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Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO_2 Capture

Yichao Lin, Qiuju Yan, Chunlong Kong & Liang Chen

Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang, 315201, P. R. China.

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Correspondence and requests for materials should be addressed to L.C. (chenliang@nimte.ac.cn) or C.K. (kongchl@nimte.ac.cn)

A series of polyethyleneimine (PEI) incorporated MIL-101 adsorbents with different PEI loadings were reported for the first time in the present work. Although the surface area and pore volume of MIL-101 decreased significantly after loading PEI, all the resulting composites exhibited dramatically enhanced CO_2 adsorption capacity at low pressures. At 100 wt% PEI loading, the CO_2 adsorption capacity at 0.15 bar reached a very competitive value of 4.2 mmol g^{-1} at 25°C, and 3.4 mmol g^{-1} at 50°C. More importantly, the resulting adsorbents displayed rapid adsorption kinetics and ultrahigh selectivity for CO_2 over N_2 in the designed flue gas with 0.15 bar CO_2 and 0.75 bar N_2. The CO_2 over N_2 selectivity was up to 770 at 25°C, and 1200 at 50°C. We believe that the PEI based metal-organic frameworks is an attractive adsorbent for CO_2 capture.

The rapidly increasing concentration of CO_2 in atmosphere, which mainly stem from the combustion of fossil fuels, is believed to be responsible for some severe global environmental crisis, such as climate change and ocean acidification. The capture and sequestration of CO_2 in an energy-efficient and economical manner is deemed as a solution to mitigate the CO_2 emission until a mature alternative new energy technology is sufficiently developed[1]. However, selective capture of CO_2 from flue gas emissions still remains challenging to date. One of the major bottlenecks is the absence of CO_2 adsorbent with high selectivity, rapid adsorption kinetics, high stability under practical conditions, high adsorption ability and low regeneration cost. Aqueous solutions of amines (20–30% concentration) are commonly used in large scale to capture CO_2 from industrial streams because they have large capacity and high selectivity for acidic gases[2]. However, high heat capacity of these aqueous solutions makes the regeneration very energy intensive and costly[3]. Instead, solid porous adsorbents are emerging as more promising candidates because the much lower heat capacity of solids can significantly reduce the regeneration energy cost. In addition, the corrosion and volatility issues, which are intrinsic to amine solutions, could be minimized in solid adsorbents.

Recently, solid metal-organic frameworks (MOFs) adsorbents have received a great deal of attention because they exhibit remarkable CO_2 adsorption capacity at high pressures owing to their extremely high surface areas and porosity[4–8]. However, the CO_2 adsorption capacities of most MOFs are unsatisfying at low pressures, especially below 0.15 bar, the condition relevant to practical applications. Some attempts have been made to enhance the CO_2 capture ability for MOFs at low pressure, such as developing MOFs with amine-functionality[9,10]. Apparently, the basic amine group is an ideal functionality to strongly interact with acidic CO_2 molecules. However, amine-functionalized MOFs have been shown to be not very successful in CO_2 capture. It was proposed that the covalent grafting of amine groups to the aromatic rings in MOFs cannot significantly enhance the affinity of CO_2 on amine groups because of the electron withdrawing effect of benzene ring[11]. Alternatively, some recent studies on incorporation of diamine to the open metal sites of MOFs have been shown to dramatically enhance CO_2 capture at low pressures. The open metal sites play an important role to anchor one end of the diamine groups and leave the other end (alkylamines) available to capture CO_2. Here we anticipate that physical impregnation of poly-alkylamines into MOFs would afford more active amine groups than diamines and maintain the strong interaction between CO_2 and alkylamine groups. Among the polyamines, polyethyleneimine (PEI) is one of the best candidates to bind CO_2 due to its high amine density and accessible primary amine sites on the chain ends[12,13]. Indeed, some recent studies reported that PEI based silica and zeolite have excellent CO_2 capture ability[3,12,14–16,9]. Ideally, the much higher pore volume, porosity and surface area of MOFs than silica or zeolite make them even more competent media to impregnate PEI for CO_2 capture. However, to date, no impregnation

of PEI into MOFs has been reported. This is partly because the complexity of MOFs including pore size and porosity would make it difficult to efficiently load PEI into the MOF pores.

In this study, we report a series of PEI modified MOF adsorbents with low molecular-weight linear PEI loaded into MIL-101(Cr)[17] for highly efficient CO_2 capture. We chose MIL-101(Cr) as the model system for MOFs because it has very large surface area (above 3000 $m^2 g^{-1}$), high porosity, excellent thermal and chemical stability, as well as high resistance to moisture. In addition, MIL-101(Cr) possesses open metal sites, which can serve as Lewis acid to anchor the Lewis basic amine groups of PEI[18,19], while leave other alkylamine groups available as reactive adsorption sites to capture CO_2 (see Figure 1). Moreover, we expect that the Cr-OH groups in MIL-101 may also anchor the amine groups. Thus, the loaded PEI can interact strongly with the pore wall of MIL-101(Cr) after the removal of solvent. Considering that short-chain and linear PEI can pass the relatively narrow MIL-101 pore windows (with diameters of 1.2–1.6 nm) more smoothly, low-molecular-weight linear PEI was chosen. As a result, solid and porous PEI-MIL-101 adsorbents with moderate surface areas were successfully assembled.

