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Swellable, Water- and Acid-Tolerant Polymer Sponges for Chemoselective Carbon Dioxide Capture

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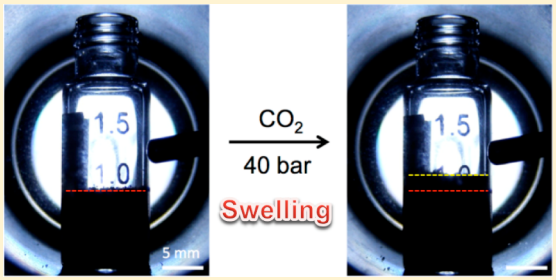
Supporting Information

ABSTRACT: To impact carbon emissions, new materials for carbon capture must be inexpensive, robust, and able to adsorb CO_2 specifically from a mixture of other gases. In particular, materials must be tolerant to the water vapor and to the acidic impurities that are present in gas streams produced by using fossil fuels to generate electricity. We show that a porous organic polymer has excellent CO_2 capacity and high CO_2 selectivity under conditions relevant to precombustion CO_2 capture. Unlike polar adsorbents, such as zeolite 13x and the metal−organic framework, HKUST-1, the CO_2 adsorption capacity for the hydrophobic polymer is hardly affected by the adsorption of water vapor. The polymer is even stable to boiling in concentrated acid for extended periods, a property that is matched by few microporous adsorbents. The polymer adsorbs CO_2 in a different way from rigid materials by physical swelling, much as a sponge adsorbs water. This gives rise to a higher CO_2 capacities and much better CO_2 selectivity than for other water-tolerant, nonswellable frameworks, such as activated carbon and ZIF-8. The polymer has superior function as a selective gas adsorbent, even though its constituent monomers are very simple organic feedstocks, as would be required for materials preparation on the large industrial scales required for carbon capture.



INTRODUCTION

The use of fossil fuels to generate electricity is the single largest anthropogenic source of CO_2 emissions. Carbon capture and storage (CCS) represent a rapidly developing set of technologies that includes precombustion capture, postcombustion capture, and oxyfuel combustion capture. CCS has the potential to achieve >90% reductions in CO_2 emissions.[1] All variants of CCS involve gas separation on multiton scales to achieve a highly concentrated stream of CO_2 for transport and subsequent storage. However, significant cost reductions are required to render CCS technologies competitive with other low-carbon generation technologies, such as renewables and nuclear power. A key target is to lower the dominant energy penalty, and therefore the cost, associated with the CO_2 separation process.

In precombustion CO_2 capture, an integrated gasification combined cycle (IGCC) power station uses the water−gas shift reaction to convert gasified fuel into a mixture of hydrogen and CO_2. The CO_2 must then be separated before using the hydrogen to drive a combined cycle turbine for electricity generation.[2] Hence, the challenge is to separate CO_2 and hydrogen (H_2) on a large scale in an energy efficient way, while minimizing hydrogen losses. The current state-of-the-art technology for precombustion capture uses physical solvent systems, such as the Selexol technology in a pressure-swing cycle.[3] Other, next-generation technologies for precombustion CO_2 separation include membranes with selective permeability[4,5] and porous adsorbents.[6,7]

There are stringent technical and economic requirements for solid adsorbents for precombustion CO_2 capture. The adsorbent must operate in a gas stream leaving the water−gas shift reactor at a total pressure of approximately 30−45 bar and at a temperature of around 40 °C. The CO_2 mole fraction would be approximately 35−40%, and hence the partial pressure of CO_2 would be approximately 12−18 bar. The major component is the gas-shifted fuel, H_2 (>60 mol %). The pressure and temperature of the gas stream make pressure-

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swing cycles particularly attractive.[8] An adsorbent must have a large CO_2 sorption capacity if it is to form part of an economically viable separation process. It must also have good selectivity for the adsorption of CO_2 with respect to other components in the gas stream in order to generate a CO_2 stream of the required purity. In particular, it must adsorb CO_2 in preference to the major component, H_2, and also other minor components such as water vapor and nitrogen (N_2). Selectivity is related to adsorption thermodynamics: the CO_2 must be adsorbed just strongly enough to facilitate the separation, without generating a large energy penalty in regenerating the adsorbent. More specifically, porous materials are required that can separate out a high-purity CO_2 stream at elevated pressures without the need for a vacuum regeneration cycle, which would add a significant energy penalty. A candidate adsorbent must also have good physicochemical stability: it must be moisture stable, thermally stable, and insensitive to corrosive acidic gases such as hydrogen sulfide over long periods. Finally, given the enormous volumes of CO_2 to be captured, candidate materials for CCS must be relatively inexpensive and their preparation must be scalable. For example, the proposed Don Valley, UK, 920 MW IGCC plant could potentially produce up to 14,000 tons of CO_2 per day in routine operation. Hence, while there have been major advances in the chemical synthesis of new porous solids with atomic precision,[9,10] most materials will fail for precombustion CCS on at least one of the five primary criteria of CO_2 capacity, CO_2 selectivity, sorption energetics, physicochemical stability, and cost.

