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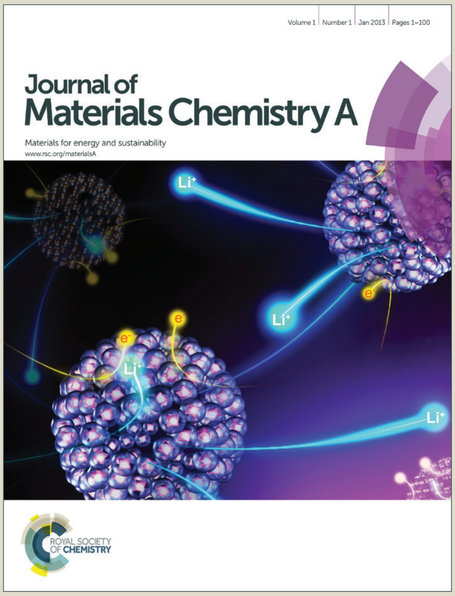

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ARTICLE TYPE

Adsorption of CO_2 on a micro-/mesoporous polyimine modified with tris(2-aminoethyl)amine

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Amine-modified sorbents are relevant to the capturing of dilute carbon dioxide from gas mixtures, and micro-/mesoporous polymers are promising substrates due to their rich chemistry. Here, we prepared an aldehyde-rich polyimine with micro- and mesopores with a Schiff-base condensation of 1,3,5-tris(4-aminophenyl)benzene and 1,3,5-benzenetricarboxaldehyde using an excess of aldehydes. The micropores were crucial to the physisorption of CO_2, while the mesopores provided space for the post-modification with tris(2-aminoethyl)amine (**tren**) that induced the chemisorption of CO_2. The amine modified polymer showed a high uptake of CO_2 at low pressures (1.13 mmol/g at 0.05 bar and 273 K) and a high estimated CO_2-over-N_2 selectivity (1.04×10^3 at 273 K for 5v%/95v% CO_2/N_2 mixture). CO_2 both physisorbed and chemisorbed on the amine-modified polyimine, which we confirmed by studying the CO_2-amine chemistry using in situ FTIR spectroscopy and solid state ^{13}C NMR spectroscopy. Carbamic acid formed during the chemisorption of CO_2, as the CO_2 reacted with the amine groups. Due to the formation of carbamic acid, the isosetric heat of adsorption was high, with values up to 80 kJ/mol at a low coverage of CO_2. It appears that amine-modified porous polymers could be relevant to the removal of CO_2 from gas streams with low concentrations.

Introduction

Carbon capture and storage (CCS) is judged to be required to reduce the emissions of CO_2 into the atmosphere and to limit serious environmental problems associated with global warming,[1-2] as fossil fuels appear to dominate the energy structure at least into the 2050s.[3-4] CCS involves CO_2 separation at point sources, transportation and long-term storage,[5] and different CCS systems have been developed. In post-combustion capture, CO_2 is captured after combustion and has the advantage that it can be retrofitted to old power plants. Today post-combustion capture is based on amine scrubbers. This approach suffers from high costs, high penalties on energy efficiency[6] and potential concerns related to amine emissions. Hence, various alternatives are actively researched. Adsorption-driven separation is one of these alternatives that appear to have the potential to reduce the cost and the environmental risks related to the emissions of amines.

