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Journal Name

ARTICLE

[Cu₃(BTC)₂]-Polyethyleneimine an efficient MOF composite for effective CO₂ separation

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The increased CO₂ concentration in earth's atmosphere results in global warming and has increased concerns towards the development of efficient strategy for carbon capture and storage. The CO₂ separation from flue gas is one of the most challenging areas. Here, Cu-BTC MOF and a series of Polyethyleneimine (PEI) incorporated Cu-BTC composites (Cu-BTC-PEI) with different loading amount of PEI have been developed for CO₂ separation. A significant increase in CO₂ adsorption capacity was observed with Cu-BTC-PEI adsorbents. Detailed characterization of developed adsorbents was done by XRD, SEM, BET surface area and IR. The synthesized adsorbents show good CO₂/N₂ selectivity for the designed flue gas composition containing 15 vol% CO₂ and balance N₂. The 2.5 wt% PEI loaded Cu-BTC (Cu-BTC-PEI-2.5) has shown CO₂ adsorption capacity 0.83 mmol g⁻¹ at pressure 0.15 bar and 25 °C which is almost double of Cu-BTC in similar conditions. But at elevated pressure of 5 bar and 25 °C, 1 wt% PEI loaded Cu-BTC (Cu-BTC-PEI-1) has performed even better with CO₂ adsorption capacity of 10.57 mmol g⁻¹. A better adsorption capacity and selectivity for CO₂ was obtained with Cu-BTC-PEI composite and are good aspirant adsorbent for CO₂ separation from flue gas.

1. Introduction

The carbon capture and storage (CCS) has attracted attention due to rising CO₂ emission from fossil fuel combustion for growing energy needs. CO₂ is the major component of emission gases which is (c.a. 60 %) of total green house gases and has major contribution toward global warming [1]. The atmospheric CO₂ concentration has reached to c.a. 403 ppm, which is significantly higher than preindustrial level of 300 ppm. The flue gas contains 14-15 % CO₂, 75-76 % N₂ and remaining H₂O, SO_x, NO_x. Therefore, adsorbent for CO₂ adsorption should possess a high CO₂ uptake and selectivity at a partial pressure

near 0.15 bar. Therefore, CO₂ separation from flue gas at room temperature and atmospheric pressure is a challenging task.

The current major requirement for any CO₂ separation process is the development of adsorbent with high adsorption capacity, selectivity, low regeneration cost and stability in actual conditions. Various solid adsorbents such as Zeolites [2], activated carbons [3], silicas [4], and new classes of porous materials [5-7] have been reported in literature for CO₂ adsorption. Among them, Metal-Organic Frameworks (MOFs) [8, 9] are emerged as potential adsorbent due to their high CO₂ storage and separation capability [10-12]. A number of MOFs materials in recent years have successfully been synthesized [13-16] focusing on their well-characterized crystalline architectures, ultrahigh porosity and the possibility of functionality. Although, designing of MOFs for CO₂ adsorption with high capacity and selectivity remains a challenge, as MOFs

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not only adsorb CO₂ but also strongly adsorb some other gases such as N₂, CH₄ and O₂. So, MOFs should be designed in such a way that pores and other functional group present in MOFs selectively and specifically adsorb CO₂. A limited number of MOFs have shown satisfactory CO₂ separation at low pressure and ambient temperature due to the weak interaction between CO₂ and framework [17, 18].

Nowadays, main emphasis in MOFs formulation is towards the enhancement of CO₂ binding capacity [19–21]. Amine grafting, introduction of strongly polarizing functional groups and open metal cation sites are mostly studied approaches. Amine functionalized zeolites and silica are already reported in literature for CO₂ adsorption [22–26]. Similarly, amine functionalization of MOFs is currently emerged as potential approach for CO₂ adsorption with low heat capacity. So, based on these studies it may be concluded that porosity and amount of amine loading determine their CO₂ adsorption capacity [23].