Results

Characterization of PEI-MIL-101. PEI-MIL-101 with different PEI loadings, corresponding to 50%, 75%, 100% and 125%, were prepared and characterized by the combination of PXRD, SEM, IR, TGA and N_2 adsorption/desorption at 77 K measurements. As shown in the PXRD patterns (Figure S1), the Bragg diffraction angles in MIL-101 and PEI-MIL-101 with different PEI loadings were essentially identical, confirming that the MIL-101 crystalline structure was preserved after loading PEI. However, we observed that the intensity of the peaks below 7° was largely reduced as the PEI loading increased. In particular, the peak at 3.44°, corresponding to the (2 2 2) plane of MIL-101, was nearly invisible in PEI-MIL-101-125. These changes are ascribed to the filling of MIL-101 pores, and indicate that PEI is not simply coated on the outer surface of MIL-101. Actually, similar phenomenon has also been observed on the SBA-15 supported PEI[12].

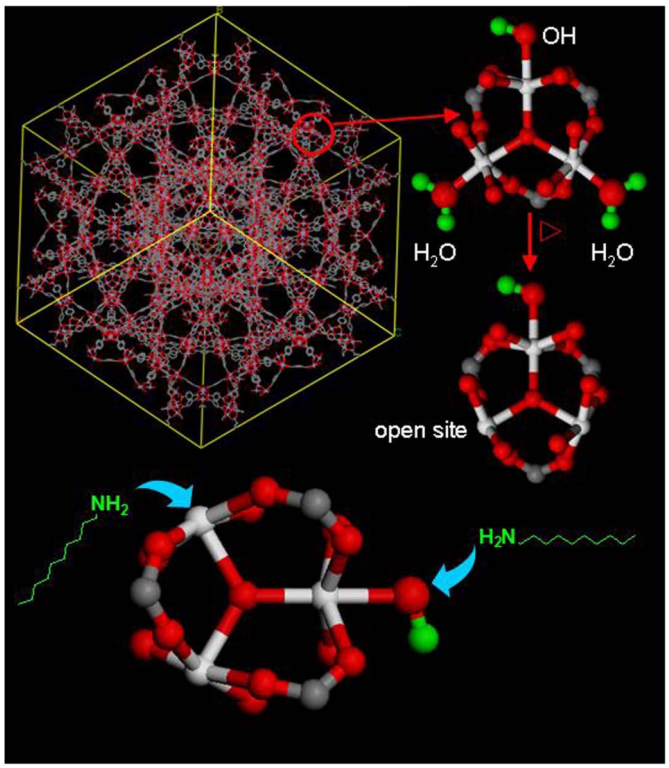


Figure 1 | The illustration of the interactions between PEI and MIL-101.

Figure 2 shows the morphologies of MIL-101 before and after loading PEI. The MIL-101 octahedral particle size was rather small (with diameters of 100–500 nm), which can sufficiently facilitate the diffusion of PEI into the MIL-101 pores. Indeed, after loading the PEI, no particle stacking was found, even at 160% loading, indicating that PEI was really loaded into MIL-101 pores. In addition, the morphologies and sizes of MIL-101 after loading the PEI remained nearly intact. To some extent, it also suggested that the MIL-101 structure was preserved after loading PEI.

To ensure the presence of PEI and detect the interactions between PEI and MIL-101, IR spectra were collected on activated PEI-MIL-101 under vacuum condition. As shown in Figure 3, the representative peaks between 3500∼2800 cm^{-1} corresponding to ν(NH) and ν(CH) stretching vibrations can be clearly observed in the IR of PEI-MIL-101 samples, which were consistent with that of pure PEI sample. The N-H bending vibration was also discernable at 1570 cm^{-1} (Figure S2). The band at 3620 cm^{-1}, which can be assigned to Cr-OH[20], was clearly observed in MIL-101. Notably, after PEI loading, this band completely disappeared. It indicated a chemical interaction between the Cr-OH groups and PEI amines, and possible formation of Cr-O-NH_3R[3]. In addition, it was reported that amine groups can bind to open Cr sites, resulting in a slight blue-shift of C-H stretching vibration adjacent to the interacting amine groups. However, in the present study, the abundant C-H groups not adjacent to the interacting amine groups would make it hard to detect the slight blue-shift of C-H stretching vibration. Nevertheless, we believe that open metal sites still play an important role to glue PEI on the MIL-101 surface.

