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Posted Date: 24 January 2024

doi: 10.20944/preprints202401.1674.v1

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Article

Functionalization of Ordered Mesoporous Silica (MCM-48) with Task Specific Ionic Liquid For Enhanced Carbon Capture

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Abstract: This work presents noble composites of AAILs@MCM-48 by functionalizing ordered mesoporous silicon MCM-48 with two amino acid-based ionic liquids (AAILs) ([Emim][Gly] and [Emim][Ala]) to improve carbon capture and selectivity of CO₂ over nitrogen. Thermogravimetric and XRD analyses of the composites show that the MCM-48 support's thermal and structural integrity was preserved after the AAILs were encapsulated. An N₂ adsorption-desorption study at 77 K also confirms AAIL encapsulation in the porous support. Under post-combustion flue gas conditions, both [Emim][Gly]@MCM-48 and [Emim][Ala]@MCM-48 demonstrated improved CO₂ adsorption in comparison to unmodified MCM-48, with a CO₂ partial pressure of around 0.15 bar. In terms of maximal CO₂ uptake, the 40wt%-[Emim][Gly] composite outperformed the others at 303K, with values of 0.74 and 0.82 mmol g⁻¹, respectively, at 0.1 and 0.2 bar. These numbers show a 10x and 5x increase, respectively, as compared to the pure MCM-48 under identical conditions. In addition, the selectivity of the composites was improved significantly, at 0.1 bar, the selectivity of composites containing 40wt% [Emim][Ala] increased to 17, compared to 2 for pristine MCM-48.

Keywords: CO₂ Capture; Mesoporous Silica; MCM-48; Amino Acid Ionic Liquid; Task-Specific Ionic Liquid

1. Introduction

For the purpose of CO₂ capture applications, ordered mesoporous silicas like SBA-15, KIT-6, and also MCM-41, MCM-48, have garnered a lot of interest owing to their high surface areas and large pore volumes, in addition to great thermal and chemical stabilities [1–4]. In spite of this, their use in the CO₂ capture process has been restricted owing to their poor CO₂ capture capabilities, which were caused by a lack of affinity towards CO₂. This is particularly true in post-combustion settings, where the partial pressure of CO₂ was close to 0.15 bar. There have been other research groups that have used procedures that include functionalizing the pore surface with amines or ionic liquids in order to improve the capabilities of CO₂ adsorption [5–8]. MCM-41 is one of the ordered mesoporous materials that has been used by a number of researchers for the purpose of surface functionalization [7,9,10]. MCM-41 has a one-dimensional pore channel, and is sensitive to restricted diffusion of guest molecules as well as pore obstruction. Alternatively, MCM-48 is known to have has a 3-dimensional cubic pore structure. MCM-48 is therefore a more desirable option than MCM-41 because it provides a better diffusion channel for the guest molecules and is less likely to get blocked [1,11]. However, details of an investigation of CO₂ capture capabilities by ionic liquid functionalized MCM-48 has not yet been demonstrated.

For this investigation, we have chosen two amino acid ionic liquids, also called task-specific ionic liquids (TSILs), to be immobilized into ordered mesoporous silica MCM-48. The goal is to create TSILs@MCM-48 composites that can enhance the ability to absorb CO₂ and increase its selectivity over N₂. The proposed TSILs are composed of 1-Ethyl-3-methylimidazolium [Emim] cations combined with Glycine [Gly] and Alanine [Ala] as anions, which are reactive amino acids (AA) that produce [Emim][Gly] and [Emim][Ala]. TSILs with an amine functional group have a greater capacity

to capture CO₂ compared to other physical ILs. Wang and co-researcher [12] showed that by encapsulating [Emim][Gly] and [Emim][Ala] inside the nanoporous polymethylmethacrylate (PMMA) microspheres, they were able to enhance the absorption of CO₂ and obtain faster CO₂ reaction rates. In our previous work, we have also demonstrated an enhanced CO₂ capture capacity by immobilization these TSILs into ZIF-8 [13] and MOF-177 [14]. To our knowledge, no research has been published addressing functionalized MCM-48 with these two TSILs. Work focused then on characterizing and investigating the composites of TSILs@MCM-48 from an engineering standpoint. Specifically, the study examined their CO₂ capture capacity, selectivity, enthalpy of adsorption, and modelled the adsorption isotherms. CO₂ adsorption isotherm was determined at three distinct temperatures (303, 313, and 323 K) and for pressures ranging from 0.10 to 10.0 bar. Furthermore, nitrogen adsorption isotherms were evaluated for both composites and the original MCM-48. This allowed for the calculation of the optimum selectivity of CO₂/N₂.

2. Materials and Methods

2.1. Materials

The solvents used were methanol, [Emim][Gly] (CAS: 766537-74-0), [Emim][Ala] (CAS: 766537-81-9) and MCM-48 (CAS: 7631-86-9) were acquired from Sigma Aldrich. The structure of cation and anion of the amino acid ionic liquids are presented in Table 1. Prior to the preparation of the sample, MCM-48 was dried at 150 °C. The TSILs and MCM-48, and their composite samples were stored within a glovebox (Clean Tech LLC) under inert atmosphere by flowing argon gas to limit moisture abs CO₂ adsorption. CO₂ (99.99 vol. %), and N₂ used in the adsorption experiments were acquired from Praxair Inc. Canada.

Table 1. Structure of cation and anions of AAILs used in this present study.

Name	Abbreviation	Structure
1-Ethyl-3-methylimidazolium	[Emim]	
Glycine	[Gly]	
Alanine	[Ala]	

2.2. Preparation of AAIL@MCM-48 composite

The MCM-48 silica support was functionalized with the AAILs using the classical wet impregnation method, with the assistance of methanol [14]. For each AAIL, three different composites were prepared by varying the content of AAIL (20, 30 and 40 weight %). The composites obtained were then labelled as X-AAILs@MCM-48, where X denotes the weight percentage of AAILs employed. For example, the composite 20-[Emim][Gly]@MCM-48 was prepared using 20 wt. % [Emim][Gly].

2.3. Characterization

Thermogravimetric analysis (TGA) of all the samples was performed using a TGA-50 instrument manufactured by Shimadzu was utilized. During all the experiments, a nitrogen flow of 50 mL per minute was maintained, while the temperature increase was set at 10 °C per minute, to a maximum of 800 °C. An estimated 10–12 mg of substance was utilized for each sample. An X-Ray diffractometer (Rigaku Ultima IV) equipped with Cu source with a wavelength of 1.54056 Å allowed for the detection of the crystal structure of the pristine MCM-48 support and AAILs@MCM-48 composites. The analysis was conducted over 2θ values with a scanning rate of ranging from 0.5 to 10° at a scanning rate of 1.2°/ min. The N₂ adsorption–desorption isotherms of MCM-48 and the composites were obtained using the Micromeritics ASAP instrument at 77 K (liquid N₂). The textural properties such as specific Brunauer–Emmett–Teller (BET) and Langmuir surface area, pore volume for each sample were computed from the corresponding N₂ adsorption-desorption data.