Porous metal−organic frameworks (MOFs) have been studied intensively as adsorbents for CCS.[11−13] Exceptional surface areas of up to 7000 m^2/g are possible in MOFs,[14] and ultralow-density frameworks, such as MOF-210, can show extraordinary CO_2 uptakes (54.5 mmol/g at 50 bar CO_2 pressure and 298 K).[15] Synthetic strategies have also been devised to optimize CO_2 selectivity, for example by using mixed organic linkers in "multivariate" MOFs.[16] However, the practical potential of most "ultraporous" MOFs, such as MOF-210, is curtailed by limited physicochemical stability and, particularly, by sensitivity to water. More stable MOFs with lower surface areas, such as zinc imidazolate frameworks (ZIFs),[17] might be better candidates for practical CCS. However, even ZIF-8, one of the more stable MOFs, has been shown undergo hydrolysis unless suitably protected.[18]

Microporous organic polymers can combine high levels of porosity with good chemical stability.[19] For example, a polyphenylene network, PAF-1, has a surface area of 5,600 m^2/g and an excess CO_2 uptake of 29.5 mmol/g at 40 bar CO_2 pressure and 298 K.[20] The physicochemical stability of PAF-1 is excellent: boiling in water for 7 days has no effect on its gas sorption properties. However, scale up may be challenging because the tetraphenylmethane-derived monomer for PAF-1 is quite expensive. More seriously, PAF-1 must be synthesized under rigorously anhydrous and anaerobic conditions, typically in a glovebox, because the stoichiometric nickel coupling reagent is air and moisture sensitive.[20] Indeed, the economics of scale-up is a general concern for porous polymer adsorbents that are prepared using precious metal reagents or catalysts, such as most conjugated microporous polymers.[21]

Extremely high surface areas may not, in fact, be a prerequisite for CCS, particularly if the sorption affinity of the adsorbent is thermodynamically attuned for CO_2 adsorption. Several studies have focused on microporous polymers with chemical functionality that was selected to improve gas selectivity, mainly in the context of postcombustion CCS where the pressure is 1 bar.[22,23] The introduction of polar functional groups into polymers can greatly improve selectivity for CO_2 over nitrogen (N_2)[23−25] by introducing specific intermolecular interactions with the CO_2 molecules.[26] However, it has also been shown that polar groups can enhance water uptake, too, thus leading to an overall decrease in CO_2 sorption capacity when measurements are performed under more realistic conditions in the presence of water vapor.[27] As such, increasing the polarity of porous polymers, while effective under laboratory conditions for perfectly dry CO_2 gas streams, will not necessarily translate into practical benefits for real-life CCS.

Hyper-cross-linked polymers[28,29] are scalable porous materials that have been produced commercially for some years. Recently, hyper-cross-linked polymers were synthesized using a formaldehyde dimethyl ether cross-linker,[30] extending the approach to a wide range of low functionality aromatic monomers. Indeed, the monomer can be as simple and inexpensive as benzene (Figure 1), and the materials cost is

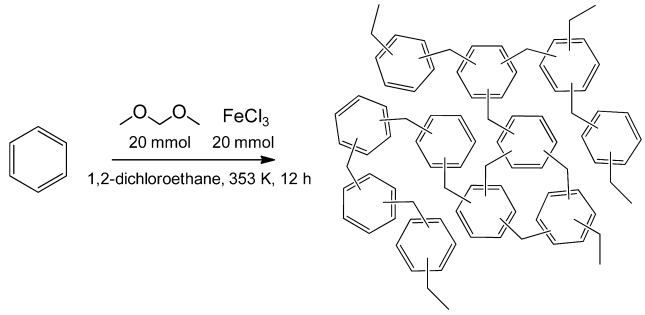

Figure 1. Synthesis of porous polymer network, **1**. Friedel−Crafts alkylation of benzene with 2 equiv of formaldehyde dimethyl acetal produces a microporous, "knitted" hyper-cross-linked polymer network.

therefore determined by the dimethyl ether cross-linker, which is used stoichiometrically, and the solvent, although it is possible that the latter could be either recycled or avoided completely: for example, by carrying out reactions in the neat aromatic monomer. Hyper-cross-linked polymers have moderate CO_2 uptakes at low pressures (1 bar), but they show more promising CO_2 uptakes at the higher pressures that are relevant to precombustion CCS.[31]

Unlike porous crystals such as MOFs and zeolites, hyper-cross-linked polymers exist in a state that is far from thermodynamic equilibrium. As synthesized, they form expanded, solvent-swollen networks. These networks then collapse upon removal of the solvent, but cannot collapse fully to a nonporous state because of the high cross-linking levels. This introduces considerable strain in the network.[32] Consequently, these materials are predisposed to swell in a wide range of solvents, including thermodynamically "bad" solvents for the polymers.[33] Carbon dioxide is known to swell nonporous aromatic polymers, such as polystyrene,[34] and we speculated, therefore, that porous hyper-cross-linked polymers might adsorb CO_2 by a chemospecific swelling mechanism that is not accessible in rigid, crystalline porous frameworks.