Adsorbents such as zeolites, activated carbons, and metal-organic frameworks (MOFs) are currently being studied for CO_2 capture and separation.[7] For an adsorption-driven capture, the function of the adsorbent is important. For example, Eddaoudi's group developed a series MOFs with tunable contracted pore size, exposed open metal sites and highly localized charge density. These functions enhanced the adsorption of CO_2 and the isosteric heat of adsorption (Q_{st}).[8-10] Such sorbents with uniformed energetic adsorption sites and relatively high Q_{st} are preferred for capturing CO_2 when its partial pressure is low. An example of such a gas mixture is the flue gases from natural gas fired turbines. They typically have a concentration of 3-4% of CO_2.[11-12] Moreover, a large Q_{st} could be relevant for a temperature-swing driven capture.[13-15] Amine modification on porous sorbents is an alternative way to enhance the energetics of CO_2 adsorption and the adsorption level at low relative pressures. The modification can be performed by: tethered amines,[16-17] amines adsorbed on the porous substrates or those filling the pores,[18] and amines polymerized within the porous framework.[19] Porous silica is a much studied substrate,[20-22] but exhibits steaming stability issues.[23] Other researched substrates are porous alumina,[23] activated carbons,[24-25] MOFs[26] and porous polymer networks.[27] For example, the MOF material of mmen-CuBTTri with the incorporation of *N,N'*-dimethylethylenediamine (mmen) had a high CO_2 uptake of 2.38 mmol/g and a high estimated CO_2-over-N_2 selectivity of 327 in a mixture of 0.15 bar CO_2 and 0.75 bar N_2 at a temperature of 298 K. The high capacity and selectivity are consequence of the exceptional large Q_{st} (96 kJ/mol) at zero coverage.[28]

Porous polymers offer some advantages over other types of substrates for the modification with amines. Post modification of porous polymers is straightforward due to the rich palette of functionalities that relate to the diverse set of synthesis routes.[29-31] These polymers can have tunable porosities and high physicochemical stability. Their highly cross-linked or interpenetrated structures can generate ultra-micropores that are relevant for the physisorption of CO_2,[32-34] but also mesopores[35-37] that offer space for further modification with alkylamines. One example is the PPN-6 with large micropores that after tethering with alkylamines exhibited a high Q_{st}, with a value up to 60 kJ/mol. This value clearly indicated a contribution from chemisorption. This modified polymer showed a high uptake of CO_2 (up to 3.04 mmol/g at 0.15 bar and 295K) and a high CO_2-over-N_2 selectivity (up to 442 at 295 K).[27] Here, we post-synthetically modified a micro-/mesoporous polymer with a tetramine, studied its uptake of CO_2 and its detailed CO_2-chemistry using *in situ* infrared spectroscopy and ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

Experimental

Materials

1,3,5-tris(4-aminophenyl)benzene (**A3**) (CAS No. 118727-34-7; > 93% purity) was purchased from TCI Europe, 1,3,5-benzenetricarboxaldehyde (**B3**) (CAS No. 3163-76-6; 98% purity) was purchased from Manchester Organics. Tris(2-aminoethyl)amine (**tren**) (CAS No. 4097-89-6; 96% purity) and all the solvents were purchased from Sigma-Aldrich. All chemicals were used without further purification.

Synthesis of PP1-2

Triamine (**A3**) (0.3 mmol, 113 mg) and 5 mL of DMSO was added to a 50 mL round flask equipped with an air cooling condenser and a magnetic stirrer. A yellow solution formed. A colorless solution of trialdehyde (**B3**) (0.6 mmol, 97 mg) dissolved in 5 mL of DMSO was drop-wise added. The temperature was ramped up from 50 ºC for the mixing (3 hours), 120 ºC (12 hours) to 200 ºC (72 hours). The mixture and precipitates gradually turned from yellow to brown on this treatment. The brown precipitates were filtered off and washed by THF and methanol for several times until the filtrate was colorless. The as-synthesized product (PP-1-2) was subsequentially dried at a temperature of 200 ºC under an atmosphere of N_2.

Synthesis PP1-2-tren

PP1-2 (100 mg) and the tetramine (**tren**) (10 ml) were added to a 25 mL round flask under an atmosphere of N_2. The flask was sealed and heated to 100 ºC for 1 day. The solid was collected and washed by THF and methanol and then dried at a temperature of 100 ºC under an atmosphere of N_2.