2.4. Adsorption Isotherms

The N₂ and CO₂ isotherms were measured utilizing a high precision intelligent gravimetric analyzer (IGA, HidenIsochema Ltd., UK). Utilizing the electro-balance principle, the IGA is a completely automated computer-controlled microbalance capable of measuring weights within 1 µg accuracy. A stainless-steel container containing a known-weight sample is suspended from a gold chain in one arm, while a reference weight is affixed to the other arm. The sample chamber is equipped with a pressure transducer (Druck PDCR4010, ± 0.008 bar) and a thermocouple (±0.05 K) for temperature measurement. The current investigation involved the measurement of CO₂ adsorption uptake at 303, 313, and 323 K, while the N₂ adsorption uptake was assessed at 313 K. The isotherms were conducted for the pressure range of 0.1 to 10 bar. Each isotherm included a quantity of material ranging from 50 to 70 mg. The sample chamber was heated to a temperature of 453 K using a water-glycol bath and evacuated to a pressure of 10 mbar using a vacuum system (Pfeiffer) until the sample weight remained constant for a duration of 1 hour. This confirmed that the solvent, moisture, and pollutants were eliminated. Following the outgassing process, the sample was brought to the desired experimental temperature by altering the temperature of the water bath. Sufficient time was allowed for the sample to reach a stable temperature. Pressure levels were pre-set from 0.1 to 10 bar in the IGASwin program and isotherm measurements began when the sample was ready. A mass flow controller (MFC) controlled CO₂ or N₂ injection into the chamber to maintain pressure. The IGASwin program provided real-time monitoring of mass, temperature, and pressure. Following a period of at least two hours allowed for the pressure to reach equilibrium, the MFC introduced more CO₂ or N₂ at the subsequent pressure level. This was done for each predetermined pressure at a specified temperature. Real-time adsorption data were adjusted for buoyancy after the experiment.

3. Results and Discussion

3.1. Characterizations of the AAILs-impregnated Sorbents

Samples were heated up to 1173 K with a N₂ flow rate of 50 mL·min⁻¹ to evaluate the thermal stability of pure [Emim][Gly], [Emim][Ala], MCM-48, and all AAILs@MCM-48 compounds. The resultant thermograms are displayed in Figure 1. The thermogram of pristine MCM-48 indicates that there is small weight loss of 1% below 373 K as visible in derivative TGA (DrTGA) profile (Figure 1), and only 2% additional loss over the temperature range of 1173 K. The fact that it remains intact at temperatures up to 1173 K shows that pure MCM-48 is thermally stable. This agrees with previous studies as well, such as the work reported by Schumacher et al. who found that MCM-48 maintains its structural integrity up to 1123 K [1,15]. The thermograms of pristine AAILs [Emim][Gly] and [Emim][Ala] showed a small weight loss of 1 to 3% below 373 K which can be ascribed to the moisture content and were stable up 473 K. The AAILs showed a dramatic decline in weight above 473 K, suggesting a quick decomposition; based on the DrTGA profile, we can estimate that the onset decomposition temperatures (T_{onset}) of [Emim][Gly] and [Emim][Ala] are around 588 and 598 K, respectively. When heated to 1175 K, both AAILs evaporated. Any residual solvent (methanol), physically adsorbed moisture, or other contaminants might explain why all of the composites showed

a weight loss at temperatures below 373 K. As seen in the DrTGA profiles (Figure 1b&d), the composites began to lose weight at a significant rate at the T_{onset} of the pristine AAILs for temperatures between 473 and 723K, as anticipated. Beyond 673 K, there was very little weight loss until 1175 K. The resulting weight reduction for the composites is likely due to the AAILs. Since pristine MCM-48 showed very little weight loss up to 1173 K, any weight loss is likely attributable to the impregnated AAILs. It can therefore be concluded that the composites are thermally stable and that thermograms show that AAILs have been successfully impregnated.

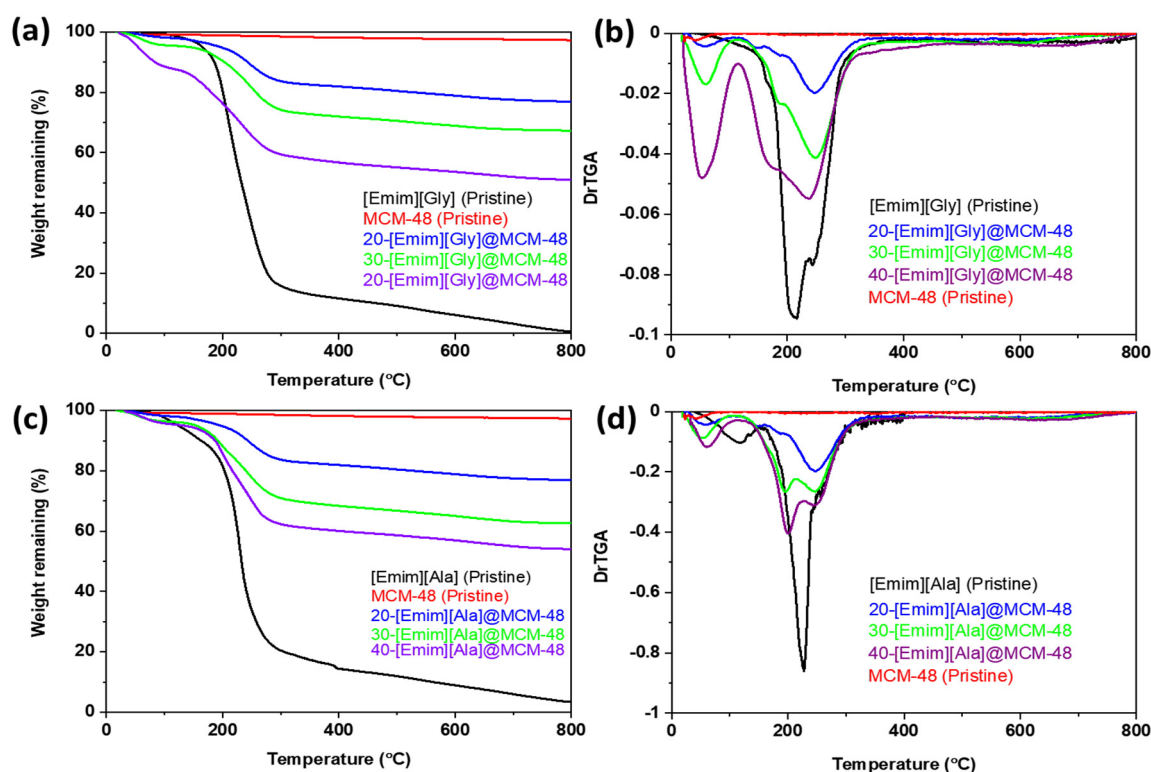


Figure 1. TGA and derivative of TGA profile for [Emim][Gly]@MCM-48 (a & b) and [Emim][Ala]@MCM-48 (c & d).

To elucidate the impact of incorporated AAILs on MCM-48 support structure, the both pristine MCM-48 and AAILs@MCM-48 composites were investigated using XRD. The analysis was performed within the angular range of 0.5° to 10° , with a scanning rate of 1.2° per minute. The resulting diffractogram is displayed in Figure 2. The unaltered MCM-48 exhibited prominent characteristic peaks at $2\theta = 2.61^\circ$ and a weak reflection peak at 4.5° , which aligns well with the findings in the existing literature [6][16]. After the addition of [Emim][Gly] and [Emim][Ala], the composites exhibited a consistent peak at around $2\theta = 2.61^\circ$ for all the various loadings. However, a subsequent decline in the peak intensity of the primary characteristic peak was detected with a higher AAILs loading. Additionally, the peak at higher indices also vanished. The decrease in intensity may be ascribed to the interaction between amine groups and MCM-48, which has previously been seen in the case of aminopropyl attached MCM-48[1] and PEI impregnated in MCM-41[17]. The XRD patterns of the composites demonstrate that the MCM-48 solid support structure remains unchanged during the impregnation procedure.