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RESULTS AND DISCUSSION

The Friedel–Crafts alkylation reaction shown in Figure 1 was carried out for four different aromatic monomers: benzene (polymer **1**), tetraphenylmethane (polymer **2**), triphenylmethane (polymer **3**), and triptycene (polymer **4**). The details of all materials are included in the Supporting Information, but only the benzene network, **1**, is discussed here. Polymers **2**–**4** did not give any real functional advantage for CCS, and their monomers are all much more expensive than benzene. All polymers were produced as insoluble dark brown solids with yields greater than 90% on a typical laboratory preparative scale of 5–10 g per batch.

The amorphous and insoluble nature of these polymers makes their structural characterizations challenging, and this relies extensively on solid-state magic angle spinning (MAS) NMR spectroscopy. Although this approach is powerful, acquisition of the NMR spectra is time-consuming (hours or days), especially when libraries of polymers are synthesized. It was shown that the sensitivity issue in solid-state NMR could be tackled with high-field dynamic nuclear polarization (DNP)[35−41] using a transfer of polarization from electrons (added to the samples as mono[35] or biradicals[42−44]) to nuclear spins at cryogenic temperatures and under adequate DNP sample preparation condition.[35,37] We have recently exploited this strategy for high-throughput structural NMR characterization of microporous organic polymers[45] where we showed that ^{13}C cross-polarization (CP) magic angle spinning (MAS) NMR could be obtained in minutes only.

The DNP enhanced ^{13}C CP MAS NMR spectra of polymer **1** obtained at a field strength of 14.1 T is given in Figure S29. This revealed the presence of substituted and nonsubstituted aromatic carbon at 137 and 130 ppm as well as the CH_2 bringing linker at 36 ppm.[30] A weak signal, hardly visible in the spectra without DNP, is also observed at 20 ppm and is assigned to a CH_3 group corresponding to the methylation of benzene with the acetal. The NMR spectra for network polymer **1** (with 3 equiv of cross-linker), the same polymer with 4 equiv of cross-linker, and polymer **3** were all very similar. They also showed a small CH_3 peak (in addition to the expected CH signal of the triphenylmethane moiety in the cages of **3** at 48 ppm).

The polymers were microporous, as indicated by a steep uptake at low relative pressures in nitrogen adsorption isotherms (Figure 2; see Figure S1 for isotherms for polymers **2**–**4**).

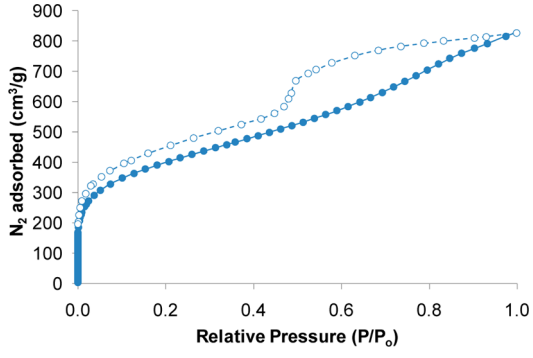

Figure 2. Nitrogen sorption isotherm for **1**. Adsorption (solid symbols) and desorption (open symbols) isotherms at 77 K indicates microporosity. The hysteresis loop suggests swelling.

The hysteresis loop in the desorption isotherm is consistent with swelling of the network during sorption analysis at 77 K.[46] The apparent BET surface area (1228 m^2/g), the total pore volume (1.54 cm^3/g), and the micropore volume (0.46 cm^3/g) were calculated from the low-pressure nitrogen isotherm. The other hyper-cross-linked polymers, **2**–**4**, had broadly similar properties (Table S1).

To evaluate its potential for precombustion CCS, polymer **1** was compared with four other porous solids: an activated carbon (Norit R2030, Norit Carbon UK; a steam-activated carbon specifically designed for CO_2 applications), a polar zeolite, zeolite 13x,[47] and two robust metal–organic frameworks, ZIF-8[17] and HKUST-1.[48] The porous properties of these materials, as derived from nitrogen sorption analyses, and their bulk densities, are given in Table 1.

Table 1. Porous Properties of the Adsorbents Tested

network	SA_{BET} (m^2/g)[a]	micropore volume (cm^3/g)[a]	bulk density (g/cm^3)
polymer 1	1228	0.46	0.35[b]
carbon	806	0.30	0.52[c]
zeolite 13x	848	0.31	0.35[c]
ZIF-8	2188	0.65	0.35[c]
HKUST-1	1896	0.73	0.48[c]

[a]Calculated from N_2 sorption isotherms measured at 77 K for "dry" samples which had been degassed at 120 °C for 15 h under high vacuum (<15 μbar). [b]Measured using mercury intrusion porosimetry at 0.31 psi. [c]Data from suppliers of materials.