Characterization

The NIR infrared spectra were recorded with a Varian 610 IR microscope coupled to a Varian 670-IR spectrometer. Thick layers (~500 µm) of the samples were placed onto KBr disc. The NIR spectra were recorded in transmission mode by accumulating 3000 scans in the spectral regime of 3800-7000 cm^{-1}. The in situ IR spectra were recorded with Varian 670-IR spectrometer equipped with a diffuse reflection accessory (DiffusIR, Pike Technologies, Madison, USA) and a diffuse reflectance cell (DiffusIR environmental chamber, Pike Technologies, Madison, USA). A small amount of PP1-2-tren was mixed with a powder of KBr and placed into the cell. Prior to the measurement the sample was degassed at a temperature of 150 ºC for 2.5 h under a flow of N_2. After this pre-treatment, a background spectrum was recorded by measuring a diffuse reflectance spectrum of the degassed sample. For recording the spectra during adsorption of CO_2, we switched the flowing gas from N_2 to CO_2. Spectra were recorded successively until they stabilized. The bands in these spectra relate to adsorbed CO_2, and occurring changes in the PP1-2-tren structure by adsorption of CO_2. To eliminate the bands for gaseous CO_2, a reference spectrum was measured with the same diffuse reflection cell with only KBr in the sample holder and by the same CO_2 flow. This reference spectrum was then subtracted from the spectra measured for adsorbed CO_2.

One of the solid-state $^{13}C\{^1H\}$ NMR spectra were recorded at a frequency of 151 MHz on a BrukerAvance III spectrometer equipped with a wide-bore superconductive magnet of 14.1 T. The other two spectra were recorded at a frequency of 100.6 MHz on another BrukerAvance III spectrometer connected to a 9.4 T magnet. To qualitative study the CO_2-amine chemistry on PP1-2-tren, a fresh prepared sample of PP1-2-tren (heated at 100 ºC for 12 h with a N_2 flow) was treated with a CO_2 flow for 12 h at room temperature. Cross-polarization (CP) $^{13}C\{^1H\}$ NMR spectra were recorded under magic angle spinning (MAS) of 14 kHz using a ramped contact pulse. SPINAL decoupling of the ^1H contributions were used during the acquisitions. A recycling delay of 3.5 s was used not to saturate the ^1H magnetization, and 7168-16384 transients were acquired for each spectrum.

Gas sorption measurements were carried out on a Micrometrics ASAP2020 analyzer. PP1-2 was degassed at a temperature of 200 ºC, and PP1-2-tren at 100 ºC for 12 h under conditions of dynamic vacuum. Surface areas were calculated from the N_2 adsorption at relative pressure (P/P_0) of 0.01-0.1 in the Brunauer–Emmett–Teller (BET) model.

Results and discussion

The micro-/mesoporous polymer (PP1-2) was synthesized by condensing the triamine (**A3**) with the trialdehyde (**B3**) with a molar ratio of 1:2 in refluxing DMSO. By an excess of **B3** a large fraction of aldehyde end-groups was introduced in PP1-2, which allowed the tethering of tetramine (**tren**) by the Schiff base condensation leading to PP1-2-tren. Scheme 1 displays the chemical reactions relating to the synthesis of PP1-2, PP1-2-tren, and its reactions with CO_2.

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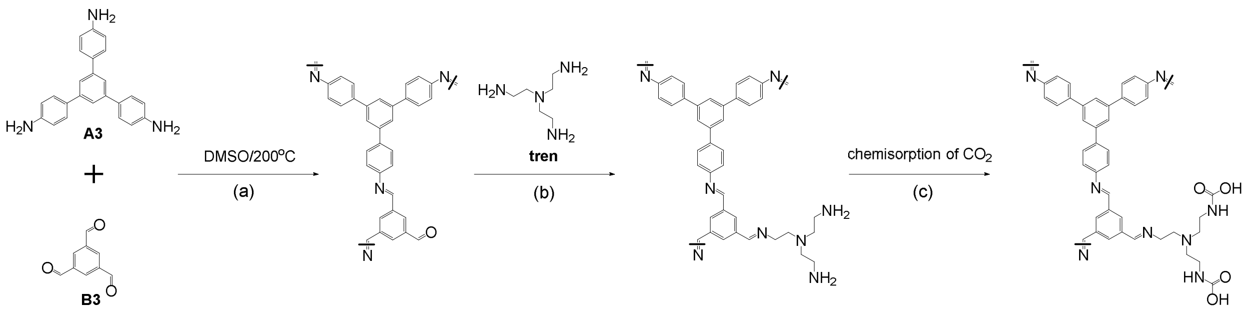

