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Impact of Water Coadsorption for Carbon Dioxide Capture in Microporous Polymer Sorbents

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Supporting Information

ABSTRACT: Alcohol-containing polymer networks synthesized by Friedel–Crafts alkylation have surface areas of up to 1015 m^2/g. Both racemic and chiral microporous binaphthol (BINOL) networks can be produced by a simple, one-step route. The BINOL networks show higher CO_2 capture capacities than their naphthol counterparts under idealized, dry conditions. In the presence of water vapor, however, these BINOL networks adsorb less CO_2 than more hydrophobic analogues, suggesting that idealized measurements may give a poor indication of performance under more realistic carbon capture conditions.

The use of microporous materials is one potential approach to the capture of greenhouse gases such as CO_2. There are several relevant classes of microporous materials, including zeolites,[1] metal–organic frameworks (MOFs),[2] porous organic molecules (POMs),[3] and microporous organic polymers (MOPs).[4–6] MOPs can exhibit high levels of permanent microporosity; in fact, the highest reported surface area for any material belongs currently to a MOP with an apparent Brunauer–Emmett–Teller (BET) surface area (S_{BET}) of more than 6400 m^2/g.[7–9] MOPs are composed entirely of organic elements and can be synthesized by many different routes, including polycondensation,[10] "click" chemistry,[11] cyclotrimerization,[12] and metal-catalyzed reactions.[13] The strong covalent bonding in MOP networks can lead to high thermal stabilities (over 500 °C), and some examples retain remarkable levels of porosity after boiling in acid.[14]

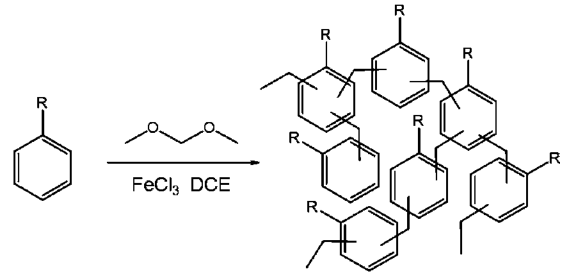
Insoluble MOP networks can physisorb gases such as hydrogen[15] and methane.[16] Linear, solution-processable MOPs have also been developed as gas separation membranes.[17] In view of their physicochemical stability and potential for "ultrahigh" surface area, MOP networks are potential candidates for postcombustion carbon capture.[18–22] For example, we showed that MOPs can have high CO_2 uptakes[18] and that isosteric heats of adsorption can be chemically tuned by changing the functional groups in these networks.[23]

A number of MOPs have also been developed as heterogeneous catalysts,[24] including networks synthesized from chiral binaphthol (BINOL) monomers.[25] For example, alkyne-functionalized BINOL monomers were polymerized by trimerization reactions using $Co_2(CO)_8$ to give MOP networks with apparent BET surface areas of up to 974 m^2/g.[25]

Recently, a versatile route to hyper-cross-linked MOPs that avoids the need for monomers with specific polymerizable functionalities was demonstrated.[26] These polymerizations involve Friedel–Crafts alkylation of aromatic monomers using a formaldehyde dimethyl acetal (FDA) cross-linker in the presence of $FeCl_3$. We subsequently demonstrated that this "knitting" approach can produce networks with BET surface areas of up to 1470 m^2/g when the tetrahedral monomer tetraphenylmethane is used.[18]

Here we demonstrate the Friedel–Crafts alkylation polymerization of a range of alcohol-containing fused aromatics using FDA in the presence of $FeCl_3$ and 1,2-dichloroethane as the solvent (Scheme 1). This simple procedure gives high-surface-area networks with CO_2 capture capacities that are among the highest reported for MOPs. Crucially, though, the best-performing networks under dry conditions do not have the highest CO_2 capacities under more realistic "wet" conditions, suggesting that such idealized laboratory measurements may not give a good indication of suitable materials for possible scale-up.