TGA measurement was employed to evaluate the thermal stability of MIL-101 before and after loading PEI (Figure S3). Interestingly, when PEI was loaded into MIL-101, the sharp weight loss of PEI took place at higher temperatures (∼225°C). Moreover, the stability of MIL-101 was also increased slightly. It suggested that the strong interactions between PEI and MIL-101, most likely on the open Cr sites and Cr-OH groups, were formed and enhanced the stability of PEI-MIL-101 composite. Indeed, no elevated decomposition temperature of PEI was found when silica was used as the support[21]. However, incorporation of Zr into the silica support can dramatically stabilize the PEI-silica composite[12].

The N_2 adsorption/desorption isotherms of MIL-101 at 77 K before and after loading PEI were measured to evaluate their surface area and pore volume. As shown in Figure 4, the original MIL-101 exhibited very high N_2 uptakes with a saturated uptake of 1000 $cm^3 g^{-1}$, which was well consistent with the values in literatures[22,23]. The corresponding BET surface area and pore volume were calculated to be 3225 $m^2 g^{-1}$ and 1629 $cm^3 g^{-1}$, respectively. After PEI was loaded into MIL-101, the N_2 uptake, surface area and pore volume decreased dramatically. As shown in Figure 5 and Table 1, the saturated N_2 uptake, surface area and pore volume of PEI-MIL-101-50 were roughly half that of pure MIL-101. Particularly, the reduced pore volume confirmed that the PEI was loaded into MIL-101 pores. When the PEI loading was continuously increased to 125 wt%, the saturated N_2 uptake drastically dropped to only 50 $cm^3 g^{-1}$. Since the pore volume of the bare MIL-101 is 1.629 $cm^3 g^{-1}$ and the density of PEI is 1.0 g/ml, the theoretical maximum PEI loading in MIL-101 pores should be approximately 160 wt%. Indeed, in the prepared PEI-MIL-101–160 sample, the resulting surface area and pore volume were only 7.4 $m^2 g^{-1}$ and 0.019 $cm^3 g^{-1}$ (Figure S4), respectively, indicating the complete pore filling of MIL-101 by PEI. Clearly, such material is incapable for gas adsorption. Therefore, in the following gas adsorption experiments, we discarded the PEI-MIL-101-160 sample and focused on the PEI-MIL-101 with 50–125 wt% loadings. Nevertheless, to the best of our knowledge, 125 wt% PEI (and correspondingly amine groups) is already the highest amount that can be loaded into the porous materials. It was expected that the more amount of PEI loaded would result in higher CO_2 adsorption capacity[24,25].

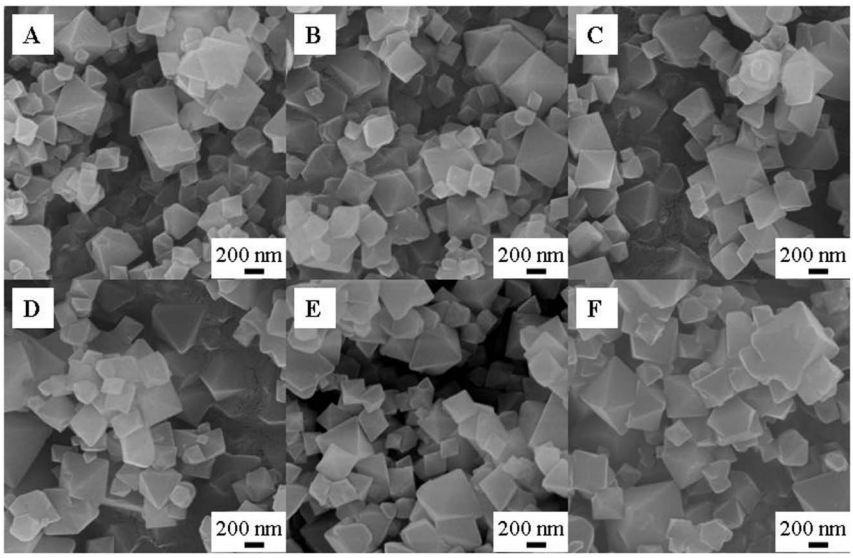


Figure 2 | The SEM images of (A) original MIL-101, (B) PEI-MIL-101-50, (C) PEI-MIL-101-75, (D) PEI-MIL-101-100, (E) PEI-MIL-101-125 and (F) PEI-MIL-101-160.