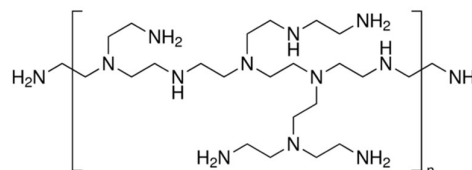
Recently, integration of diamine or polyamine into open metal sites of MOFs have been reported to increase the CO₂ adsorption capacity at low pressure and room temperature [27–29]. The dispersion of polyamine in MOFs framework allows diffusion and adsorption of CO₂ molecule which results in high CO₂ adsorption capacity with MOFs/polyamine composite. Pure polyamine is found in gel form which hinders the diffusion of CO₂ molecule and interaction with amine group. MOFs act as support and dispersion surface for polyamines to determine the enhanced CO₂ adsorption capacity and selectivity. Polyethyleneimine (PEI) is one of suitable polyamine for loading in MOFs due to its high amine density and accessible primary amine sites at chain ends [23, 30]. The higher pore volume, porosity and surface area of MOFs than silica or zeolite make them more suitable for PEI impregnation with high CO₂ adsorption capacity. The PEI impregnation into MOFs is recently reported by Chen et al. [27, 31] which is only available literature for MOFs-PEI composites.

Cu₃(BTC)₂ (also known as HKUST; btc=1,3,5-benzenetricarboxylic acid) is chosen as MOFs because it has large surface area, high pore volume, chemical stability and the Lewis acidity of open metal sites [32, 33]. Post synthetic modification of Cu-BTC by coordinating 4-(methylamino)-pyridine to the Cu-center has been reported by Ingleson et al. [34] while few reports are available in literature on the modification of organic linker H₃btc by methyl, ethyl group [35] and amine group [36, 37]. Herein, we report the loading of branched PEI into Cu-BTC framework for enhanced CO₂ adsorption capacity. The PEI is anchored to the open metal sites of Cu-BTC to form Cu-BTC-PEI composite adsorbent. The used branched PEI of molecular weight (Mw=1,300) possesses more primary amine groups (-NH₂-) that could show higher affinity for CO₂ than secondary amine (-NH-) [38].

2. Experimental

2.1. Materials

Benzene-1,3,5-tricarboxylic acid (H₃BTC, Sigma-Aldrich), cupric nitrate trihydrate (Spectral, India), Ethanol (Fisher) and Methanol (SRL, India) were used as received without further purification. Branched polyethyleneimine (50 wt % in H₂O, Mw ≈ 1300, Sigma-Aldrich) was used in the present study. The PEI structure is as follows



2.2. Synthesis of Cu-BTC [Cu₃(BTC)₂]

Cu₃(BTC)₂ was synthesized according to the procedure reported by Chui *et al* [39]. The ethanolic solution of H₃BTC (1.2 g, 5mmol in 20mL) was slowly added on continuous stirring to the aqueous solution of Cu(NO₃)₂·3H₂O (2.17 g, 9 mmol in 20mL). The resulting reaction mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 120 °C for 18 h. After cooling to ambient temperature, blue crystals of Cu-BTC were isolated by filtration, and repeatedly washed with deionized water followed by ethanol. Finally, Cu-BTC was dried under vacuum at 130 °C for 12 h.

2.3. Synthesis of Cu-BTC-PEI composites

The Cu-BTC-PEI composite MOFs were synthesized by following wet impregnation method. Before impregnation Cu-BTC MOF was activated at 130 °C for 12 h under vacuum to remove foreign molecules and to make free cavities available for loading of desired molecules. PEI corresponding to 1.0, 2.5 and 5.0 wt % loading respectively was dissolved in anhydrous methanol. Then Cu-BTC (0.5 g) was added in steps to above solutions and stir for 1 hr. The resulting gel was dried overnight at room temperature under nitrogen protection. Obtained material was dried at 110 °C for 12 h under vacuum. Eventually a porous solid Cu-BTC-PEI were obtained corresponding to 1.0, 2.5 and 5.0 wt % loading of PEI and abbreviated as Cu-BTC-PEI-1, Cu-BTC-PEI-2.5 and Cu-BTC-PEI-5, respectively.