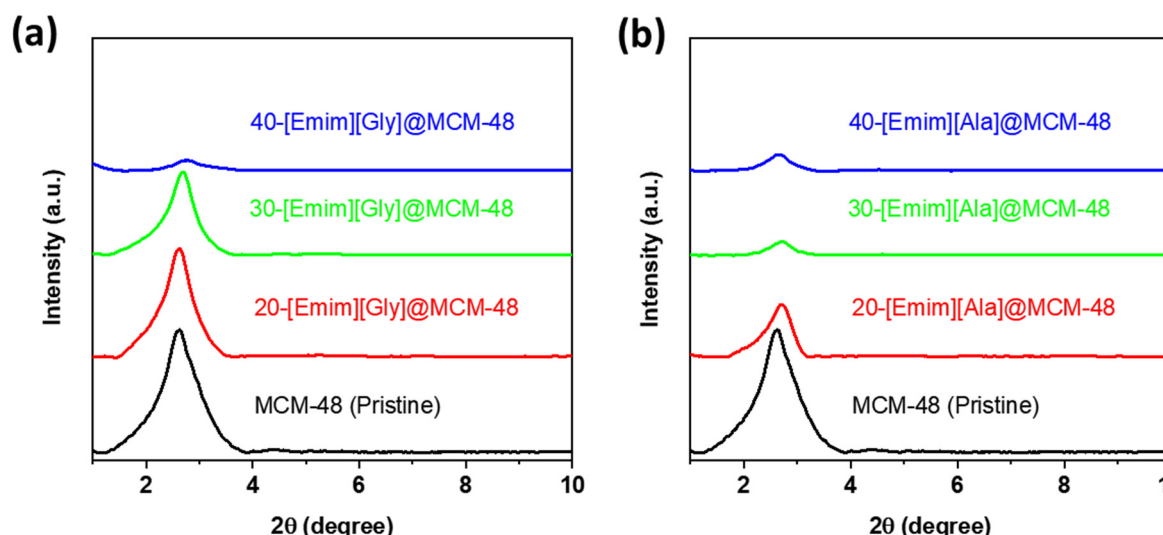


Figure 2. XRD profile of pristine MCM-48 and composites: (a) Emim][Gly]@MCM-48; (b) [Emim][Ala]@MCM-48.

To unfold the textural properties of the composites upon encapsulation of the AAILs into the pore of MCM support, N_2 adsorption-desorption isotherms of MCM-48 and AAILs@MCM-48 composites were obtained at liquid nitrogen temperature of 77 K, which are displayed in Figure 3. From the corresponding N_2 isotherm data the textural properties such as specific Brunauer-Emmett-Teller (BET) and Langmuir surface area, pore volume for each sample was calculated which are tabulated in Table 2. Unmodified MCM-48 support displayed typical type IV reversible isotherm characteristics of mesoporous material with sharp steps for the pressure range of $P/P_0 = 0.2$ to 0.3 associated to capillary condensation and without noticeable hysteresis. Similar isotherm for MCM-48 is also reported in previous literature [1][15][18]. The composites displayed significantly reduced N_2 adsorption compared to the original MCM-48. The isotherms also indicated hysteresis between P/P_0 values of 0.5 and 0.9, which may be ascribed to the filling of the pores and the blockage of the pore network by the encapsulated AAILs. According to Table 2, increasing the loading of AAILs leads to a further drop in both surface area and pore volume. For example, the BET surface area of composites 40-[Emim][Gly]@MCM-48 and 40-[Emim][Ala]@MCM-48 surface area decreases to 50 and 29 $m^2 \cdot g^{-1}$, respectively, and the pore volume decreases to 0.07 and 0.04 $cm^3 \cdot g^{-1}$. This suggests that when a large amount of AAILs is loaded, the pores of the MCM-48 support are essentially occupied by the enclosed AAILs.

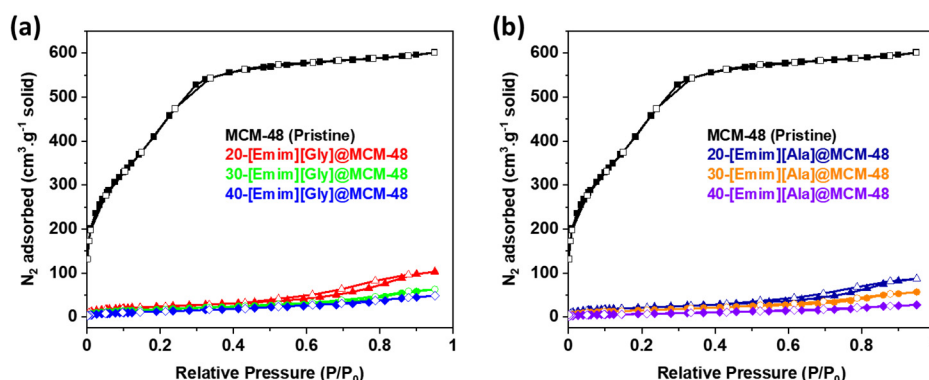


Figure 3. N_2 adsorption-desorption isotherms at 77 K for the pristine MCM-48 and composites [Emim][Gly]@MCM-48 (a) [Emim][Ala]@MCM-48 (b). Filled symbols represent the adsorption and unfilled symbols the desorption isotherms.

Table 2. Textural properties of pristine MCM-48 and AAILs@ MCM-48 composites computed from the N₂ adsorption-desorption isotherms at 77.

Samples	S _{BET} (m ² ·g ⁻¹)	S _{Langmuir} (m ² ·g ⁻¹)	Pore Volume (cm ³ ·g ⁻¹)
MCM-48	1,638	2,700	0.93
20-[Emim][Gly]@ MCM-48	87	287	0.16
30-[Emim][Gly]@ MCM-48	66	192	0.10
40-[Emim][Gly]@ MCM-48	50	155	0.07
20-[Emim][Ala]@ MCM-48	79	236	0.13
30-[Emim][Ala]@ MCM-48	60	196	0.09
40-[Emim][Ala]@ MCM-48	29	117	0.04

3.2. CO₂ Adsorption Isotherms

CO₂ absorption capacities were measured at 303, 313, and 323 K and pressures ranging from 0.1 to 10 bar for the pristine MCM-48, [Emim][Gly] @MCM-48, and [Em-im][Ala]@MCM-48 composites. Figure 4 illustrates the outcomes for the low-pressure range (0.1 to 1.0 bar), whereas Figure 5 displays the findings for the complete range of pressures (0.1 to 10 bar). CO₂ uptake of pristine MCM-48 was 0.07 and 0.14 mmol·g⁻¹ for 0.1 and 0.2 bar at 303K, respectively. CO₂ uptake increases linearly with the increase in pressure indicating that the process flowed a physisorption. [Emim][Gly] incorporated composite [Emim][Gly]@MCM-48 exhibited enhanced CO₂ uptake than the pristine MCM-48 at pressure below 2 bar. As an example, CO₂ adsorption capacity for 20%-[Emim][Gly]@MCM-48 sample was 0.19 mmol·g⁻¹ at 0.2 bar and 303 K. CO₂ uptake increases further with the increment of the loading at lower pressure. For 40 wt% loading of [Emim][Gly], the composite exhibited CO₂ uptakes of 0.74 and 0.82 mmol·g⁻¹ for 0.1 and 0.2 bar at 303 K, respectively, which are over 10- and 5-folds increase over the pristine MCM-48 at the same conditions.