Scheme 1 Structure formulas for the: (a) porous polymer PP1-2 and (b) amine modified porous polymer PP1-2-tren (**tren**: tris(2-aminoethyl)amine); (c) the formation of carbamic acid species on PP1-2-tren during the chemisorption of CO_2.

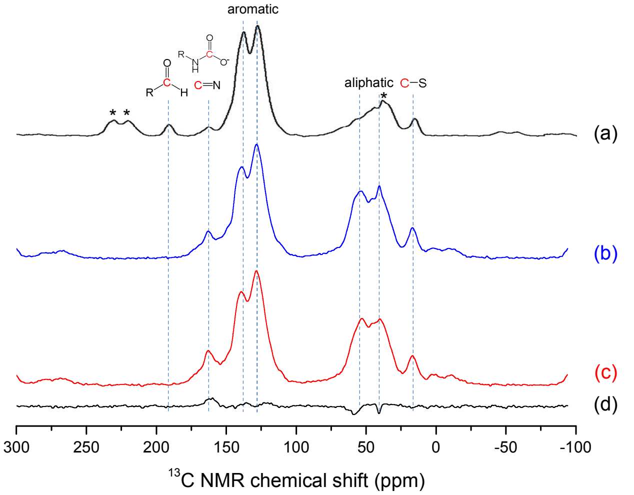

Fig. 1 Solid state $^{13}C\{^{1}H\}$ cross coupling magic angle spinning (MAS) nuclear magnetic resonance spectra of (a) PP1-2, (b) PP1-2-tren, (c) CO_2 adsorbed PP1-2-tren and (d) differences between b and c. Spectrum (a) was measured at 151 MHz and (b-c) at 100.6 MHz. The MAS rate was 14 kHz.

The molecular details of PP1-2, PP1-2-tren and CO_2 reacting with PP1-2-tren were examined by both FTIR and solid state $^{13}C\{^{1}H\}$ cross-polarization (CP) magic angle spinning (MAS) NMR spectroscopy. The $^{13}C\{^{1}H\}$ CPMAS NMR spectrum of PP1-2 shows peaks for the carbonyl carbons of aldehyde end groups at a chemical shift of 193 ppm and for the carbons of imine groups at 161 ppm, see Fig. 1a. The aromatic carbons have two broad bands at shifts of 120-140 ppm, and the decomposition products of DMSO have bands in the range of 20-60 ppm. The spectrum in Fig. 1a is similar to that of one of our earlier studies, where we studied microporous polymers formed from triamines and dialdehydes.[38] The imine bonds in PP1-2, and PP1-2-tren were confirmed by a band in the infrared spectra (corresponding to the C=N stretching: 1660 cm^{-1}) (Fig. S1). The IR, NIR and solid state ^{13}C NMR spectra of PP1-2-tren jointly confirmed that the **tren** molecules were successfully tethered to the porous polymer. The NMR spectrum of PP1-2-tren in Fig. 1b shows no carbonyl carbons, and a large intensity of the carbons of the imine groups. Hence, additional imine bonds were formed between the **tren** and aldehyde end groups of PP1-2 during the post-synthetic modification. The NIR spectrum of PP1-2-tren clearly shows a combination band (at 4930 cm^{-1}) and an overtone band (at 6512 cm^{-1}) from the primary amine groups (Fig. S2). NIR spectra of primary amines show such bands.[39] The alkyl groups of tethered **tren** were detected by both IR and NMR spectroscopy. In the solid state ^{13}C NMR spectrum in Fig. 1b, the chemical shifts at 40 and 54 ppm are assigned to the CH_2 groups in **tren** (the signal of the alkyl groups at 40 ppm partly overlapped with the side bands). In the IR spectrum in Fig. S1 the bands at 2923 cm^{-1} and 2846 cm^{-1} are assigned to the C–H stretching modes in the CH_2 groups of the **tren** moiety.