2.4. Characterization

Powder XRD data of the product were collected on a Bruker D8 Avance diffractometer using CuKα radiation at room temperature in angular range of 5 – 30° (2θ) with a step size of 0.02°/sec (2θ). IR spectra of the samples were recorded as KBr pellets in a Thermo Nicolet 8700 spectrometer. Cu-BTC and Cu-BTC-PEI samples were activated under vacuum conditions for IR analysis. Thermo gravimetric analyses of the complexes were carried out using Perkin Elmer's Diamond under nitrogen

atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ up to $600\text{ }^{\circ}\text{C}$. Before TGA measurement all samples were activated at $130\text{ }^{\circ}\text{C}$ for 6 h. The morphology of adsorbents was examined using a Field Emission Scanning Electron Microscope (FE-SEM). Transmission Electron Microscopy (TEM)-elemental mapping and TEM-EDX analysis was performed on JEOL model no JEM 2100. The surface area, and pore volume measurements were performed using a surface area analyzer (Micromeritics Tristar II). All samples were out gassed under vacuum at $130\text{ }^{\circ}\text{C}$ for about 12 h prior to measurement of N_2 isotherms at 77 K. For surface area calculation the relative pressure (P_s/P_o) range was between 0.05 and 0.2.

2.5. Sorption Experiments

Adsorption equilibrium isotherms of CO_2 and N_2 on the Cu-BTC and Cu-BTC-PEI composites were measured gravimetrically on Rubotherm Magnetic Suspension balance at 25, 40 and $55\text{ }^{\circ}\text{C}$ respectively. Prior to adsorption isotherm experiment each adsorbent was activated at $130\text{ }^{\circ}\text{C}$ for 12 hr under vacuum. During the gaseous sorption measurements, the sample mass were monitored until equilibrium achieved at each pressure. The buoyancy volume required for the corrections was obtained using helium as a non-adsorbing reference gas at $25\text{ }^{\circ}\text{C}$. Buoyancy corrections were applied to raw measurements recorded by balance, to calculate excess amount adsorbed [40]. In typical adsorption equilibrium measurement, the adsorption equilibrium was determined by observing the plateau in the uptake curve. The equilibrium was assumed to have been achieved when the gas uptake was within $\pm 5\text{ }\mu\text{g}$ between two subsequent measuring points taken by the microbalance software automatically. At a given pressure point it took 45 to 60 minutes to reach equilibrium as per above criterion.

The CO_2 adsorption isotherm data was fitted with Langmuir model as described in equations 1 and 2. Langmuir is a thermodynamically consistent model which reduces to Henry's law at low pressure.

$$q = \frac{q_0 b P}{1 + b P} \quad \text{.....Eq. 1}$$

The parameter b follows an Arrhenius like temperature dependence which is given as equation 2.

$$b = b_0 \exp\left(\frac{-\Delta H}{RT}\right) \quad \text{.....Eq. 2}$$

where, q and q_0 are adsorbed amount and monolayer adsorption capacity in mmol/g , respectively. Where b and b_0 are langmuir and temperature independent langmuir parameter at temperature T (bar^{-1}); P is pressure (bar), $-\Delta H$ corresponds to heat of adsorption (J/mol), R is universal gas constant and temperature, T (K).

The CO_2/N_2 adsorption selectivity of all samples were calculated by using the following equation

$$\alpha = \frac{Q_{\text{CO}_2}/P_{\text{CO}_2}}{Q_{\text{N}_2}/P_{\text{N}_2}}$$

where, Q_i is the adsorption capacity of the component i , P_i is the partial pressure of the component i .