A similar surge in CO₂ uptake was observed for [Emim][Ala] composites when CO₂ uptake increased with the increase in [Emim][Ala] loading (Figure 5). 40wt.% loaded [Emim][Ala]@MCM-48 exhibited the highest CO₂ adsorption of 0.65 and 0.74 mmol·g⁻¹ at 0.1 and 0.2 bar at 303 K, respectively, which are 9- and 5-fold increase relative to pristine MCM-48 . It is important to highlight that under identical temperature and pressure, the CO₂ adsorption capacity of [Emim][Ala]@MCM-48 composites was marginally lower than that of [Emim][Gly]@MCM-48 composites with an equivalent AAIL loading.

The substantial increase in CO₂ sorption capacity of the AAILs@MCM-48 sorbent following AAIL impregnation under post-combustion conditions (P_{CO₂} ≈ 0.15 bar) can be attributed to CO₂'s strong affinity for the amino group attached to the anion of the [Emim][Gly] and [Emim][Ala] that were introduced into the pore. According to published research [19–21], the amino group of AAILs reacts with CO₂ via a mechanism analogous to that of aqueous amine solution. According to Wang et al. [12], the reduced size of the cation and anion of [Emim][Gly] enables them to approach an amino group and undergo a reaction resulting in the formation of carbamate with a stoichiometry of 1:2 (Scheme 1). Hence, it can be hypothesized that the amino groups present in composites of [Emim][Gly]@MCM-48 and [Emim][Ala]@ MCM-48 engage in comparable interactions, culminating in the formation of carbamate via a reaction with CO₂. This process enhances the CO₂ uptake capacity of [Emim][Ala]@ MCM-48 relative to its pristine counterpart below a pressure of 1 bar.

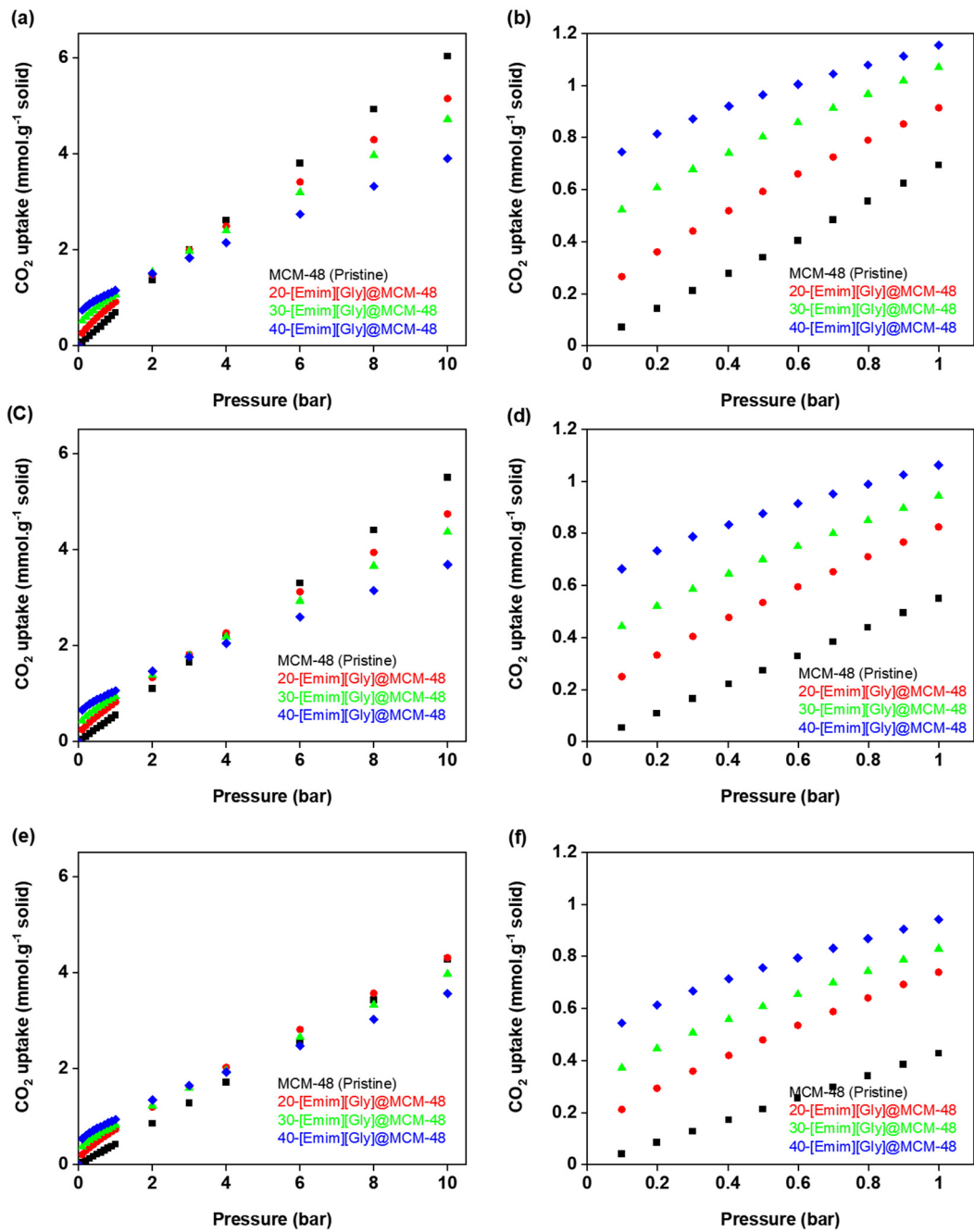


Figure 4. CO₂ equilibrium adsorption capacity of MCM-48 and [Emim][Gly]@MCM-48 composites at 303 K (a & b), 313 K (c & d) and 323 K (e & f).