Scheme 1. Friedel–Crafts "Knitting" Polymerization of Aromatic Monomers Using Formaldehyde Dimethyl Acetal



The polymerization of hydroxyl-containing fused aromatics (Scheme 1) with 3 or 4 equiv of FDA (depending on the

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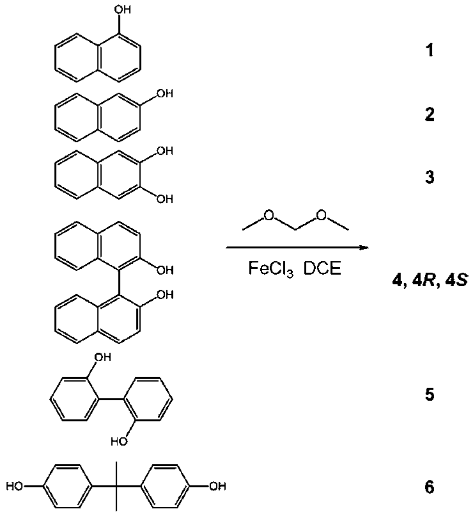
number of aromatic protons available) produced brown, insoluble powders in quantitative yields on 2 g (10 mmol) scales. These polymers are significantly less expensive in terms of monomers and reagents than conjugated microporous polymers (CMPs).[27] In some cases, yields in excess of 100% were obtained, which may be due to the trapping of iron residues within the networks or adsorbed molecules such as water and CO_2 within the micropores (many MOPs and porous organic crystals adsorb at least 5 wt % H_2O at ambient temperature and humidity). In addition to a racemic BINOL-based network, the two enantiomers of BINOL were also polymerized to give chiral networks **4*R*** and **4*S*** (Scheme 2).

Scheme 2. Synthesis of Hydroxyl-Containing MOP Networks via Friedel−Crafts Alkylation with FDA at 80 °C for 18 h



The MOP networks were initially characterized by FT-IR spectroscopy (Figures S1.1−S1.8 in the Supporting Information). The networks showed broad −OH bands due to the presence of the alcohols within the network structures. SEM images (Figures S2.1−S2.8) showed that most of the networks were composed of a fused-sphere morphology, like that reported previously for a phenol network.[26] Networks **3** and **6** had a different morphology, comprising rough particles similar to those observed in CMP networks.[27]

To characterize the porosity in the networks, nitrogen adsorption/desorption isotherms were collected for all of the MOPs at 77 K (Figure 1a). The isotherms for networks **1**−**5** can be classified as broadly type I, showing adsorption of large quantities of gas (>100 cm^3/g) at low relative pressures, indicative of adsorption into micropores. Network **4** displays a further gradual filling of mesopores at higher relative pressures. Most of the other networks adsorbed only small amounts of gas at higher relative pressures. Network **6** shows a type-IV isotherm. All of the networks except **4** showed little hysteresis upon desorption. The hysteresis in **4** is similar to that seen in other MOPs, which has been attributed to network swelling.[28] From the nitrogen adsorption isotherms, pore volumes for the networks were calculated at P/P_0 = 0.99 and 0.10, corresponding to the total pore volume (V_{tot}) and the micropore volume ($V_{0.1}$), respectively (Table 1). Network **4** showed the highest pore volumes (V_{tot} = 0.62 cm^3/g and $V_{0.1}$ = 0.40 cm^3/g), while networks **1**−**3** showed the lowest V_{tot} (0.26, 0.28, and 0.30 cm^3/g, respectively).

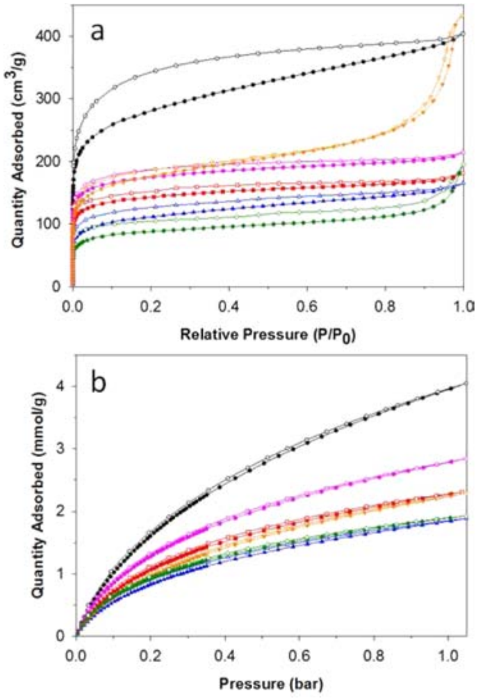


Figure 1. (a) N_2 adsorption (solid symbols)/desorption (open symbols) isotherms at 77 K and (b) CO_2 adsorption/desorption isotherms at 273 K. Networks: **1** (blue), **2** (red), **3** (green), **4** (black), **5** (pink), and **6** (orange).