3. Results and discussion

3.1. Characterization of Cu-BTC and Cu-BTC-PEI composites

The lab synthesized Cu-BTC and Cu-BTC-PEI composites were characterized by N_2 adsorption, desorption at 77 K, Scanning electron microscopy (SEM), Powder X-ray diffraction (PXRD), Thermo Gravimetric Analysis (TGA) and Infrared spectroscopy (IR). SEM of Cu-BTC and PEI impregnated Cu-BTC were recorded to understand the morphological changes occurring at various levels of syntheses. The scanning electron microscopy images of Cu-BTC and Cu-BTC-PEI composites are shown in Fig.1. The prepared bare Cu-BTC has square planar trigonal bipyramidal shape with smooth surface. On PEI loading the basic structure of Cu-BTC was conserved with some roughening due to interaction of Cu-BTC with PEI. Change in surface of Cu-BTC after loading of PEI suggest the change in nature of surface of Cu-BTC. The morphological change on surface was also ratified by PXRD as shown in Fig.2. Further, the presence of amine in terms of nitrogen is confirmed by TEM elemental mapping and TEM-EDX analysis of Cu-BTC and Cu-BTC-PEI composite (ESI Fig. S1-S4). The pure Cu-BTC has not shown the presence of nitrogen at its surface, while PEI impregnated Cu-BTC shows the presence of nitrogen which is clearly visible and increasing with loading amount of PEI.

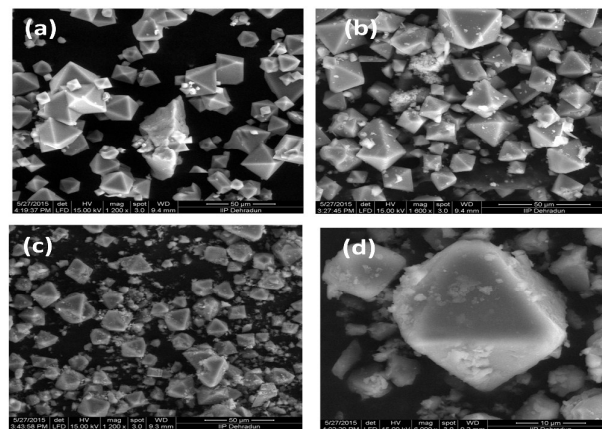


Fig. 1: SEM micrographs of (a) Cu-BTC, (b) Cu-BTC-PEI-1, (c) Cu-BTC-PEI-2.5 and (d) Cu-BTC-PEI-5

The diffraction pattern of as synthesized Cu-BTC was in accordance with published literature data [32, 41]. Powder XRD

patterns of Cu-BTC and Cu-BTC-PEI composites are essentially identical indicating that Cu-BTC crystal structure is well maintained after loading of PEI. The peak at 6° in Cu-BTC is disappeared because of the PEI loading into the pores of Cu-BTC. As amount of PEI loading increases decrease in peak intensity above 7° in Cu-BTC-PEI composites were observed, also suggest the loading of PEI into the pores of Cu-BTC. The decrease in intensity also indicate roughness and interaction of PEI with Cu-BTC which level to low crystallinity. These changes in XRD peak intensity and crystallinity indicates that PEI loading into inter crystalline void space as well as also covering the surface of Cu-BTC. Decrease in peak intensity after loading of PEI onto Cu-BTC indicates the loading of PEI at the surface of Cu-BTC. Similarly, decrease in surface area as well as pore volume indicates the loading of PEI into the pores of Cu-BTC. PEI loaded SBA-15 has also exhibited similar type of behaviour [23].

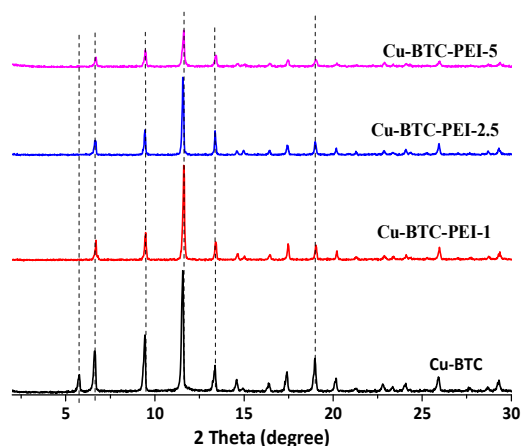


Fig. 2: Powder XRD pattern of Cu-BTC and Cu-BTC-PEI with different loading amount of PEI.