CO_2 uptake. The CO_2 isotherms of MIL-101 and PEI-MIL-101 samples obtained at low-pressures and 25°C are presented in Figure 5. All isotherms were fitted with the Langmuir-Freundlich model[26–28]. It can be seen that all PEI-MIL-101 samples exhibited significantly enhanced CO_2 adsorption compared to the original MIL-101. At 1 bar, PEI-MIL-101-50 can adsorb 4.0 mmol g^{-1} of CO_2, representing a ~150% improvement in gravimetric capacity relative to MIL-101. When the PEI loading was increased to 75 and 100 wt%, the CO_2 adsorption uptake was further enhanced at all tested pressures. An outstanding uptake of 5.0 mmol g^{-1} was achieved at 1 bar, which is on par with that of recently reported MOFs appended with diamines[29,30]. However, when the PEI loading was further increased to 125 wt%, decreased CO_2 adsorption uptakes were found. The PEI-MIL-101-125 can adsorb 4.35 mmol g^{-1} of CO_2 at 1 bar, about 13% lower than that of PEI-MIL-101-100. At higher pressure, the decrease is even more significant. Actually, as aforementioned, the surface areas of PEI-MIL-101-125 dropped to only 182.9 m^2 g^{-1}, indicating that some pores were completely filled and thus not accessible to CO_2 molecules at room temperature. Furthermore, incorporation of PEI into MIL-101 would increase the framework density, which is also negative to the improvement in CO_2 gravimetric capacity. Although we do not show the data at higher pressures (>2 bar), but the trend can be clearly seen that the adsorption uptake at higher pressures would follow the sequence: MIL-101 > PEI-MIL-101-50 > PEI-MIL-101-75 > PEI-MIL-101-100 > PEI-MIL-101-125 (i.e., proportional to the surface area). Therefore, it is necessary to carefully balance the PEI loading and adsorbents surface area to achieve the desired CO_2 adsorption capacity at specific pressures.

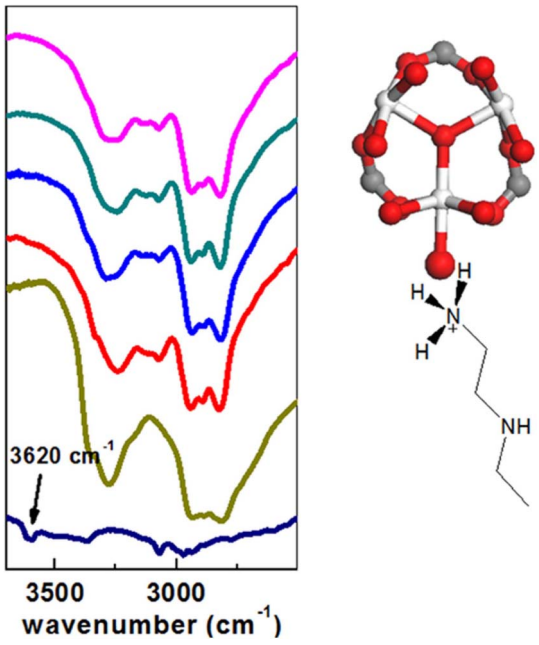


Figure 3 | IR spectra of the pure PEI and MIL-101 before and after loading PEI. From bottom to top: MIL-101, pure PEI, PEI-MIL-101-50, PEI-MIL-101-75, PEI-MIL-101-100, PEI-MIL-101-125.

To investigate the influence of elevated temperature on CO_2 adsorption behaviors of the PEI-MIL-101 adsorbents, we further measured the CO_2 adsorption isotherms of the PEI-MIL-101 samples at 50°C (Figure S5). Interestingly, at 50°C, PEI-MIL-101-125 displayed the highest CO_2 uptakes at all tested pressures. Moreover, the CO_2 adsorption capacity of PEI-MIL-101-125 at 50°C was also higher than its adsorption capacity at 25°C. Actually, a similar phenomenon has also been observed when PEI was loaded into SBA-15[3]. Indeed, due to the high elasticity of PEI, some pores in PEI-MIL-101-125 that were not accessible to CO_2 molecules at low temperature, would become accessible at elevated temperatures. Furthermore, the high kinetic barrier for the diffusion of CO_2 from the surface into the filled pores would be overcome by the intense thermal motion at higher temperature. Apparently, upon PEI impregnation, the original window size (1.2–1.6 nm) and pore size (2.9–3.4 nm) of MIL-101 were reduced so that CO_2 diffusion would be more difficult. On the other hand, it is worth mentioning that the small and unstacked PEI-MIL-101 particles in this study would sufficiently facilitate the diffusion of CO_2 from the gas phase to the surface and inner pores of the sorbents.