Our strategy was to evaluate all of these materials in terms of four key properties that might define their performance in precombustion CCS, namely; (i) CO_2 sorption capacity; (ii) tolerance to water and acids; (iii) CO_2/H_2 selectivity; and (iv) CO_2/N_2 selectivity. The results of these measurements are summarized in Table 2.

First, the single component CO_2 isotherms were measured for all samples in the "dry", thoroughly degassed state up to a pressure of 40 bar using high-purity CO_2. Total pressures of around 40 bar are relevant to precombustion CCS[12] (even higher-pressure systems might be developed in the future), but we also analyzed these data in terms of sorption capacities at 17.5 bar, which is more reflective of the likely partial pressure of CO_2 in precombustion CCS.

Of the five materials tested, polymer network **1** has the highest gravimetric CO_2 capacity of 15.32 mmol/g in the "dry" state at 40 bar, as compared to values in the range 6.91–9.30 mmol/g for the other four materials. It also has the highest gravimetric CO_2 capacity at the lower pressure of 17.5 bar (8.66 mmol/g). Polymer **1** does not, however, have the highest apparent BET surface area or micropore volume, as measured by N_2 adsorption: both of the MOFs, ZIF-8 and HKUST-1, have higher porosity as measured in that way (Table 1). The isosteric heat of adsorption for CO_2 was measured for **1** and was found to be 28–30 kJ/mol at low CO_2 coverage (Figure S2): this is comparable with other porous polymers and not high enough to introduce large energy penalties for CO_2 desorption.

These "dry" measurement conditions involve rigorous degassing of the sample before analysis (<15 × 10^{-6} bar, 120 °C, 15 h). Such high vacuum conditions would be prohibitively expensive for CCS. Also, in real CCS, the adsorbent would not be exposed to high-purity CO_2. Instead, the regenerated

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Table 2. Key Functional Properties for Porous Adsorbents for Precombustion CCS[a]

network	CO_2 uptake (mmol/g)[b]		H_2 uptake (mmol/g)[b]		N_2 uptake (mmol/g)[b]		CO_2/H_2 selectivity[d]	CO_2/H_2 selectivity[d]	CO_2/N_2 selectivity[d]	swelling in CO_2[e] (%)	volumetric CO_2 uptake ($mmol/cm^3$)
	dry[c]	wet[c]	dry[c]	wet[c]	dry[c]	wet[c]	dry[c]	wet[c]	dry[c]		wet[f]
polymer 1	15.32	13.17	0.68	0.58	2.65	2.43	22.5	22.7	5.8	11.2	4.61 [3.63][h]
	(8.66)	(7.12)	(0.29)	(0.30)	(1.61)	(1.42)	(29.9)	(23.7)	(5.4)	(4.3)	(2.50) [2.39][h]
carbon	6.91	5.75	1.35	0.61	3.50	1.96	5.1	9.4	2.0	0	2.99
	(6.33)	(3.10)	(0.61)	(0.34)	(2.39)	(1.25)	(10.4)	(9.1)	(2.6)	(0)	(1.61)
zeolite 13x	8.03	0.46	0.56	–[g]	2.89	–[g]	14.3	–[g]	2.8	0	0.16
	(7.40)	(0.19)	(0.26)	–[g]	(2.09)	–[g]	(28.5)	(–)[g]	(3.5)	(0)	(0.07)
ZIF-8	9.30	8.78	0.84	0.67	2.32	2.21	11.1	13.1	4.0	0	3.07
	(7.74)	(6.99)	(0.32)	(0.33)	(1.31)	(1.19)	(24.2)	(21.2)	(5.9)	(0)	(2.45)
HKUST-1	7.91	2.19	0.96	–[g]	3.23	–[g]	8.2	–[g]	2.4	0	1.05
	(7.37)	(0.67)	(0.44)	–[g]	(2.18)	–[g]	(16.8)	–[g]	(3.4)	(0)	(0.32)

[a]Polymer **1** outperforms the other materials significantly in terms of gravimetric CO_2 uptake and CO_2/H_2 selectivity (both dry and wet conditions; see also Figure 3f. [b]Gravimetric CO_2 capacity as measured in pure CO_2 at 40 bar, 298 K; in all cases, figures in parentheses refer to data measured at 17.5 bar, reflecting the likely partial pressure of CO_2 in precombustion CCS. [c]"Dry" samples were degassed under dynamic vacuum at 120 °C ($<15 \times 10^{-6}$ bar) for 15 h before analysis; "wet" samples were equilibrated with air for 48 h and were *not* degassed before analysis. [d]Ideal molar gas selectivities as calculated from independent sorption isotherms for pure gases; the ratios were calculated at 40 bar, 298 K. [e]Change in sample volume between 1 and 40 bar, as estimated using a high-pressure view cell (±1.3%). [f]Calculated from "wet" CO_2 sorption data using the material density values given in Table 1; in real CCS, it would be the packed pellet density, rather than the bulk material density used here, that will determine the size of the CO_2 capture unit. [g]Gas uptake under these conditions was too low to be quoted with precision. [h]Figures in square brackets are data corrected to allow for volume increase in the sample upon polymer swelling, reflecting the fact that sample volume determines the overall size of the capture unit required.