The IR spectra of Cu-BTC and Cu-BTC-PEI composites are shown in Fig. 3. The band observed around 1715 cm^{-1} can be assigned to acidic C=O stretching vibration present in the BTC, which after complexation with Cu^{2+} is shifted to 1665 cm^{-1} . The characteristic vibration at 725 cm^{-1} is attributed to Cu–O stretching vibration because of the coordination of oxygen atom with Cu. The vibration at 1574 cm^{-1} is due to -NH bending and indicates the interaction between Cu-OH and PEI amine group.

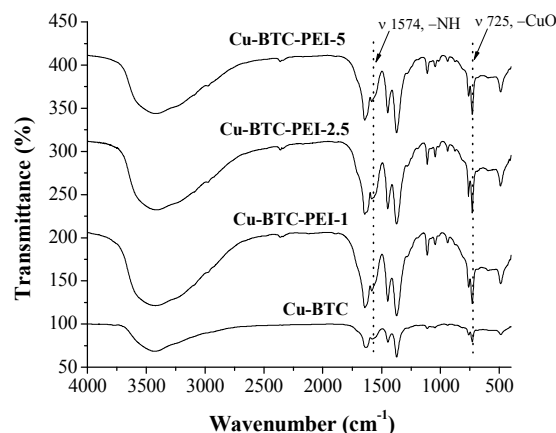


Fig. 3 IR spectra of (a) Cu-BTC, (b) Cu-BTC-PEI-1, (c) Cu-BTC-PEI-2.5 and (d) Cu-BTC-PEI-5

The thermal stability of Cu-BTC and Cu-BTC-PEI composite with respect to temperature was studied by TGA (Fig. 4). As per Fig. 4 the initial weight loss at 100°C can be attributed to loss of moisture which continues upto 150°C . With PEI loading of 5 wt. %, a sharp decrease in weight was observed from 280°C onward, which could be attributed to loss of loosely bound PEI. It may be mentioned that at lower PEI loading i.e. 1.0 and 2.5 wt. %, such loss occurs at higher temperature. This TGA behaviour clearly indicates that at lower loading, PEI is more strongly interacted with CuBTC framework. The weight loss from 220 to 360°C is may be due to decomposition of organic benzene tricarboxylate linker and collapsing of MOF structure.

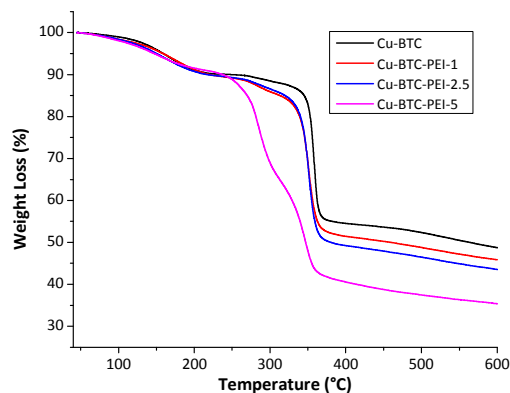


Fig. 4 TGA Profile of Cu-BTC and PEI impregnated Cu-BTC

The surface area and pore volume measurements of Cu-BTC and PEI impregnated Cu-BTC were obtained from N_2 adsorption/desorption isotherms at 77K. The surface area of the Cu-BTC was calculated as 1080 and $1566\text{ m}^2\text{g}^{-1}$ using the

multipoint BET and the Langmuir equation, respectively and specific pore volume was $0.57\text{ cm}^3\text{ g}^{-1}$. The surface area and pore volume of Cu-BTC-PEI composites were calculated on the basis of N_2 isotherm and shown in Fig. 5, Table 1. The impregnation of PEI on the Cu-BTC surface leads to decrease in pore volume and surface area. With increase in PEI loading, probability of pore blockage increases and some pores are not accessible for N_2 adsorption which also results in decrease of pore volume. Similar type of changes in surface area and pore volume have been studied with PEI loaded silica [42].