Table 1. Gas Sorption Properties

network	S_{BET} (m^2/g)[a]	V_{tot} (cm^3/g)	$V_{0.1}$ (cm^3/g)	CO_2 uptake (mmol/g)[b] 273 K	CO_2 uptake (mmol/g)[b] 298 K
1	414	0.26	0.16	1.85	1.25
2	538	0.28	0.21	2.28	1.46
3	333	0.30	0.13	1.89	1.24
4	1015	0.62	0.40	3.96	2.27
4*R*	927	0.58	0.37	3.46	2.21
4*S*	981	0.55	0.39	3.50	2.21
5	657	0.33	0.26	2.79	1.80
6	650	0.67	0.25	2.24	1.41

[a] Apparent BET surface areas calculated over the relative pressure range P/P_0 = 0.015−0.1. [b] Measured at a pressure of 1 bar.

The apparent BET surface areas for the networks (Table 1) were calculated over a the relative pressure range P/P_0 = 0.015−0.1, which was found to give a positive value of *C* in the BET equation. The highest apparent BET surface area was calculated to be 1015 m^2/g for network **4**, while networks **1** and **3** showed lower surface areas of 414 and 333 m^2/g, respectively.

The apparent BET surface areas for networks **4*R*** and **4*S*** were also calculated to be 927 and 981 m^2/g, slightly lower than for the racemic network but within the batch-to-batch variation for such polymerizations. To date, there have been only a few reports of chiral microporous networks,[25,29] and these have either given low levels of porosity[29] or required a number of synthetic steps in order to functionalize the monomers.[25] This Friedel−Crafts method is therefore advantageous because it provides a much simpler route to chiral microporous networks while giving high levels of porosity (S_{BET} $\approx$ 1000 m^2/g).

The presence of alcohol groups has previously been shown to lead to improved CO_2 uptake in MOPs.[21] Hence, we collected the CO_2 isotherms at 273 K (Figure 1b) and 298 K for these networks. Networks **1** and **2** showed uptakes of 1.25 and 1.46 mmol/g, respectively, at 298 K and 1 bar. Network **4** showed a significantly higher uptake of 2.38 mmol/g CO_2 at 1 bar and 298 K, while the amount adsorbed at 273 K was measured to be 3.96 mmol/g. This is among the highest reported CO_2 uptakes for MOPs at 298 K, slightly higher than that for the alcohol-functionalized network POP1B (2.14 mmol/g) but lower than those for the benzimidazole networks BILP-1 (2.98 mmol/g),[19] and BILP-6 (3.30 mmol/g).[30]

The isosteric heats of adsorption for CO_2 (Figure S7) were calculated to be 28−31 kJ/mol at low coverage for all of the networks. These values are similar to the highest heats seen for other MOPs, such as CMPs[23] and also porous, electron-rich covalent organonitridic frameworks (PECONFs).[31] The Friedel−Crafts-alkylated MOPs retain these heats of adsorption with increasing quantities of adsorbed CO_2, which enhances the level of CO_2 capture despite the relatively modest surface area.[9]

The CO_2/N_2 selectivities (Figures S6.1−S6.4) were calculated for these MOPs using the slopes at low pressure in the Henry's law region for both CO_2 and N_2 at 298 K. Selectivities of up to 26:1 were calculated for network ***4R***. The naphthol networks **1** and **2** showed lower selectivities of 16:1 and 23:1, respectively. The selectivities of these alcohol networks are lower than those reported for the PECONF series (up to 51:1 at 298 K).[31]

Scale-up to 50 mmol was carried out for the best-performing network, **4**, to produce 18.2 g of the racemic BINOL network. An apparent BET surface area of 921 m^2/g was calculated, and the CO_2 uptake at 1 bar and 298 K was found to be 2.05 mmol/g. This material was examined further using thermogravimetric analysis (TGA) to test its sorption under more practically relevant conditions (Figure 2a).