Above we discussed the CO_2 adsorption uptakes of PEI-MIL-101 materials at 1 bar. Actually, the CO_2 uptake at near 0.15 bar is a more important parameter because the flue gas usually contains ~15% CO_2[31]. Hence, the CO_2 adsorption uptakes of the PEI-MIL-101 samples at 0.15 and 1 bar are summarized in Table 1 for comparison. Fortunately, it is found that the CO_2 adsorption uptakes of PEI-MIL-101 increase extremely fast with respect to pressure in the range of 0–0.2 bar, which make them very advantageous for low-pressure CO_2

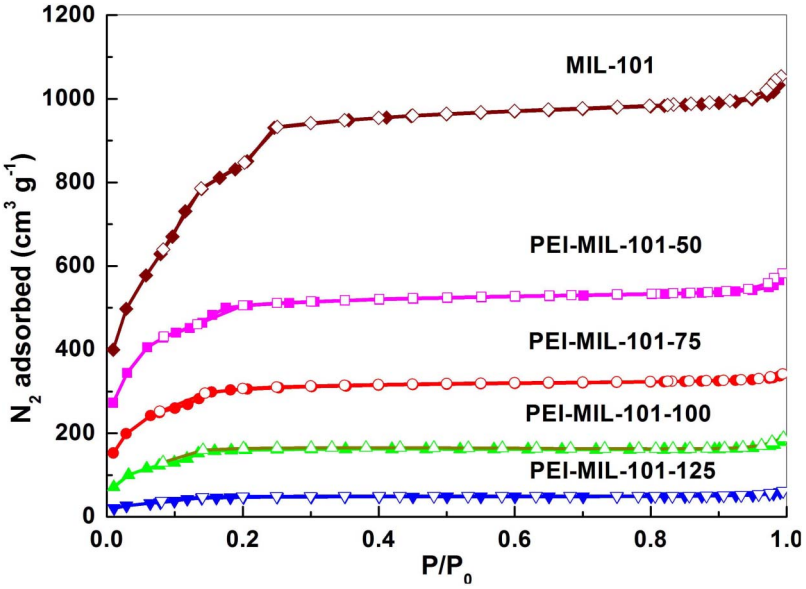


Figure 4 | N_2 adsorption-desorption isotherms at 77 K. The symbols: Filled, adsorption; Blank, desorption.

capture. On the PEI-MIL-101 samples with higher loadings (>75 wt%), CO_2 uptakes rapidly reached a considerable amount at 0.15–0.2 bar. At 0.15 bar and 25°C, PEI-MIL-101-100 displayed the best CO_2 adsorption performance with a value of 4.2 mmol g^{-1}. Under the same conditions, the original MIL-101 can only capture 0.33 mmol g^{-1} CO_2, respectively. Thus, PEI-MIL-101-100 can adsorb about 12 times more CO_2, even though the surface is reduced by 80%. The capacity value of PEI-MIL-101-100 is ~220% higher than the saturation absorption capacity (1.32 mmol g^{-1} CO_2) of 30% MEA solution at 25°C and 0.15 bar, which is commonly used in coal-fired power plants[2,29,32]. Very recently, PEI/Zr-SBA-15 was reported to show excellent CO_2 adsorption performance, with a CO_2 capacity of 1.65 mmol g^{-1} at a partial pressure of 0.1 bar and 25°C. Here, at 0.1 bar and 25°C, PEI-MIL-101-100 can adsorb about 140% more amount (4.0 mmol g^{-1}) of CO_2 owing to the higher loading of PEI. The performance of PEI-MIL-101-100 for CO_2 capture at 0.15 bar is on par with that of the best functionalized solid materials reported to date, particularly the MOF-based materials[3,29,30,33,34]. In addition, we also measured the CO_2 adsorption capacity of humid PEI-MIL-101-100, which was exposed to moisture. No decreased CO_2 adsorption capacity was observed, indicating the high moisture stability of the PEI-MIL-101 materials.

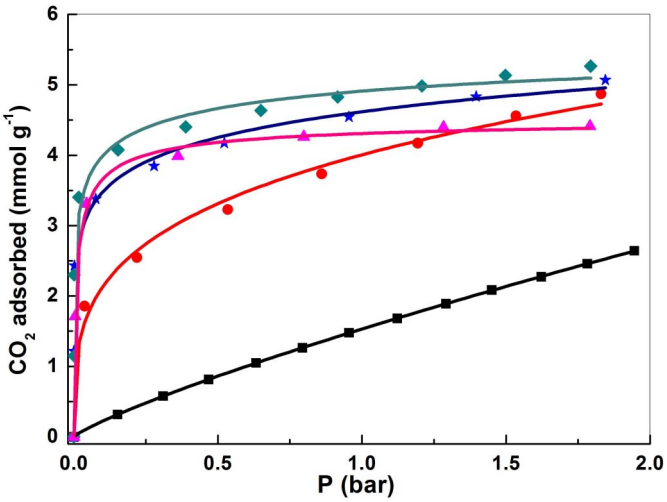


Figure 5 | **The CO_2 adsorption isotherms of the MIL-101 before and after loading PEI at 25°C. Symbol: ■ MIL-101, ● PEI-MIL-101-50, ★ PEI-MIL-101-75, ◆ PEI-MIL-101-100, ▲ PEI-MIL-101-125.** Lines are the fitted isotherms.