The CO_2 adsorption capacity increases with PEI loading though there is a decrease in surface area and pore volume of adsorbent [43] compared to the unimpregnated Cu-BTC. The enhancement in CO_2 capacity can be attributed to the higher affinity of amine groups for CO_2 . As the PEI loading increases no further enhancement in CO_2 uptake is observed at 5 bar pressure. This phenomena could be due to decrease in surface area and pore volume of the adsorbent with increased PEI loading. It also indicates that for a given partial pressure there is an optimum amount of PEI loading with maximum enhancement of CO_2 loading.

Table 1: Textural properties for the synthesis of Cu-BTC before and after loading of PEI

Adsorbent	Surface Area (m^2/g)		Pore Volume (cm^3/g)
	BET	Langmuir	
Cu-BTC	1080.00	1566.02	0.57
CuBTC-PEI-1	1034.05	1497.21	0.54
CuBTC-PEI-2.5	885.73	1276.76	0.47
CuBTC-PEI-5	877.61	1266.75	0.46

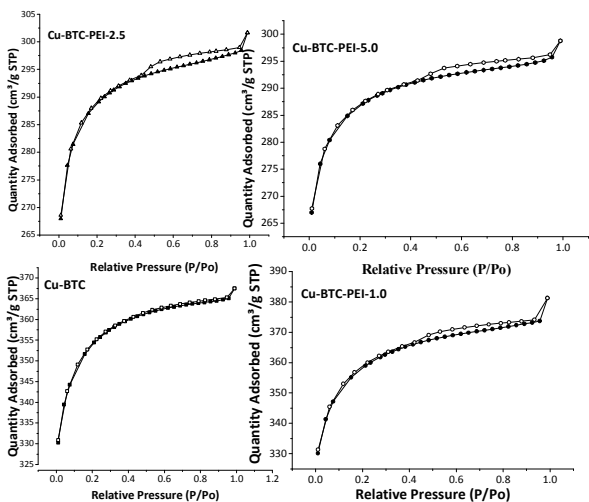


Fig. 5 N_2 Adsorption, desorption isotherms at 77 K. The symbols: Filled, adsorption; Blank, desorption

3.2. CO_2 , N_2 Adsorption Isotherms

The adsorption isotherms for CO_2 , N_2 were measured gravimetrically in Rubotherm gravimetric balance at 25, 40 and 55 °C up to 5 bar pressure. The experimental isotherm data was also fitted with Langmuir isotherm model and fitting parameters of Cu-BTC and Cu-BTC-PEI adsorbents are shown in Fig. 6 and Table 2.

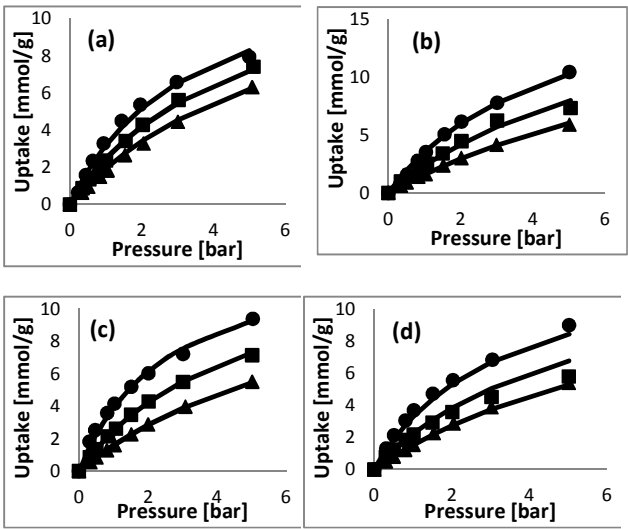


Fig. 6 Experimental CO_2 Isotherms and Corresponding Langmuir Fit of (a) Cu-BTC (b) Cu-BTC-PEI-1.0 (c) Cu-BTC-PEI-2.5 and (d) Cu-BTC-PEI-5.0 (Symbol Description- $\bullet$: 25 °C, $\blacksquare$ 40 °C, $\blacktriangle$ 55 °C and Solid Line: Corresponding Langmuir Fit)