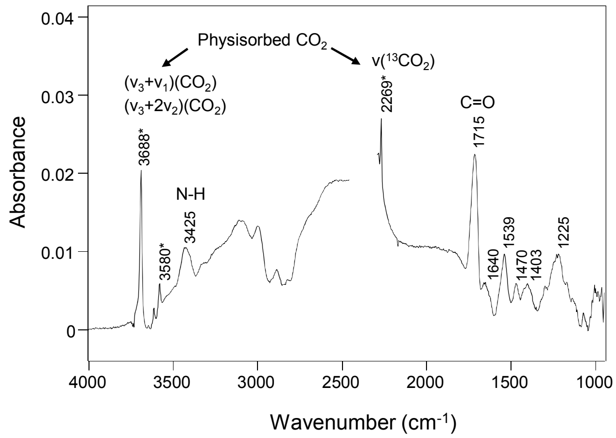

Fig. 2 In situ difference infrared spectrum of adsorbed CO_2 on PP1-2-tren. (A degassed sample was used to measure the IR background spectrum and the bands in the difference spectrum relate to the changes upon CO_2 adsorption)

The bands in the difference IR spectrum in Fig. 2 show that CO_2 was both chemisorbed and physisorbed onto PP1-2-tren. Chemisorbed CO_2 was detected by the bands in the range of 1100-1715 cm^{-1} and 3425 cm^{-1}. The band with the highest intensity at 1715 cm^{-1} was assigned to carbonyl groups with a frequency suggestive of carbamic acids (or a similar compound with a carbonyl group). The band at 3425 cm^{-1} was assigned to an N–H stretching mode in carbamic acid. The broad band between 3600 and 2500 cm^{-1} was assigned to the O–H stretching modes typical for hydrogen bonded acids. As the **tren** moieties of PP1-2-tren have a pKb of ~4, the chemisorption of CO_2 was expected. When amines and CO_2 react at dry conditions ammonium carbamate ion pairs usually form.[40] If the amines are immobilized, the close proximity of the primary or secondary amine groups needed to form these ion pairs. The long distances between the amine groups within the **tren** molecules appeared to have hindered ammonium carbamates ion pairs from forming. Possibly the protophilic nature of the polymer backbone could also have stabilized the carbamic acid.[40,41] Consistently, no strong characteristic bands of NH_3^+ and $(NH)COO^-$ moieties were observed. Such characteristic bands would have been observed at ~1484, 1633 cm^{-1} for NH_3^+ and 1580 cm^{-1} for $(NH)COO^-$, respectively.[40] Previously, it has been shown that the amine-CO_2 chemistry in amine-modified silica is complex with the possible formation of ammonium carbamates, surface bound carbamates or carbamic acid depending on the nature of amines, amine concentrations, the distance between amines, humidity, etc.[20,40,42-44] Physisorbed CO_2 is also visible in the IR spectrum in Fig. 2. The bands at frequencies of 2269 (antisymmetric stretching band for $^{13}CO_2$), 3580 and 3688 cm^{-1} (combination bands) correspond to physisorbed CO_2 molecules. (The antisymmetric stretching band at a frequency of ~2340 cm^{-1} should have had the highest intensity, but it was hidden by the full absorption of the IR radiation by gaseous and adsorbed CO_2).