CO_2 adsorption Kinetics and cycling measurements. As mentioned, one of the major bottlenecks for deliverable CO_2 adsorbents is the slow adsorption kinetics. Thus, it is very necessary to measure the CO_2 adsorption kinetics of PEI-MIL-101 materials. As shown in Figure 6, CO_2 adsorption capacity in PEI-MIL-101-100 could reach 4.2 mmol g^{-1} within the first 5 minutes. Afterwards, the PEI-MIL-101-100 sample seemed completely saturated. The corresponding pressure drop (to around 0.15 bar) in the sample holder also indicated a very rapid adsorption behavior (Figure S7). The CO_2 adsorption kinetics for PEI-MIL-50, 75 and 125 (Figure S8–S10) were similar to that of PEI-MIL-101-100. Hence, PEI-MIL-101 materials exhibited rather good kinetics for CO_2 adsorption.

To ensure the regenerability of PEI-MIL-101 materials, we further performed CO_2 adsorption cycling measurements. In our experiments, we found that the CO_2 captured in PEI-MIL-101 materials can be completely desorbed at 110°C under vacuum condition for 1 hour, which is confirmed by the equal mass of PEI-MIL-101 materials before adsorption and after desorption measurements (Table S1). Therefore, between each cycle measurement, the sample was degassed at 110°C for 1 hour under vacuum condition. It can be obviously observed that, after five adsorption/desorption cycles, the CO_2 adsorption capacity of the prepared PEI-MIL-101 was well retained.

CO_2/N_2 selectivity. Motivated by the observation that increasing PEI loading would reduce the N_2 adsorption uptake but enhance CO_2 sorption uptake, we anticipate that this kind of materials could be an exceptional candidate for post-combustion CO_2 capture. For coal-fired power stations, the main flue gas components by volume are N_2 (~75%) and CO_2 (~15%). Thus, the CO_2 selectivity for a gas mixture with 0.15 bar CO_2 and 0.75 bar N_2 is often used to evaluate the CO_2 capture ability. Therefore, the adsorption isotherms for N_2 in MIL-101 before and after loading the PEI were also measured (Fig S11–12), and the molar selectivity of MIL-101 before and after loading the PEI in the designed gas mixture were further calculated according to the previously reported equation[29,30,35]. Similar to the N_2 adsorption at 77 K, PEI-MIL-101 adsorbed less N_2 than pure

Table 1 | The measured properties of the PEI-MIL-101 adsorbents at 0.15 and 1 bar

					CO_2 adsorbed (mmol g^{-1})			
					25°C		50°C	
	PEI loading (wt%)	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	Occupancy [a] (%)	0.15 bar	1 bar	0.15 bar	1 bar
MIL-101	0	3125.4	1.629	0	0.33	1.60	0.20	1.00
PEI-MIL-101-50	50	1802.7	0.901	31	2.40	4.00	1.86	3.07
PEI-MIL-101-75	75	1112.6	0.526	46	3.67	4.64	3.17	4.02
PEI-MIL-101-100	100	608.4	0.292	61	4.20	5.00	3.40	4.14
PEI-MIL-101-125	125	182.9	0.095	77	3.85	4.35	3.95	4.51

[a]The total volume of MIL-101 divided by the volume of loaded PEI, the density of PEI was 1 ml/g.

MIL-101 at all tested pressures and temperatures due to the significantly reduced surface area. Figure 7 depicts the calculated CO_2/N_2 selectivities at 25 and 50°C. Indeed, PEI-MIL-101 materials show dramatically enhanced CO_2/N_2 selectivities. For example, the CO_2/N_2 selectivities for PEI-MIL-101-100 were calculated to be 600 at 25°C, 750 at 50°C. Further, the CO_2/N_2 selectivities for PEI-MIL-101-125 reached 770 at 25°C, 1200 at 50°C. To the best of our knowledge, these values represent the highest CO_2/N_2 selectivity in flue gas by zeolite and MOF-based adsorbents reported in literatures.

In addition, the mole of CO_2 adsorbed at 0.15 bar divided by the mole of N_2 adsorbed at 0.75 bar is also often employed to evaluate CO_2/N_2 selectivity. Therefore, the corresponding CO_2/N_2 selectivities for the PEI-MIL-101 materials were calculated using this method (Table S2). The calculated selectivities at 25°C for PEI-MIL-101-100 and PEI-MIL-101-125 were 120 and 150, respectively, both of which are much higher than that of PPN-6-SO_3Li[34] (selectivity = 17) and metal-inserted MOF-253[33] (selectivity = 12).

The separation performance of PEI-MIL-101 material for CO_2/N_2 was further tested in a breakthrough experiment performed at 25°C using an equimolar CO_2/N_2 mixture. As shown in Figure S13, N_2 eluted rapidly from the column, whereas CO_2 only started to elute after a period of time. Clearly, the distinct breakthrough data of the two components suggested the strong interaction between CO_2 and PEI-MIL-101 materials and corroborated the high CO_2/N_2 selectivity calculated from single component gas adsorption.