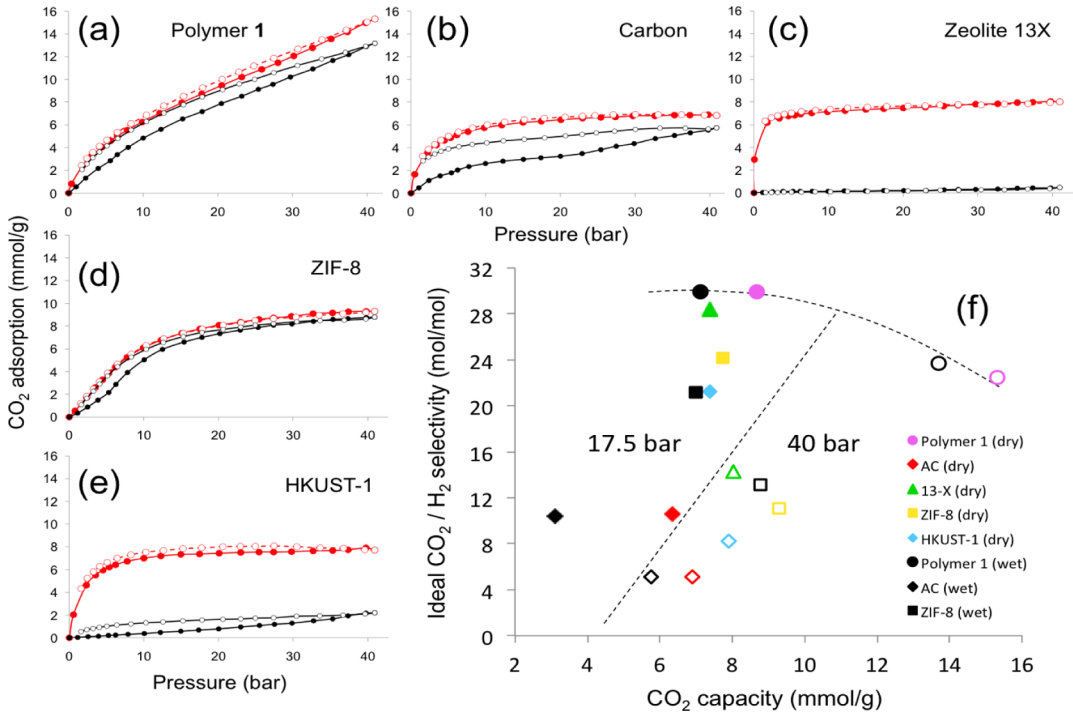

Figure 3. Gas sorption isotherms for wet and dry adsorbents (a–e) and their ideal CO_2/H_2 selectivities (f). For (a–e), the *x*-axis represents pressure (in bar), and the *y*-axis represents CO_2 adsorption in mmol/g. Adsorption (solid circles) and desorption (open circles) isotherms (100% CO_2) for both "dry" (red) and "wet" (black) samples of (a) benzene polymer **1**; (b) activated carbon R2030; (c) zeolite 13x; (d) ZIF-8; and (e) HKUST-1. (f) The ideal CO_2/H_2 selectivity plotted against CO_2 capacity, as measured at 40 bar (open symbols to right of dashed straight line) and 17.5 bar (likely CO_2 partial pressure in precombustion CCS; closed symbols to left of line). Colored symbols denote "dry" measurements and black symbols the corresponding "wet" measurements. Wet uptakes for HKUST-1 and zeolite 13x are not plotted because both CO_2 and H_2 uptakes are very low in the presence of physisorbed water. Polymer **1** (circle points) forms the upper performance bound for the five materials, as illustrated by the curved, dotted line.

adsorbent would be exposed to a mixture of CO_2 with other components such as H_2, N_2, and water vapor. We showed previously that exposure to atmospheric water vapor can have a large, negative influence on the CO_2 capacity of otherwise promising porous polymer adsorbents for postcombustion CCS.[26] Hence, the CO_2 capacities of all samples were remeasured after exposure to air for 48 h (22 °C, 35–45% relative humidity), in the absence of the high-vacuum degassing step, to more closely mimic real-life CCS conditions. In some cases, the CO_2 capacities in the "wet" samples were dramatically