Solid state NMR spectroscopy can also detect CO_2 that is chemisorbed in amine modified sorbents, which was shown by Pinto *et al.* and Huang *et al.*[45-46] The solid state $^{13}C\{^1H\}$ CPMAS NMR spectrum of a PP1-2-tren sample subjected to CO_2 (in Fig. 1c) shows the additional increased intensity of a signal at a chemical shift of ~160-165 ppm in comparison with the spectrum of fresh PP1-2-tren (in Fig. 1b). This was consistent with the formation of the carbonyl group in PP1-2-tren on chemisorption of CO_2. (the signals of carbonyl and imine bond are partly overlapped in the same area) There is also a reduced intensity in the amine signals in Fig. 1c, which could relate to a change in the CP dynamics during the formation of carbamic acid. The difference spectrum of Fig. 1b and Fig. 1c is presented in Fig. 1d. Due to the sample preparation of the PP1-2-tren subjected to CO_2, the NMR results showed they were treated as qualitative. In conjunction with the IR and ^{13}C NMR spectra, we conclude that carbamic acid was formed during the chemisorption of CO_2 in PP1-2-tren (Scheme 1).

The N_2 isotherm for PP1-2 in Fig. 3a shows typical steep uptakes at low pressure regimes ($P/P_0<0.05$), which were reduced significantly upon tethering for the PP1-2-tren sample. The specific surface area was reduced from 405 to 72 m^2/g and the total pore volume was reduced from 0.54 to 0.27 cm^3/g upon tethering with **tren**. According to the pore size distribution analysis using the N_2 adsorption isotherms in Fig. 3b, the micropores with centred at 0.7 and 1.3 nm in the PP1-2 vanished after grafting the **tren** which can be attributed to a pore blocking effect by the bulky amines. The decreases in surface areas, pore volumes and pore size were also detected in related amine-modified sorbents.[27,30] The high pressure regimes ($P/P_0>0.9$) show a steep uptake of N_2 for both samples, and a corresponding hysteresis, which is typical for a sample with large mesopores or interparticle voids.[47] Such steep N_2 uptakes at high relative pressures are commonly observed in related porous polymers.[37,48-50]

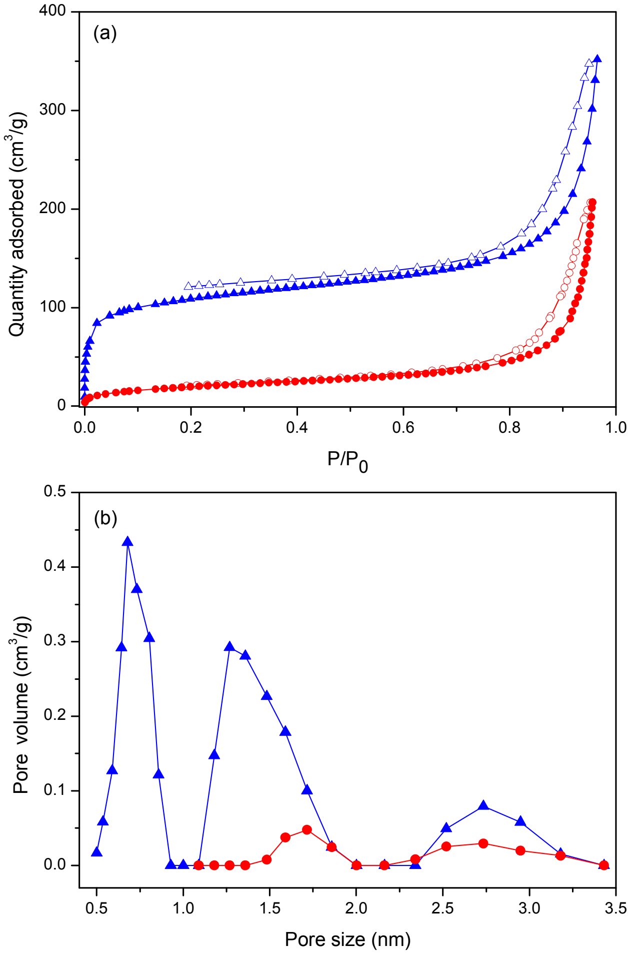

Fig. 3 (a) N_2 adsorption and desorption isotherms of PP1-2 (blue triangles) and PP1-2-tren (red circles). (b) Pore size distribution of PP1-2 (blue triangles) and PP1-2-tren (black blanks) analyzed on N_2 adsorption isotherms measured at 77 K using the DFT model. PP1-2 and PP1-2-tren were degassed at 200 and 100 °C for 12 h before the measurement.