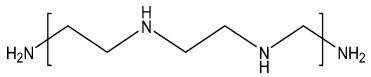
Discussion

In conclusion, the impregnation of PEI into MOFs afforded a new and high-performance sorbent for post-combustion CO_2 capture at low pressures. It possesses excellent CO_2 adsorption capacity, rapid adsorption kinetics, together with very high CO_2/N_2 selectivity in flue gas. We believe that PEI modified MOF is a more promising MOF-based material, considering that many pure MOF adsorbents are unsatisfying at low pressures, especially below 0.15 bar, which greatly hinders the practical application. Overall, the present study has demonstrated the first successful combination of polymeric amine and MOFs for post-combustion CO_2 capture. We anticipate that some others MOFs with large surface area and open metal sites, such as NU-100[36] and MOF-177[37], can also be excellent supports for PEI.

Methods

Materials. The chemicals are of analytical grade and used without further purification in this study. Deionized water and alcohol was employed as solvent. The PEI (purity, 99%) used in the present study was a linear polymer with an average molecular weight of 300 g/mol. Due to the hydroscopic property , the PEI was placed in glove box.

The PEI molecular formula:



Synthesis of MIL-101. MIL-101 was prepared by a hydrothermal reaction following the procedure reported by Ferey and coworkers with minor difference: the hydrofluoric acid was replaced with hydrochloric acid. The detailed synthesis was as follows: chromic nitrate (800 mg, 2 mmmol), terephthalic acid (332 mg, 2 mmol), 12 M hydrochloric acid (164 μL, 2 mmol), and deionized water (10 ml) were mixed in a Teflon-lined stainless steel autoclave and kept at 220°C for 8 h. After the synthesis, the autoclave reactor was slowly cooled down to room temperature for 3 h in order to obtain larger crystals of the unreacted terephthalic acid. After cooling, the reaction mixture was filtered using a large pore paper filter to eliminate the recrystallized free acid. Water and MIL-101(Cr) powder can pass through the filter, whereas the free acid would stay inside or on the paper filter. After that, the product was recovered by centrifugation. To remove the free acid lying in the MIL-101(Cr)

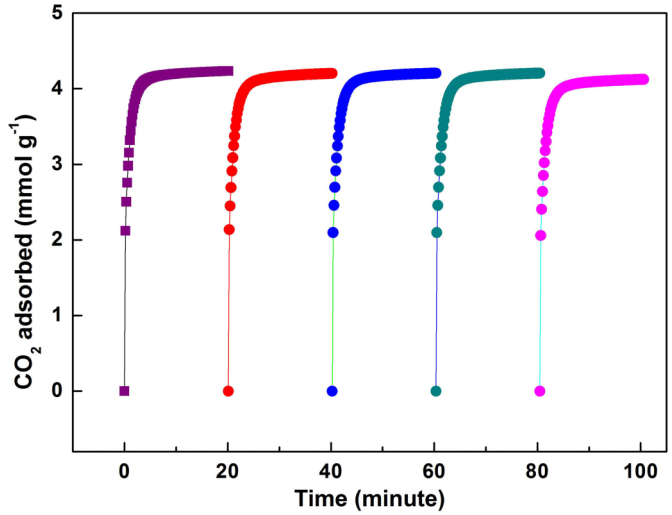


Figure 6 | Cycling CO_2 adsorption kinetics of PEI-MIL-101-100. For clarity, the kinetics for the cycle 2, 3, 4 and 5 were shifted horizontally by 20, 40, 60 and 80.

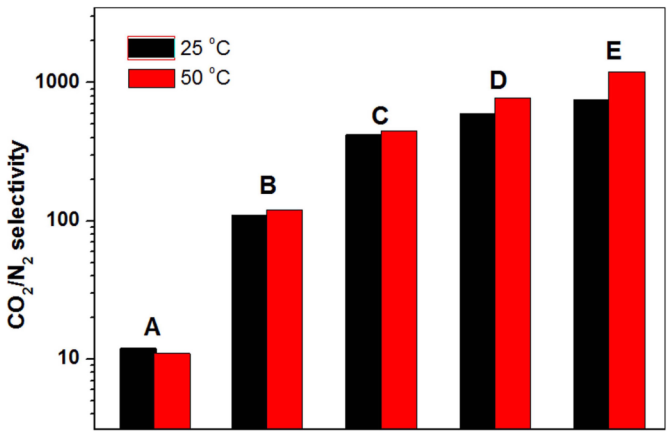


Figure 7 | The CO_2/N_2 ideal selectivity for a gas mixture with 0.15 bar CO_2 and 0.75 bar N_2. (A) MIL-101, (B) PEI-MIL-101-50, (C) PEI-MIL-101-75, (D) PEI-MIL-101-100, (E) PEI-MIL-101-125.

pores, a solvothermal treatment of the product was employed by using hot ethanol (95% EtOH, 5% water) in an autoclave at 80°C for 8 h. The resulting solid was cooled down, centrifuged, and finally dried over night at 80°C under air atmosphere. For the following experiments, about 2 g MIL-101(Cr) samples were prepared by the above procedure.