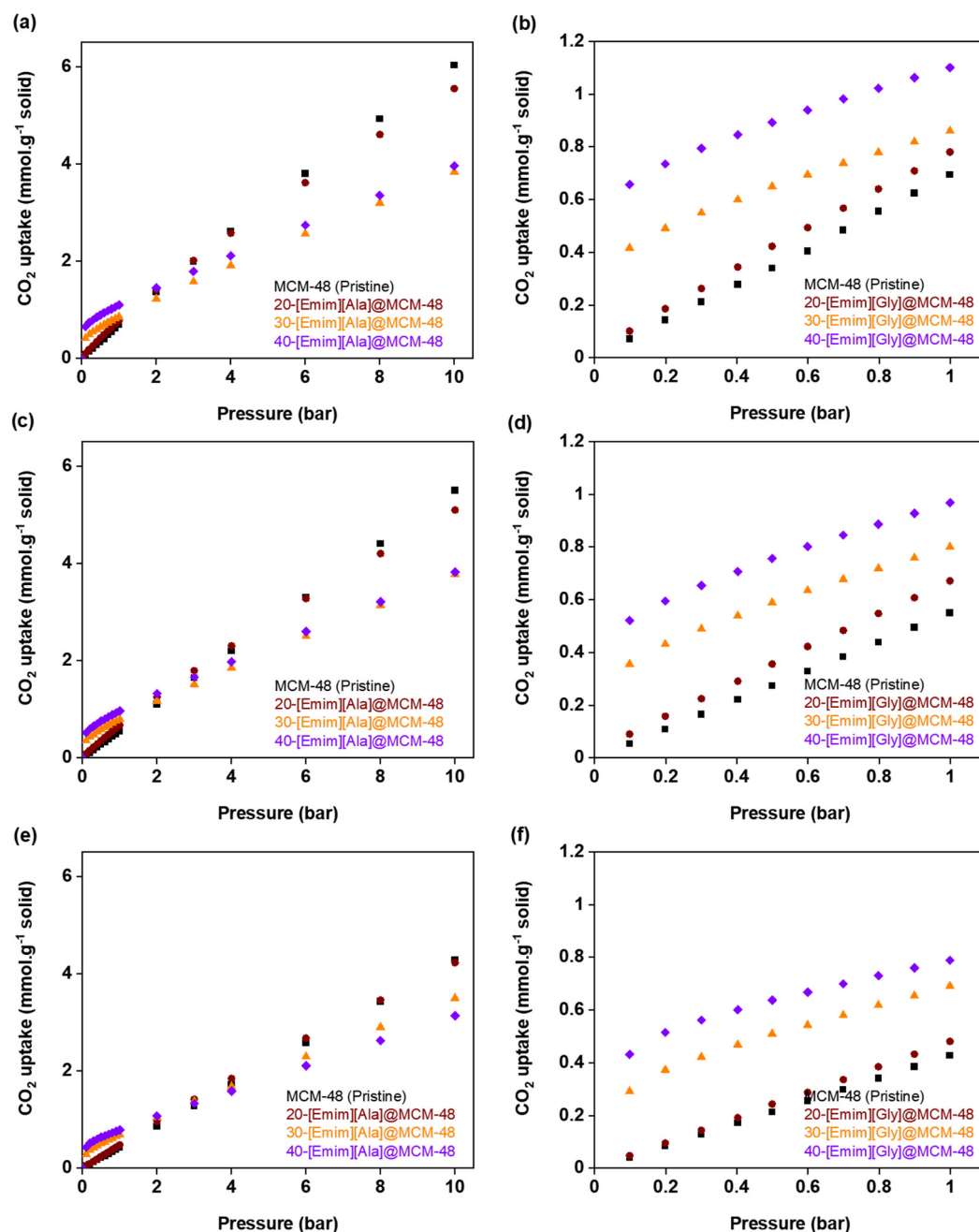
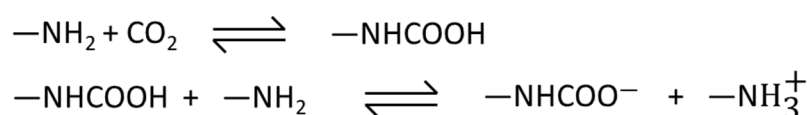


Figure 5. CO₂ equilibrium adsorption capacity of MCM-48 and [Emim][Ala]@MCM-48 composites at 303 K (a & b), 313 K (c & d) and 323 K (e & f).

Hence, although surface area and pore volume diminished significantly upon encapsulation of [Emim][Gly] and [Emim][Ala] but they provide the chemical active sites to attract CO₂. As a result, at lower pressure chemisorption act as a dominating factor. However, as the pressure increases, there are less chemical active sites available as those are already occupied, then the available surface area and pore volume plays a dominator role over the pressure at 2 bar and higher the loading of AAILs, lower the available active surface available. As the pressure rises to the moderate and high levels, the adsorption capacity of the sorbent is determined not only by the active chemical adsorption sites inside the sorbent but also by the physical adsorption sites that are present [22]. Hence can be observed from Figures 4 and 5, at a pressure above 2 bar, CO₂ uptake was lower for all AAILs@MCM-48 composites compared to pristine MCM-48 at the three temperatures studied. CO₂ uptake decreased across the board for all composites when the temperature ramped up to 423 K from 403 K at the same pressure.



Scheme 1. Schematic representation of the reaction between carbon dioxide (CO₂) and ionic liquids containing amino groups (AILs) impregnated on a solid substrate.[20].

3.3. Selectivity for CO₂/N₂

For an effective solid sorbent in the post-combustion capture process, it is crucial to have excellent selectivity of CO₂ over other gases, particularly N₂. Therefore, in order to determine the selectivity of CO₂/N₂, we conducted measurements of N₂ adsorption isotherms at a temperature of 40 °C. The pressure range for each isotherm spanned from 0.1 to 10 bar. The optimal selectivity may be determined by many approaches, one of which involves computing the selectivity based on the isotherms of individual components. This technique relies on adsorption of the components at the identical pressure, as shown in Equation (1) [23].

$$S = \frac{q_{\text{CO}_2}}{q_{\text{N}_2}} \quad (1)$$

where S denoted the selectivity and q_{CO_2} and q_{N_2} symbolize the adsorption of CO₂ and N₂ in mole, respectively. The computed ideal CO₂/N₂ selectivity from the isotherms of CO₂ and N₂ at 313 K of [Emim][Gly]@MCM-48 and [Emim][Ala]@MCM-48 composites are displayed in Figure 6. It was found that the pristine MCM-48 exhibited almost constant CO₂/N₂ selectivity of about 2 for the entire pressure range. Whereas [Emim][Gly] and [Emim][Ala] encapsulated MCM-48 composites displayed higher CO₂/N₂ selectivity at lower pressure below 2 bar and selectivity increases with the increase of loading. Out of all the composites containing [Emim][Gly]@MCM-48, the 40wt%- [Emim][Gly]@MCM-48 composite exhibited the best selectivity of 11 and 8 at pressures of 0.1 and 0.2 bar, respectively. However, the selectivity steadily decreased as the pressure increased. Likewise, 40 wt% [Emim][Ala]@MCM-48 exhibited the highest selectivity among all [Emim][Ala]@MCM-48 composites, reaching 17 and 11 at 0.1 and 0.2 bar, respectively.

The significant surge in CO₂/N₂ selectivity for the composites compare to pristine MCM-48 can be attributed to the presence of encapsulated amino acid base liquid into the pore of MCM-48. As stated earlier, the loading of AAILs resulted in a significant increase in the amount of CO₂ that was taken in. This may be due to the active chemical sorption sites for carbon dioxide provided by the amino acids. It is hypothesized that these sites generate an N-C bond that is similar to the interaction that occurs between CO₂ and alkanolamine. Even though the occupied ionic liquid resulted in a decrease in the surface area and pore volume, the amount of CO₂ captured was dramatically enhanced. On the other hand, owing to the physical nature of adsorption, which is reliant on the surface area that is available, N₂ does not have any affinity for the amino group and was therefore not adsorbed. The final outcome is a higher CO₂/N₂ selectivity because, at low pressure, the absorption of carbon dioxide is more prevalent than the uptake of nitrogen. However, as the pressure is increased, the adsorption capacity is also governed by the physical adsorption sites present. This is in addition to the active chemical adsorption sites that are present in the sorbent. As a consequence, the selectivity of the composites for CO₂/N₂ diminishes as the pressure increases, and it reaches a level that is lower than that of the pristine MCM-48 when the pressure is more than 2 bar.