Note that inefficient pore blocking by the amines in the substrate PP1-2 could remain or generate a certain amount of ultramicropores in the amine modified polymer PP1-2-tren. It is relatively common that such ultramicropores in porous polymers cannot be detected by N_2 sorption at 77 K.[51] Using CO_2 sorption at 273 K is a feasible way to probe the ultramicropores;[52] however, porosity analysis by CO_2 adsorption isotherms for PP1-2-tren is not appropriate because of strong chemisorption.

The PP1-2-tren showed a distinct uptake of CO_2 at low pressures due to the chemisorption to the basic **tren** moieties. The CO_2 isotherm of PP1-2 in Fig. 4 shows a much smaller gradient at low pressures compared with that of PP1-2-tren. For the amine modified polymer, the uptake of CO_2 at a pressure of 0.15 and 0.05 bar was relatively high (1.45 and 1.13 mmol/g at 273 K), 61% and 144% higher than that of the substrate polymer of PP1-2 (0.90 mmol and 0.46 mmol/g at 273 K). It surpassed most porous polymers and was comparable with some top performing sorbents with the same or similar conditions (0.15 bar), such as PPF-1 (1.80 mmol/g),[49] mPMF-5 (1.93 mmol/g),[50] BILP-4 (1.99 mmol/g)[53] and PPN-6-CH_2DETA (3.04 mmol/g, 295 K).[27]

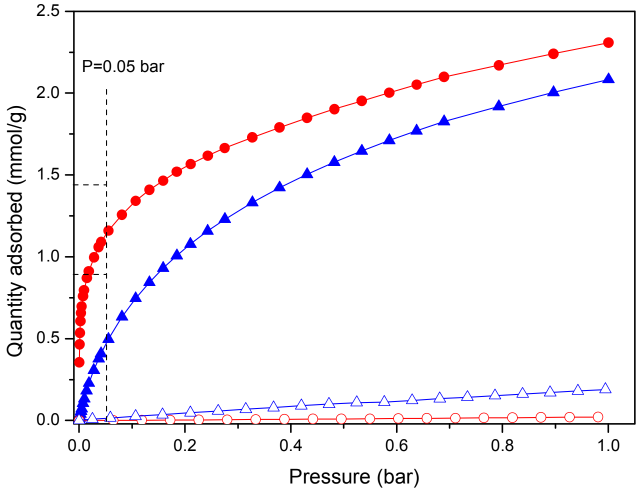

Fig. 4 CO_2 and N_2 adsorption isotherms of PP1-2 (▲: CO_2; △: N_2) and PP1-2-tren (●: CO_2; ○: N_2) at 273 K.

The isosteric heat of adsorption is relevant for potential applications towards CCS. The amine-modified porous polymer, PP1-2-tren had a very high Q_{st} of ~80 kJ/mol at a low coverage of CO_2, and remained at a relatively high level of ~45 kJ/mol for a higher coverage of CO_2, as can be seen from the trend in Fig. 5. We interpret this reduction in Q_{st} as the accessible **tren** moieties reacting with CO_2, and the remaining CO_2 physisorbed in ultramicropores. As expected, the substrate PP1-2 had a lower Q_{st} value of ~28 kJ/mol at low coverage, which is typical for the physisorption of CO_2. The curves in Fig. 5 were derived from CO_2 adsorption isotherms recorded at different temperatures modeled in a dual-site Langmuir model[54] (Tables S1-2, Fig. S4-5). Similar heat sorption dependencies were derived from experimental adsorption isotherms using the Clausius-Clapeyron relation (Fig. S7-8). The linearity of the isosters confirmed the accuracy of the Q_{st} calculated from the temperature dependent CO_2 adsorption isotherms. To the best of our knowledge, ~80 kJ/mol is the highest Q_{st} for CO_2 reported for porous polymers. As shown by spectroscopy, the high value of Q_{st} is related to the formation of carbamic acids and could certainly be relevant to applications where CO_2 needs to be captured at relatively low pressures.[55] One the other hand, the high Q_{st} indicates that the CO_2 capacities in the sorbents are strongly dependent on temperature.[28] Hence, PP1-2-tren and related sorbents should primarily be regenerated by temperature swings.