The CO₂ adsorption capacity of Cu-BTC at 25 °C was obtained as 7.56 mmol g⁻¹ at 5 bar which decreased to 6.31 mmol g⁻¹ on further increase in temperature to 55 °C. After impregnation of PEI to Cu-BTC increase in CO₂ adsorption capacity was observed. The Cu-BTC-PEI-1 was exhibited CO₂ adsorption capacity of 3.95 mmol g⁻¹ at 1 bar which on increment of PEI amount to 2.5 wt % increased to 4.15 mmol g⁻¹ but on further increase in PEI loading to 5 wt % a decrease in CO₂ adsorption capacity to 3.65 mmol g⁻¹ was observed. At 5 bar pressure, Cu-BTC-PEI-1 shows 10.47 mmol g⁻¹ of CO₂ adsorption capacity at 25 °C, which is higher than bare Cu-BTC. At same conditions a decreased CO₂ adsorption capacity was obtained with increased PEI loading i.e. 2.5 and 5 wt %, may be due to decreased surface area and pore volume.

Table 2: Langmuir isotherm parameters for adsorption on Cu-BTC

Adsorbent	q _o (mmol /g)	b _o (bar ⁻¹)	-ΔH (kJ/mo l)	Sum of Square Error (mmol/g) ²
Cu-BTC	13.832	3.830E-04	16.500	0.69
Cu-BTC-PEI-1.0	19.745	1.140E-05	24.398	1.47
Cu-BTC-PEI-2.5	14.099	2.110E-06	30.000	0.483
Cu-BTC-PEI-5.0	13.868	1.276E-05	25.000	2.155

CO₂ adsorption isotherms was also carried out at 40 and 55 °C respectively to observe the effect of temperature on CO₂ adsorption capacity. CO₂ adsorption capacity at different temperatures for Cu-BTC and Cu-BTC-PEI adsorbents is shown in Table 3. At 40 °C Cu-BTC-PEI adsorbents has shown increased CO₂ adsorption capacity while at 55 °C a negligible increase in CO₂ adsorption capacity has been observed (Table 3). The CO₂ adsorption at high temperature has negative effect on the adsorption because CO₂ adsorption onto PEI is an exothermic process [23]. CO₂ molecules at high temperature tend to have high kinetic energy. So, higher adsorption capacity is expected to be achieved at lower temperature.

The CO₂ adsorption capacities at c.a. 0.15 bar corresponding to flue gas CO₂ for Cu-BTC and PEI impregnated Cu-BTC was also tabulated in Table 3. The PEI impregnated Cu-BTC has shown fast increment in CO₂ adsorption capacity than bare Cu-BTC in the pressure range of 0 – 0.15 bar. The Cu-BTC with a PEI loading of 2.5 wt % has CO₂ adsorption capacity 0.83 mmol g⁻¹ while Cu-BTC has shown only 0.42 mmol g⁻¹ at same conditions.

The CO₂ adsorption capacity has been decreased with the increased amount of PEI as the primary amine groups bind more CO₂ as compare to secondary amine group. Also, the PEI being used has branched chains and it would wrap on the surface as well as block the pores of Cu-BTC. This is also consistent with the surface area, SEM and XRD data.

Table 3 CO₂ adsorption capacity and CO₂/N₂ selectivity with Cu-BTC and PEI impregnated Cu-BTC