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lower than the corresponding dry measurements. For example, the MOF sample, HKUST-1, retained only 28% of its dry CO_2 capacity at 40 bar when wet,[49] although we note that other studies show an enhancement in CO_2 uptake in HKUST-1, at least at lower pressures, at certain levels of framework hydration.[48] Water was also shown by others to have a highly deleterious effect on CO_2 sorption for the magnesium MOF, Mg-MOF-74.[51] The effect on zeolite 13x is even more striking: it has just 6% of its dry CO_2 capacity at 40 bar when wet, not because it is unstable to water but because the material is strongly hydrophilic. It is a much better adsorbent for water than for CO_2, and dehydration is energy intensive. By contrast, the three more hydrophobic materials, polymer **1**, activated carbon, and ZIF-8, retain between 83% and 94% of their dry CO_2 capacity at 40 bar when wet (86% for **1**). Similar conclusions can be drawn from CO_2 sorption data at 17.5 bar.

In addition to retaining CO_2 selectivity under moist conditions, more hydrophobic materials may also exhibit better chemically stability to water and to acidic impurities in the gas stream. To demonstrate this, samples of polymer **1** were boiled in both water and in aqueous sulfuric acid (1 M) for 1 h. This had no effect on either the porosity or the CO_2 uptake (Figures S3 and S4), indicating excellent stability, both to water and to acid. Analysis by Fourier transform infrared (FTIR) spectroscopy also showed no chemical change to the polymer after boiling in concentrated acid (Figure S5). By contrast, many porous inorganic materials or hybrid MOFs would be rendered nonporous or dissolved by boiling in acidic solutions.

Water adsorption isotherms were also measured for polymer **1** at 1 bar and 298 K, and this showed that there is very little water uptake until humidity reaches a high level (Figure S6), which is consistent with the selective adsorption of CO_2 over water in **1**. Taken together, these data suggest a strong advantage for more hydrophobic adsorbents for precombustion CCS in terms of avoiding the energy penalties associated with rigorous drying of either the adsorbent or the gas stream.

The CO_2 sorption isotherms for the various dry and wet samples are shown in Figure 3. In addition to its higher CO_2 capacity, the relative shapes of the isotherms reveal another advantage for polymer **1**. The working capacity, rather than the absolute capacity, will define the performance of an adsorbent. The working capacity is defined as the difference between the quantity of CO_2 adsorbed at the adsorption pressure, and the residual adsorbed CO_2 at the desorption pressure, in the pressure swing cycle.[41] In general, the introduction of larger pressure swings in CCS introduces additional energy penalties, and hence materials that can adsorb and release large amounts of CO_2 over a small operational pressure window are desirable. The greater slope of the adsorption/desorption isotherms for **1** at higher pressures is therefore an advantage in a pressure-swing adsorption/desorption cycle. This is related to swelling effects, as discussed below.

For precombustion CO_2 capture, good CO_2:H_2 selectivity at high pressures is paramount. We therefore measured the H_2 isotherms for this set of materials over the same pressure range, 1−40 bar (Figure S7). From these data, it was possible to calculate an ideal CO_2:H_2 selectivity, defined simply as the ratio of the CO_2 and H_2 uptakes at a given pressure. This is shown for all five materials at two pressures, 17.5 and 40 bar, in Figure 3f. The "wet" H_2 sorption capacities reflected the trends found for CO_2, with substantial reductions in the H_2 uptakes for the wet HKUST-1 and zeolite 13x samples. Of the three more hydrophobic materials, polymer **1** has the lowest H_2 uptake under wet conditions. Coupled with its higher CO_2 uptake, this gives **1** the highest ideal CO_2:H_2 selectivity of 22.5 (wet) and 29.9 (dry) at a pressure of 40 bar. This selectivity is four times higher than activated carbon under dry conditions, and twice as high as HKUST-1 (Table 2). Polymer **1** was also found to have the highest "wet" and "dry" ideal CO_2/H_2 selectivities at 17.5 bar, although the advantage was less pronounced because the degree of swelling is reduced at this lower pressure. However, unlike polymer **1**, the material with the next best gas selectivity at 17.5 bar, zeolite 13x, loses most of its CO_2 capacity under "wet" conditions. Thus, polymer **1** has the most promising combination of gravimetric CO_2 capacity, moisture tolerance, acid tolerance, and CO_2:H_2 selectivity for precombustion CCS of any of the materials tested. This polymer defines the upper performance bound for these five materials in terms of combining CO_2/H_2 selectivity with gravimetric CO_2 capacity, as shown in Figure 3f.

While CO_2:N_2 selectivity is a less crucial parameter than CO_2:H_2 selectivity for precombustion CCS, air ingress or incomplete air separation can lead to some nitrogen impurities in the gas stream. We therefore also calculated ideal CO_2:N_2 selectivities for each of these materials at 40 bar and at 17.5 bar (Table 2; Figure S8). As for hydrogen, the ideal wet and dry CO_2:N_2 selectivities for polymer **1** were better than for the other adsorbents, with the exception of ZIF-8, which showed similar CO_2:N_2 selectivity at 17.5 bar (Table 2).