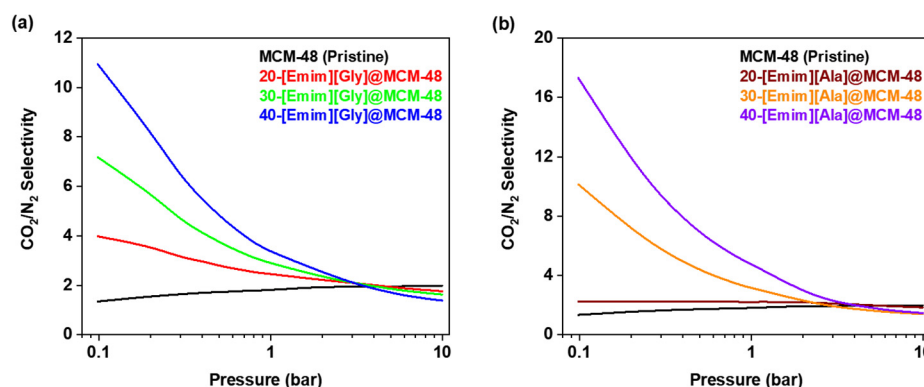


Figure 6. CO₂/N₂ selectivity of [Emim][Gly]@MCM-48 (a) and [Emim][Ala]@MCM-48 (b) composites at 313 K.

A closer look at both AAILs composites reveals that the 40 wt%-[Emim][Ala]@MCM-48 exhibited higher CO₂/N₂ selectivity than the 40wt%-[Emim][Gly]@MCM-48 although CO₂ uptake of 40 wt%-[Emim][Gly]@MCM-48 was higher than that of 40 wt%-[Emim][Ala]@MCM-48. This can be attributed to the less N₂ uptake by 40 wt%-[Emim][Ala]@MCM-48 with lower surface area and pore volume available than 40 wt%-[Emim][Gly]@MCM-48 as explained earlier. Hence despite lower CO₂ uptake by 40 wt%-[Emim][Ala]@MCM-48, CO₂/N₂ selectivity was higher.

3.4. Equilibrium Isotherm Modeling

Equilibrium isotherm modeling is crucial for accurately representing the experimental data in the design of adsorption and desorption processes. The composite in this work exhibits both robust and weak binding sites as a result of the inclusion of encapsulated AAILs inside the pore of MCM-48. Therefore, after considering many models, the Dual-site-Langmuir model (DSL) [25,26] was determined to be appropriate. This model integrates the Langmuir adsorption at two different sites, and the overall adsorption is the sum of the adsorption at each individual site, as shown in Equation (2) [24]

$$N_e = \frac{N_A b_A P}{1 + b_A P} + \frac{N_B b_B P}{1 + b_B P} \quad (2)$$

where, N_e represents CO₂ uptake (mmol·g⁻¹), P represents the pressure (bar), N_A , N_B , b_A , b_B represent the DSL parameters. The regressed parameters for the composites [Emim][Gly]@MCM-48 and [Emim][Ala]@MCM-48 are, respectively, presented in Tables 3 and 4. These figures depict the fitting contours of the DSL model (Figures 7 and 8). The model provided an exceptional fit to the experimental data, as indicated by the close proximity of R^2 values to unity. Consequently, the enthalpy of adsorption will be calculated using the model data in the following section.

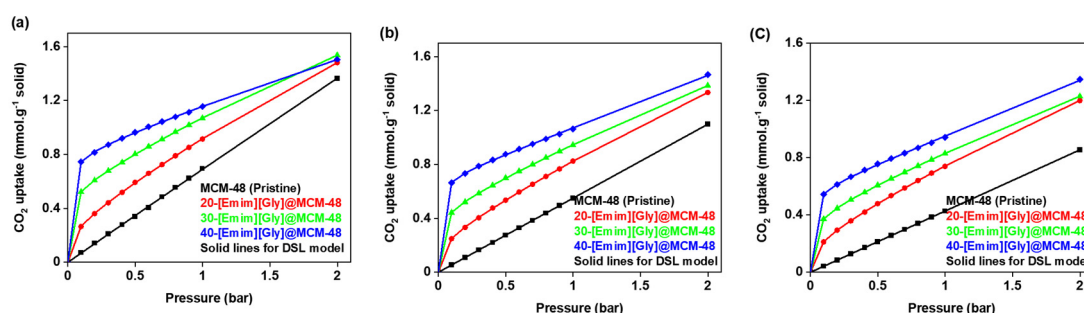


Figure 7. CO₂ equilibrium uptake of MCM-48 and [Emim][Gly]@MCM-48 composites fitted using the DSL model (Solid line) at various loadings of [Emim][Gly] at temperatures of 403 K (a), 413 K (b), and 423 K(c), with a pressure range of 0.1 to 2.0 bar.

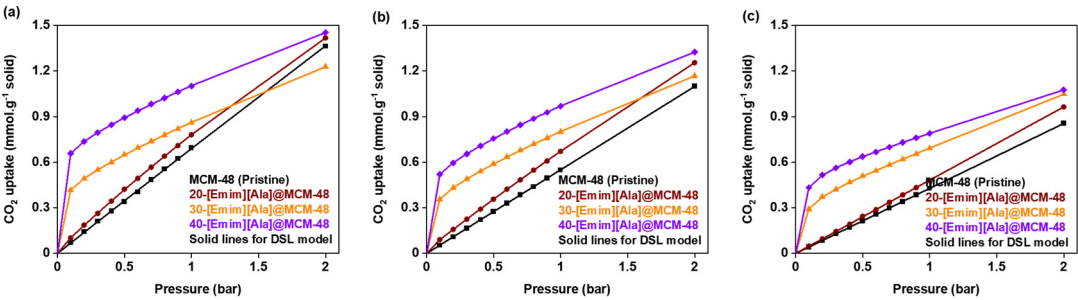


Figure 8. CO₂ equilibrium uptake of MCM-48 and [Emim][Ala]@MCM-48 composites fitted using the DSL model (Solid line) at various loadings of [Emim][Ala] at temperatures of 403 K (a), 413 K (b), and 423 K (c), with a pressure range of 0.1 to 2.0 bar.

Table 3. DSL model parameters for the MCM-48 and [Emim][Gly]@MCM-48 composites at 303 K, 313 K and 323K for the pressure range of 0.1 to 2.0 bar.

Model Parameters	20-[Emim][Gly]@MCM-48			30-[Emim][Gly]@MCM-48			40-[Emim][Gly]@MCM-48		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
N _A	7.277	0.239	6.204	0.520	0.450	0.390	0.780	0.691	0.572
b _A	0.102	37.406	0.095	83.374	67.387	52.263	95.804	101.737	81.843
N _B	0.248	7.722	0.209	5.896	7.090	7.041	7.017	731.290	531.196
b _B	36.92	0.083	29.783	0.105	0.076	0.068	0.058	0.001	0.001
R ²	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Table 4. DSL model parameters for the MCM-48 and [Emim][Ala]@MCM-48 composites at the temperature of 303 K, 313 K and 323K for the pressure range of 0.1 to 2.0 bar.

