelerates adsorption kinetics, ensuring adsorption equilibration within the stipulated 20 min cycle duration. For a more meaningful comparison of these materials, the average working capacity across ten cycles was calculated. Analysis of low-pressure isotherms revealed that the initial cycle in each PSM material exhibited the highest estimated working capacity. However, from the second cycle onward, working capacity experienced a decline due to the chemical sorption of CO_2. Evaluation of the average working capacities under both dry and wet conditions demonstrated that the majority of these MOFs exhibited commendable regenerability and stability, even in the presence of H_2O vapor. Despite some PSM materials demonstrating higher CO_2 adsorption capacities at 0.05 bar during low-pressure experiments, their working capacities in cycling experiments fell short of those observed in MIL-101(Cr)-NH_2. It is noteworthy that when comparing these results with the CO_2 uptakes of MIL-101(Cr)-NH_2 at temperatures of 45°C and above, most of the modifications exhibited improved performance during cycling. MIL-101(Cr)-NH_2, known for its attractive H_2O adsorption capability with a measured uptake of 8.55 wt%, showcased superior performance. The PSM modifications resulted in diminished H_2O uptakes, consistent with the reduction in pore volumes. Despite similar pore volumes in MIL-101(Cr)-NH_2-DETA-88 and MIL-101(Cr)-NH_2-ED-128, the

ED-modified framework exhibited significantly higher H_2O uptake compared to the DETA-modified framework. This observation aligns with the loss of ED during the experiment. Notably, DETA and PEI modified materials demonstrated comparable or slightly higher CO_2 working capacities under wet conditions, affirming the regenerability of these materials in cycling scenarios. These findings contribute valuable insights into the performance and potential applications of these MOFs, especially in the context of environmental and industrial considerations.

Conclusion

In conclusion, an amine-functionalized MOF, MIL 101(Cr)-NH_2, was successfully synthesized and functionalized using various types of amins. The structure and morphology of MOFs was determined by using analytical methods, confirming successfully synthesized MOFs. The investigation revealed that Metal-Organic Frameworks (MOFs) function as a renewable CO_2 adsorbent, demonstrating commendable stability across repeated cycling experiments. This valuable insight enhances our understanding of the MOFs' suitability for sustainable and enduring carbon capture applications.

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