The large CO_2 uptake for polymer **1** relative to its modest apparent BET surface area (Table 1) suggested that swelling was occurring, and that swelling was the underlying cause of both the isotherm shape (Figure 3a) and the high CO_2:H_2 selectivity for this polymer. This was confirmed by images recorded using a high-pressure view cell (S10 − S13). Polymer **1** swells by 11.2% (±1.3%) at 298 K and 40 bar pressure in pure CO_2, while activated carbon, and the other materials tested here, show no apparent swelling under the same conditions. At higher CO_2 pressures (60 bar), polymer **1** swells even more, by up to 55 ± 3% of the original sample volume (Figure S13). Polymer **1** also swells in CO_2 at 17.5 bar by ∼4.3% (Figures S14 and S15). Approximately, the bulk polymer volume increases linearly as a function of CO_2 density (Figure S16). Next-generation gasifier technologies have been proposed to function at total system pressures up to 60 bar, and under those conditions, polymer **1** might perform even better than the rigid sorbents, all of which, with the exception of ZIF-8, saturate with CO_2 at a partial CO_2 pressure of 10−15 bar (Figure 3).

The swelling profile rationalizes the shape and magnitude of the CO_2 sorption isotherm in Figure 3a, and the fact that **1**, uniquely, does not reach saturation even at 40 bar. At elevated pressures, therefore, these hyper-cross-linked polymers adsorb CO_2 by a fundamentally different mechanism compared to rigid adsorbents. This explains the superior precombustion CCS properties for polymer **1**. The absence of this swelling mechanism in **1** at lower pressures also rationalizes the more modest sorption CO_2 capacities observed at 1 bar.[30] This swelling in CO_2 is totally and rapidly reversible over multiple pressure cycles, and hence deswelling contributes to the slope of the desorption isotherm shown in Figure 3a. The energetics (heat flow) of this swelling phenomenon might be also important in a real-life process, but this was not studied here.

Swelling enhances the working capacity of **1** with respect to nonswellable materials for pressure-swing desorption because an additional effect, deswelling, contributes to the expulsion of

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CO_2 from the material during depressurization. The polymer does not swell in either H_2 or N_2 at 298 K and 40 bar (Figure S17 and S18) and hence the uptake of these gases is low, even though the low-temperature sorption isotherm for **1** (Figure 2) does suggest some swelling in liquefied N_2 at 77 K. Even allowing for the increase in sample volume with swelling, the volumetric CO_2 capacity for polymer **1** at 40 bar CO_2 (4.61 mmol/cm^3; Table 2) is higher than the other adsorbents tested. The degree of swelling in pure CO_2 is proportional to the number of equivalents of cross-linker used: fewer cross-links allow more swelling (Figure S19). This could be used, potentially, to tune this behavior if more or less swelling was desired for practical application. With high equivalents of dimethyl ether, the swelling in CO_2 can be effectively shut off.

The selectivities quoted so far are ideal selectivities, calculated from separate, single-component isotherms for pure gases. In a mixed gas stream, it is conceptually possible that the additional surface area that is generated by CO_2-induced swelling could also contribute to H_2 or N_2 sorption, thus lowering the actual gas selectivity. Likewise, the polymer is likely to swell less in CO_2 that is diluted with H_2 or N_2. To test this, the swelling of **1** was measured in a gas stream comprising both CO_2 and N_2 (30:70 mol/mol) using a high-pressure view cell. This showed that the polymer also swells in a mixed gas system, but the degree of swelling was decreased as a result of the nitrogen diluent (Figure S20). The same measurement was carried out for a CO_2 and H_2 (40:60 mol/mol) mixed gas stream, which is more representative of a likely precombustion gas stream. Again, the polymer was observed to swell, but to a lesser extent than in pure CO_2 (Figure S21).

We also carried out experiments for polymer **1**, with the same mixed gas streams, using *in situ* ATR-FTIR spectroscopy[53] that is sensitive only to CO_2 sorption, but not to N_2 or H_2 sorption (Figure 4a; Figures S22, S23). As expected, the relative CO_2 uptake measured with 30 mol %, nitrogen-diluted CO_2, and 40 mol % hydrogen-diluted CO_2 were lower than for pure, 100 mol % CO_2. However, the reduction in CO_2 uptake was not proportional to the change in the molar gas composition. At 40 bar total pressure, the CO_2 uptake in polymer **1** for 30 mol % CO_2 was 73%, and for 40 mol % was 88%, of the CO_2 uptake measured using the same spectroscopic method for pure, 100 mol % CO_2 (Figure 4b; Figure S24). This demonstrates true chemoselectivity for polymer **1** in mixed gas streams, as required for real-life precombustion CCS.