Model Parameters	20-[Emim][Ala]@MCM-48			30-[Emim][Ala]@MCM-48			40-[Emim][Ala]@MCM-48		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
N _A	0.026	0.023	349.867	0.433	0.374	0.357	0.679	0.531	0.525
b _A	53.033	10000	0.000	58.632	48.183	26.971	90.057	79.650	34.622
N _B	8.784	12.152	579.453	4.647	4.692	227.845	3.908	3.753	94.954
b _B	0.094	0.056	0.001	0.104	0.102	0.002	0.124	0.135	0.003
R ²	1.000	0.999	1.000	1.000	1.000	1.000	1.000	1.000	1.000

3.5. Isosteric heat of adsorption (*Q_{st}*)

The isosteric heat of adsorption (adsorption enthalpy, *Q_{st}*), is a crucial metric in the adsorption-based CO₂ capture process. It discloses the attraction and intensity of the interaction between the gas molecules being adsorbed and the host. Therefore, it signifies the magnitude of the energy needed for the adsorption-desorption process. The adsorption enthalpy (*Q_{st}*) was calculated based on the CO₂ isotherms obtained at 303, 313, and 323 K. The DSL model was employed to initially fit the isotherms, as mentioned in the previous section. Following this, the Clausius–Clapeyron equation, represented by equation (3), was used [24].

$$(\ln P)_N = -\left(\frac{Q_{st}}{R}\right)\left(\frac{1}{T}\right) + C \tag{3}$$

where, *P* stands for pressure (bar), *N* for CO₂ uptake, *R* is the universal gas constant and *T* for temperature (K). According to the equation, graphs of (ln *P*) vs 1/*T* were plotted at a constant CO₂ uptake. The slope of the plots represents the *Q_{st}* corresponding to the CO₂ uptake. The calculated *Q_{st}* for pristine MCM-48 and AAILs@MCM-48 composites are illustrated in Figure 9. The *Q_{st}* values for pristine MCM-48 were approximately 20 kJ·mol⁻¹ which also confirms the physisorption nature of

CO₂ adsorption whereas a sharp increase of Q_{st} was observed for [Emim][Gly] and [Emim][Ala] incorporated into MCM-48 composites. An upward trend in the isosteric heat of adsorption was noted as the concentration of AAILs on both sorbents increased incrementally. The maximum values of Q_{st} were -71 and -77 kJ·mol⁻¹, respectively, for 40 wt%-[Emim][Gly]@MCM-48 at 0.7 mmol·g⁻¹ CO₂ uptake and 0.6 mmol·g⁻¹ CO₂ uptake, respectively. Q_{st} values reached their maximum at low pressures ranging from 0.1 to 0.2 bar, at the initial stage of CO₂ adsorption. The observed rise in Q_{st} can be ascribed to a substantial increase in CO₂ adsorption within the low-pressure range, which leads to a greater release of heat throughout the adsorption process. As previously described, the amino group of the anion of the TSIL is capable of forming N-C bonds and, as a result, liberating a greater quantity of energy during CO₂ adsorption [24]. With additional CO₂ adsorbed, the value of Q_{st} decreases significantly after the peak, reducing the number of amine sites with the highest affinity that are available for CO₂ molecules to occupy. Comparable trends in Q_{st} variations were detected upon incorporating [Bmim][Ac] and [Emim][Ac] into ZIF-8, consistent with findings reported in a previous investigation conducted by our research group. [26]

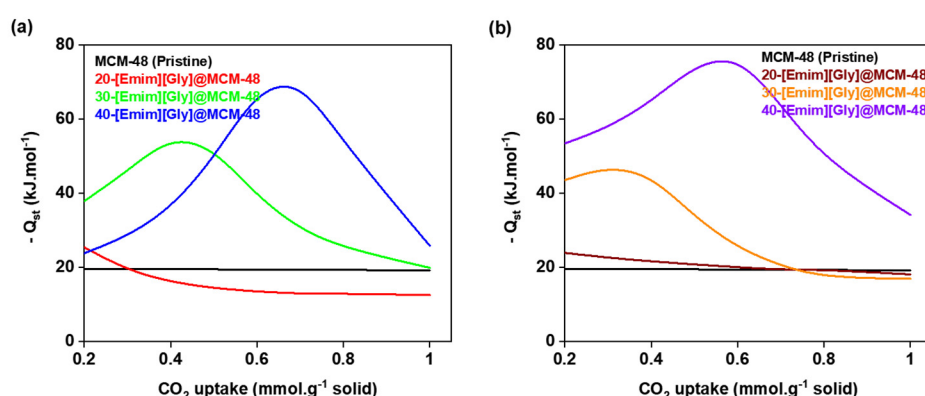


Figure 9. CO₂ adsorption enthalpy (Q_{st}) of (a) [Emim][Gly]@MCM-48 and (b) [Emim][Ala]@MCM-48 composites.

4. Conclusions

The objective of this work was to enhance the capacity for capturing CO₂ and the selectivity of CO₂ over N₂ by encapsulating amino acid-based ionic liquids (AAILs) [Emim][Gly] and [Emim][Ala] into ordered mesoporous silica MCM-48, resulting in the formation of AAILs@MCM-48 composites. The thermogravimetric and XRD characterization of the composites indicates that the thermal and structural integrity of the original MCM-48 support remained unchanged after the AAILs were encapsulated. An N₂ adsorption-desorption analysis conducted at 77 K revealed a substantial decrease in surface area and pore volume as the support's pores were almost entirely filled with increasing AAIL loading. This finding further verifies the effective encapsulation of AAILs inside the porous support. Both [Emim][Gly]@MCM-48 and [Emim][Ala]@MCM-48 showed enhanced CO₂ adsorption compared to the unmodified MCM-48 at post-combustion flue gas conditions, with a CO₂ partial pressure of around 0.15 bar. Among the composites, the 40 wt%-[Emim][Gly] composite showed the maximum CO₂ uptake of 0.74 and 0.82 mmol·g⁻¹ at 0.1 and 0.2 bar, respectively, at 303 K. These values represent an increase of nearly 10- and 5-fold compared to the pristine MCM-48 under the same circumstances. Composites demonstrated both enhanced CO₂ absorption and increased CO₂/N₂ selectivity. The selectivity of 40 wt% [Emim][Ala]@MCM-48 composites significantly increased to 17 at 0.1 bar, while the selectivity of the pristine MCM-48 was only 2. It can therefore be inferred that AAILs@MCM-48 composites possess significant potential to be considered as candidates for the post-combustion CO₂ capture.

Author Contributions: **Firuz A. Philip:** Conceptualization, Methodology, Material synthesis, Characterization, Experimental analysis, Validation, Data analysis, Writing-Original draft preparation, **Amr Henni:**

Conceptualization, Resources, Funding acquisition, Writing-Review& Editing, Project administration, Supervision.

Funding: This research was funded by a grant provided to the second author by The Natural Sciences and Engineering Research Council of Canada (NSERC) - Discovery Grant (RGPIN-2018-06805)

Institutional Review Board Statement: Not applicable

Informed Consent Statement: Not applicable

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are not available from the authors.