The CO_2-over-N_2 selectivity is very important to CCS capture. It was estimated from single component adsorption data and the equation of $S=(q_A/q_B)/(p_A/p_B)$ (S: selectivity; q: uptake; p: partial pressure; A, B: gas component).[27,56] PP1-2-tren had very high selectivities (456 and 1040) for gas mixtures of CO_2/N_2 with compositions of 15v%/85v% and 5v%/95v%, respectively at 273 K (Table S3). The high selectivity of PP1-2-tren is consistent with the formation of carbamic acid and is possibly an added kinetic contribution from separation in ultramicropores. The substrate (PP1-2) had moderate selectivities of 31 and 48.

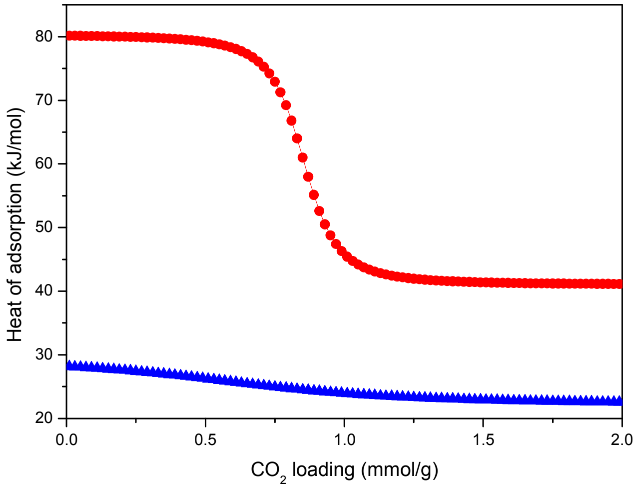

Fig. 5 Heat of adsorption of CO_2 for PP1-2 (blue triangles) and PP1-2-tren (red circles) calculated by the dual-site Langmuir model.

Conclusions

In conclusion, porous organic polymers with hierarchical pore structures are promising substrates for amine-based sorbents for CO_2 capture. The alkylamine tethered sorbents studied here had a high uptake of CO_2 at low pressures (<0.05 bar) of CO_2. The high Q_{st} for CO_2 adsorption and high CO_2-over-N_2 selectivity make them potentially relevant for CO_2 capture at quite low pressures of CO_2. The amine groups and most probably the ultramicropores played an important role for the adsorption of CO_2. The high heat of adsorption could have problems for the regeneration and cycling behaviours of the modified polymers. The quantitative modification of the polymers to optimize and balance the heat of adsorption, uptakes and selectivities could be important aspects for future studies.

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Notes and references

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Electronic Supplementary Information (ESI) available: NIR and IR spectra, fitting of CO_2 adsorption isotherms and the calculation of isosteric heat of adsorption. See DOI: 10.1039/b000000x/

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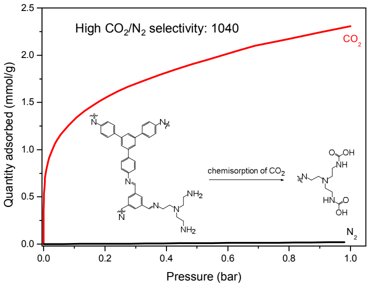

Tris(2-aminoethyl)amine modified micro-/mesoporous polyimine show high CO_2 uptakes at low partial pressures and high estimated CO_2-over-N_2 selectivity up to 1040.