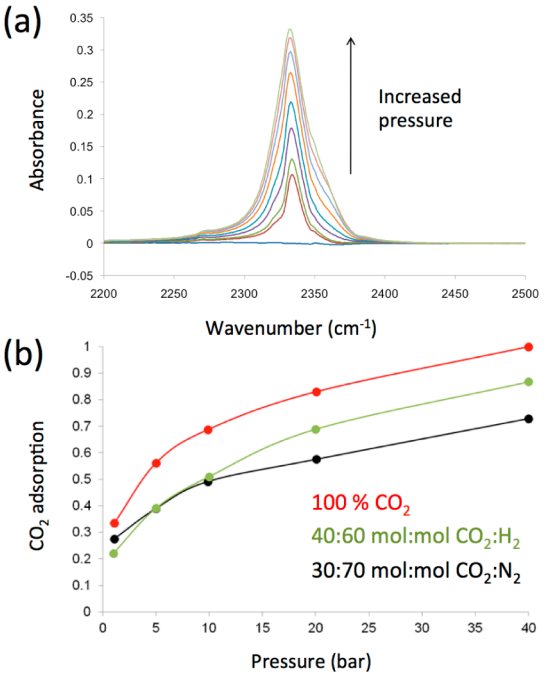

Figure 4. (a) *In situ* ATR-FTIR spectra showing the asymmetric stretching mode of physisorbed CO_2 at 2334 cm^{-1} in polymer **1** in the 0−40 bar pressure range. This was used to calculate the CO_2 uptake in **1** as a function of increasing pressure, both for pure CO_2 and for mixed CO_2/N_2 and CO_2/H_2 systems. Neither N_2 nor H_2 have any absorbance in this region. (b) Calculated CO_2 adsorption in **1** as a function of pressure for 100 mol % CO_2 (red circles), a CO_2:H_2 mix (40:60 mol/mol) (green circles), and a CO_2:N_2 mix (30:70 mol/mol) (black circles), as measured by *in situ* ATR-FTIR. The measurements are not precisely quantitative because the refractive index of the polymers is unknown. Hence, the 30 and 40 mol % CO_2 data are normalized relative to the 100 mol % CO_2 data. The reduction in CO_2 adsorption for the diluted CO_2 mixtures is not proportional to the change in the molar gas composition, suggesting chemoselectivity toward CO_2.

CONCLUSIONS

A hyper-cross-linked polymer has been shown to swell in CO_2, leading to an unusual isotherm shape and high CO_2:H_2 selectivity. A number of factors remain to be explored in terms of scale up. It would be necessary to produce pellets of this polymer with sufficient mechanical robustness for use in large scale CCS. In terms of process engineering, physical swelling of the adsorbent might present challenges, although this swelling appears to be tunable to some extent (Figure S19). The detailed kinetics of swelling/deswelling should also be investigated, although preliminary view-cell studies suggest that this is both reversible and rapid (time scale of seconds). Likewise, the energetics of swelling and deswelling, and their impact on the pressure-swing process, would also need to be explored. It would certainly be preferable to devise a synthetic route that could avoid the use of large volumes of organic solvents, perhaps by synthesizing the material in a solvent-free bulk reaction, and then stripping off unreacted aromatics.

Hence, as for all new porous adsorbents, there is potential for one or more of these cost or engineering factors to thwart scale up. Nonetheless, based on a range of relevant practical criteria, hyper-cross-linked polymers such as **1** appear to have strong potential as adsorbents for precombustion CCS. The polymers are robust, exceptionally tolerant to water and even to concentrated acid and, unlike many microporous polymers, polymer **1** can be prepared without using precious metal catalysts. While not tested here, this aromatic polymer should also have good stability toward corrosive impurities, such as hydrogen sulfide, which could cause problems with other porous frameworks.

Another potential advantage is cost. One of the monomers for **1**, benzene, is among the cheapest organic feedstocks possible for materials of this type, and the dimethyl acetal, while more expensive, is also a simple, commodity chemical. Analogous polymers might be produced from even cruder feedstocks, such as benzene−toluene−xylene (BTX) mixtures obtained directly from the catalytic reforming of naphtha. However, despite its synthetic simplicity, this acid-stable polymer strongly outperforms the other materials tested here in terms of both CO_2 capacity and ideal CO_2:H_2 selectivity. It also does this in the presence of adsorbed impurities, such as water vapor, which can totally undermine the CCS performance of more polar adsorbents, even if they are water-stable.

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The underlying swelling mechanism is a unique feature of hyper-cross-linked polymers that has not, hitherto, been appreciated in connection with precombustion CCS. Other porous polymers have been shown recently to adsorb similar amounts of CO_2, and it is possible that swelling also occurs in these cases.[54,55] This chemoselective swelling phenomenon might also prove useful in applications other than precombustion CO_2 capture, such as CO_2 storage or purification at moderate pressures.

■ ASSOCIATED CONTENT

Supporting Information

Details of the polymer synthesis, DNP sample preparation, characterization, further gas sorption data, IR data, and ^{13}C CP MAS NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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