References

- Kim, S.; Ida, J.; Gulians, V. V.; Lin, J.Y.S. Tailoring Pore Properties of MCM-48 Silica for Selective Adsorption of CO₂. *J. Phys. Chem. B* **2005**, *109*, 6287–6293, doi:10.1021/jp045634x.
- Samanta, A.; Zhao, A.; Shimizu, G.K.H.; Sarkar, P.; Gupta, R. Post-Combustion CO₂ Capture Using Solid Sorbents: A Review. *Ind. Eng. Chem. Res.* **2012**, *51*, 1438–1463.
- Yu, C.-H.; Huang, C.-H.; Tan, C.-S. A Review of CO₂ Capture by Absorption and Adsorption. *Aerosol Air Qual. Res.* **2012**, *12*, 745–769, doi:10.4209/aaqr.2012.05.0132.
- Ünveren, E.E.; Monkul, B.Ö.; Sarioğlu, Ş.; Karademir, N.; Alper, E. Solid Amine Sorbents for CO₂ Capture by Chemical Adsorption: A Review. *Petroleum* **2017**, *3*, 37–50.
- Yue, M.B.; Chun, Y.; Cao, Y.; Dong, X.; Zhu, J.H. CO₂ Capture by As-Prepared SBA-15 with an Occluded Organic Template. *Adv. Funct. Mater.* **2006**, *16*, 1717–1722, doi:10.1002/adfm.200600427.
- Huang, H.Y.; Yang, R.T.; Chinn, D.; Munson, C.L. Amine-Grafted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas. *Ind. Eng. Chem. Res.* **2003**, *42*, 2427–2433, doi:10.1021/ie020440u.
- Wei, J.; Liao, L.; Xiao, Y.; Zhang, P.; Shi, Y. Capture of Carbon Dioxide by Amine-Impregnated as-Synthesized MCM-41. *J. Environ. Sci.* **2010**, *22*, 1558–1563, doi:10.1016/S1001-0742(09)60289-8.
- Chen, H.; Liang, Z.; Yang, X.; Zhang, Z.; Zhang, Z. Experimental Investigation of CO₂ Capture Capacity: Exploring Mesoporous Silica SBA-15 Material Impregnated with Monoethanolamine and Diethanolamine. *Energy and Fuels* **2016**, *30*, 9554–9562, doi:10.1021/acs.energyfuels.6b01298.
- Xu, X.; Song, C.; Andresen, J.M.; Miller, B.G.; Scaroni, A.W. Novel Polyethylenimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO₂ Capture. *Energy and Fuels* **2002**, *16*, 1463–1469, doi:10.1021/ef020058u.
- Wang, X.; Chen, L.; Guo, Q. Development of Hybrid Amine-Functionalized MCM-41 Sorbents for CO₂ capture. *Chem. Eng. J.* **2015**, *260*, 573–581, doi:10.1016/j.cej.2014.08.107.
- Santos, S.C.G.; Pedrosa, A.M.G.; Souza, M.J.B.; Cecilia, J.A.; Rodríguez-Castellón, E. Carbon Dioxide Adsorption on Micro-Mesoporous Composite Materials of ZSM-12/MCM-48 Type: The Role of the Contents of Zeolite and Functionalized Amine. *Mater. Res. Bull.* **2015**, *70*, 663–672, doi:10.1016/j.materresbull.2015.05.037.
- Wang, X.; Akhmedov, N.G.; Duan, Y.; Luebke, D.; Li, B. Immobilization of Amino Acid Ionic Liquids into Nanoporous Microspheres as Robust Sorbents for CO₂ Capture. *J. Mater. Chem. A* **2013**, *1*, 2978–2982, doi:10.1039/c3ta00768e.
- Philip, F.A.; Henni, A. Enhancement of Post-Combustion CO₂ Capture Capacity by Incorporation of Task-Specific Ionic Liquid into ZIF-8. *Microporous Mesoporous Mater.* **2021**, *111580*, doi:10.1016/j.micromeso.2021.111580.
- Philip, F.A.; Henni, A. Incorporation of Amino Acid-Functionalized Ionic Liquids into Highly Porous MOF-177 to Improve the Post-Combustion CO₂ Capture Capacity. *Molecules* **2023**, *28*, 7185, doi:10.3390/molecules28207185.
- Schumacher, K.; Ravikovitch, P.I.; Du Chesne, A.; Neimark, A. V.; Unger, K.K. Characterization of MCM-48 Materials. *Langmuir* **2000**, *16*, 4648–4654, doi:10.1021/la991595i.

16. Xu, J.; Luan, Z.; He, H.; Zhou, W.; Kevan, L. A Reliable Synthesis of Cubic Mesoporous MCM-48 Molecular Sieve. *Chem. Mater.* **1998**, *10*, 3690–3698, doi:10.1021/cm980440d.
17. Thi Le, M.U.; Lee, S.Y.; Park, S.J. Preparation and Characterization of PEI-Loaded MCM-41 for CO₂ Capture. *Int. J. Hydrogen Energy* **2014**, *39*, 12340–12346, doi:10.1016/j.ijhydene.2014.04.112.
18. Boote, B.; Subramanian, H.; Ranjit, K.T. Rapid and Facile Synthesis of Siliceous MCM-48 Mesoporous Materials. *Chem. Commun.* **2007**, 4543–4545, doi:10.1039/b706633c.
19. Bates, E.D.; Mayton, R.D.; Ntai, I.; Davis, J.H. CO₂ Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927, doi:10.1021/ja017593d.
20. Ren, J.; Wu, L.; Li, B.G. Preparation and CO₂ Sorption/Desorption of N -(3-Aminopropyl)Aminoethyl Tributylphosphonium Amino Acid Salt Ionic Liquids Supported into Porous Silica Particles. *Ind. Eng. Chem. Res.* **2012**, *51*, 7901–7909, doi:10.1021/ie2028415.
21. Gurkan, B.E.; De La Fuente, J.C.; Mindrup, E.M.; Ficke, L.E.; Goodrich, B.F.; Price, E.A.; Schneider, W.F.; Brennecke, J.F. Equimolar CO₂ Absorption by Anion-Functionalized Ionic Liquids. *J. Am. Chem. Soc.* **2010**, *132*, 2116–2117, doi:10.1021/ja909305t.
22. Ferreira, T.J.; Ribeiro, R.P.P.L.; Mota, J.P.B.; Rebelo, L.P.N.; Esperança, J.M.S.S.; Esteves, I.A.A.C. Ionic Liquid-Impregnated Metal-Organic Frameworks for CO₂/CH₄ Separation. *ACS Appl. Nano Mater.* **2019**, *2*, 7933–7950, doi:10.1021/acsanm.9b01936.
23. Lin, Y.; Kong, C.; Zhang, Q.; Chen, L. Metal-Organic Frameworks for Carbon Dioxide Capture and Methane Storage. *Adv. Energy Mater.* **2017**, *7*, 1601296, doi:10.1002/aenm.201601296.
24. Sumida, K.; Rogow, D.L.; Mason, J.A.; McDonald, T.M.; Bloch, E.D.; Herm, Z.R.; Bae, T.-H.; Long, J.R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 724–781, doi:10.1021/cr2003272.
25. Kinik, F.P.; Altintas, C.; Balci, V.; Koyuturk, B.; Uzun, A.; Keskin, S. [BMIM][PF₆] Incorporation Doubles CO₂ Selectivity of ZIF-8: Elucidation of Interactions and Their Consequences on Performance. *ACS Appl. Mater. Interfaces* **2016**, *8*, 30992–31005, doi:10.1021/acsami.6b11087.
26. Mohamedali, M.; Ibrahim, H.; Henni, A. Incorporation of Acetate-Based Ionic Liquids into a Zeolitic Imidazolate Framework (ZIF-8) as Efficient Sorbents for Carbon Dioxide Capture. *Chem. Eng. J.* **2018**, *334*, 817–828, doi:10.1016/j.cej.2017.10.104.

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