Synthesis of PEI-MIL-101 adsorbent. The PEI-MIL-101 adsorbent was prepared by wet impregnation method. The detailed process was as follows. First, before the impregnation, the MIL-101 (Cr) powders were heated at 160°C under vacuum condition for 12 h, removing the adsorbed water and coordinated water. Second, the desired amount of PEI was dissolved in 1 mL anhydrous methanol under stirring for 10 min, and then 0.2 g MIL-101 (Cr) powders were added step by step into the PEI/methanol solution under stirring. Finally, the resulting gel was dried over night under room temperature and nitrogen protection, and then the temperature of the sample was increased at programmed rate and held at 110°C for 12 h under vacuum condition. After that, a porous and solid PEI-MIL-101 (Cr) adsorbent was obtained. Herein, four PEI-MIL-101 samples with different PEI loadings were prepared, corresponding to 50%, 75%, 100% and 125%. To confirm the accurate PEI loading, the mass of MIL-101(Cr) was measured immediately after activated, and the mass of PEI was measured in glove box. The loading of PEI was calculated by the following equation:

$$\text{PEI loading} = \frac{\text{mass}_{PEI}}{\text{mass}_{MIL-101}} \times 100\% \quad (1)$$

In addition, the PEI loading amount was further verified by element analysis (see Table S3).

Gas adsorption measurement. The adsorption isotherms and of the probe gas CO_2 (purity, 99.999%) and N_2 (purity, 99.999%) were measured using volumetric technique by an apparatus from SETARAM France (PCTpro-E&E). Before each measurement, the sample was evacuated at 110°C for 12 h. Pressure as a function of the amount of CO_2 adsorbed was determined using the Langmuir-Freundlich fit[26–28] for the isotherms:

$$\frac{N}{N_m} = \frac{B \times P^{(1/t)}}{1 + B \times P^{(1/t)}} \quad (2)$$

Here, N is the amount of CO_2 adsorbed (mmol g^{-1}), p is the pressure, N_m is the amount of CO_2 adsorbed at saturation, B and t are constants. To solve the exact pressures, p, corresponding to constant amount of CO_2 adsorbed, the above equation can be rearranged to:

$$P = \left(\frac{N/N_m}{B - B \times N/N_m}\right)^t \quad (3)$$

CO_2 selectivity calculations. The CO_2 selectivities (S) of samples were evaluated by the following equation which was previously reported[29,30,35]:

$$S = \frac{q_{CO_2}/p_{CO_2}}{q_{N_2}/p_{N_2}} \quad (4)$$

where q_i is the adsorption capacity of i component, p_i is the partial pressure of i component. The adsorption capacities of the components are defined to be molar excess adsorption capacities determined without correction for absolute adsorption.

CO_2 adsorption kinetics measurement. The CO_2 adsorption kinetics of the probe gas CO_2 were also measured using volumetric technique by the apparatus from SETARAM France (PCTpro-E&E). Before each measurement, the sample was evacuated at 110°C for 12 h. In a simple procedure, the apparatus first give a desired pressure CO_2 gas to the sample holder, and record the pressure values in the sample holder and calculated the adsorbed CO_2 amount.

Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA) was measured using a system provided by Mettler Toledo (model TGA/DSC1), in air at a heating rate of 5°C/min up to 600°C. Before the TGA measurement, the samples were first activated and then placed in atmosphere for the same time (~5 days). The PEI was immediately measured after moving from the glove box.

Infrared spectra (IR). IR of the samples were recorded on KBr/sample pellets in a Thermo model Nicolet 6700 spectrometer to determine the amine. IR spectra were collected on activated PEI-MIL-101 and MIL-101 samples under vacuum condition. IR spectra of pure PEI are also shown for comparison.

Other physical measurements. For structure analysis, powder x-ray diffraction (PXRD) data of the samples was collected on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation at room temperature. The 77 K nitrogen adsorption/desorption isotherm was measured on ASAP 2020 M apparatus. The Brunauer-Emmett-Teller (BET) surface area was calculated over the range of relative pressures between 0.05 and 0.20 bar. Before the 77 K N_2 adsorption/desorption measurements, samples were pretreated under vacuum at 110°C for 12 h. The as-prepared samples morphologies were examined using a field emission scanning electron microscope (SEM) (Hitachi, S-4800).

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Author contributions

L.C., C.K. and Y.L. designed the project; Y.L. carried out the experiments; Y.L. wrote the manuscript. All authors discussed the results and commented on the manuscript.

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