Adsorbent	CO ₂ Adsorption Capacity (mmol/g) at 25 °C			CO ₂ Adsorption Capacity (mmol/g) at 40 °C			CO ₂ Adsorption Capacity (mmol/g) at 55 °C			CO ₂ /N ₂ selectivity, at 1 bar	
	0.15 bar	1 bar	5 bar	0.15 bar	1 bar	5 bar	0.15 bar	1 bar	5 bar	at 25 °C	at 55 °C
Cu-BTC	0.42	3.22	7.56	0.37	2.35	7.42	0.28	1.82	6.31	1.26	2.08
CuBTC-PEI-1	0.59	3.95	10.47	0.42	2.52	7.33	0.26	1.61	5.89	1.52	2.48
CuBTC-PEI-2.5	0.83	4.15	9.37	0.45	2.61	7.13	0.26	1.60	5.50	2.04	2.18
CuBTC-PEI-5	0.63	3.67	8.97	0.38	2.17	5.77	0.24	1.52	5.38	1.77	2.29

The CO₂/N₂ selectivity was calculated for gas mixture with CO₂ 0.15 bar and N₂ 0.85 bar considering the flue gas compositions which contains CO₂ (15 vol. %) and balance N₂ as main components. As shown in Table 3 PEI impregnated Cu-BTC has shown increased CO₂ adsorption capacity at experimental temperatures. Cu-BTC-PEI-2.5 has shown approximately double CO₂/N₂ selectivity ca. 1.0 than Cu-BTC at 25 °C.

The N₂ adsorption isotherm has also been measured with Cu-BTC before and after impregnation with PEI at 25, 40 and 55 °C as shown in Fig. 7. The PEI impregnated Cu-BTC has shown lower adsorption capacity for N₂ as compare to Cu-BTC at 1 bar and 25 °C.

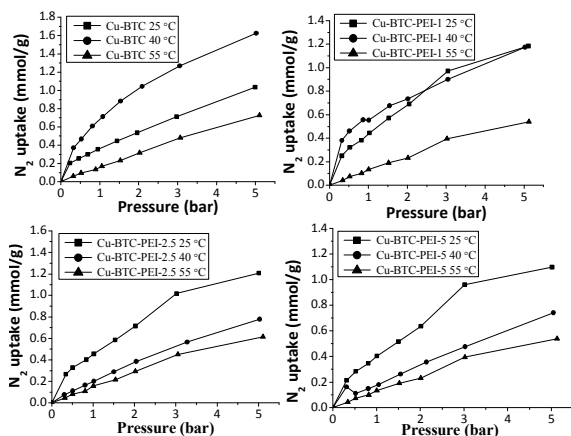


Fig. 7 N_2 adsorption isotherms with (a) Cu-BTC, (b) CuBTC-PEI-1, (c) CuBTC-PEI-2.5 and (d) CuBTC-PEI-5 at 25, 40, 55 °C

The N_2 adsorption capacity decreases due to weak van der Waals interaction. The kinetic diameter of CO_2 is 3.3 Å which is smaller than N_2 (3.64 Å). Due to small diameter CO_2 were able to access the inner pore and strong interaction of PEI with CO_2 enhance the possibility of CO_2 adsorption. However, high CO_2/N_2 selectivity of PEI impregnated Cu-BTC were also observed at high temperature.

4. Conclusions

PEI impregnated Cu-BTC has successfully been synthesized and characterized by XRD, SEM, Surface area properties. Adsorption isotherms for CO_2 and N_2 were carried out at different temperatures with Cu-BTC and Cu-BTC-PEI adsorbents. The Cu-BTC-PEI-2.5 shows increased adsorption capacity of 0.83 mmol g^{-1} compared to 0.42 mmol g^{-1} for Cu-BTC at 0.15 bar and 25 °C and this also shows higher CO_2 capacity at 40 °C. But at temperature of 55 °C PEI impregnated Cu-BTC does not show increased CO_2 adsorption capacity due to pore blocking of MOF. At high pressure of 5 bar Cu-BTC-PEI-1 shows CO_2 adsorption capacity of 10.5 mmol g^{-1} which is also higher as compare to Cu-BTC at 25 °C. So, the PEI impregnated Cu-BTC will be a high performance adsorbent at low pressure with increased adsorption capacity, CO_2/N_2 selectivity in flue gas. Future work will be focused on the development of Pressure/Vacuum Swing Adsorption (PVSA) based process for CO_2 separation from flue gas.

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