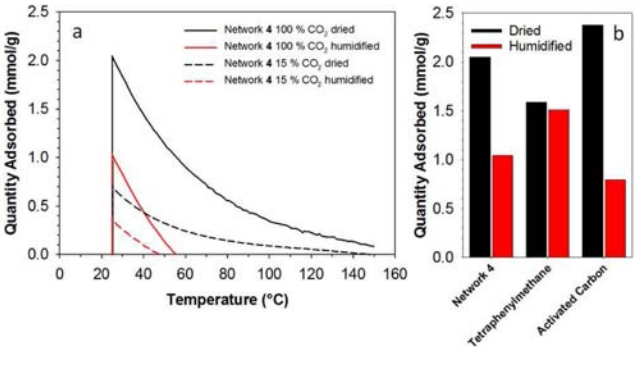


Figure 2. (a) TGA of network **4** in 100% CO_2 (black) and 15% CO_2 in nitrogen (red) after drying (solid lines) and under "wet" conditions (dashed lines). (b) "Wet" and dry uptakes of CO_2 at 298 K and 1 bar for **4**, a tetraphenylmethane analogue,[18] and activated carbon.

First, the network was pretreated to remove any physisorbed molecules in the pores in order to mimic as closely as possible the conditions used for the volumetric sorption measurements. In a stream of 100% high-purity CO_2, the uptake at 298 K was again calculated to be 2.05 mmol/g, thus demonstrating comparability with the volumetric analyses. When the temperature was increased, the CO_2 uptake dropped to 1.43 mmol/g at 313 K and just 0.36 mmol/g at 373 K. In comparison, Mg-MOF-74 has a much higher uptake under pure CO_2 (5.28 mmol/g at 313 K and 0.15 bar[32]).

Additional TGA experiments were carried out to evaluate the potential of network **4** under conditions closer to those that would be experienced in postcombustion CO_2 capture. Because the cost of drying the gas stream would be prohibitive, sorbents for postcombustion CO_2 capture would inevitably be exposed to moisture.[33] This is a potential problem, since more polar sorbents with high CO_2 affinities might be expected to have even higher affinities for water. To probe the influence of water vapor, network **4** was pretreated as above and then exposed to the atmosphere for 24 h and allowed to equilibrate with any moisture, N_2, and CO_2 (~50% relative humidity conditions). The "humidified" sample was then remeasured in 100% CO_2. The amount of CO_2 adsorbed by the humidified sample was 1.04 mmol/g, which represents a 50% drop relative to the outgassed network. Large drops in CO_2 capacity have also been reported for Mg-MOF-74,[34] one of the best-performing MOFs, at 1 bar and 298 K.[35] Mg-MOF-74 shows only 16% of its native CO_2 capacity under a relative humidity of 70% (0.85 mmol/g vs 5.36 mmol/g for the dried sample).[34] In principle, the competitive sorption of water can be suppressed by rendering the sorbent more hydrophobic. Hence, we also investigated a network prepared from tetraphenylmethane[18] using the same Friedel−Crafts "knitting" approach. Although this network has a lower uptake than network **4** under dry conditions, it loses only 5% of its capacity when measured under wet conditions (Figure 2b). This results in a net quantity of CO_2 adsorbed that is *higher* than for network **4** when measured under more practically relevant conditions. Finally, we directly compared both networks to activated carbon, which showed an even more pronounced drop in capacity under humid conditions (Figure 2b and Figure S11).

These observations are important from the perspective of designing materials for postcombustion CO_2 capture, since they show that the relative performance of sorbents can be modified and even inverted when the presence of physisorbed water is considered. The high adsorption of CO_2 afforded by the polar alcohol groups in these networks also increases the affinity of the materials for water, presumably via hydrogen bonding. TGA of these two networks under a flow of nitrogen (Figure S9) showed mass losses of 5.53% for network **4** and 3.65% for the tetraphenylmethane-based network at 120 °C. This corresponds to roughly one molecule of water per BINOL or tetraphenylmethane unit. However, it is likely that the water molecules in network **4** are preferentially bound to the alcohol sites, rendering these sites unavailable to bind to CO_2, whereas in the tetraphenylmethane-based network, there are no specific polar binding sites. Water adsorption isotherms were collected for both network **4** and an activated carbon (Figure S10), both of which show reduced CO_2 uptakes under humid conditions (Figure 2). Both materials adsorb significant quantities of water. At a relative humidity of 10%, which is close to those found in postcombustion gas streams,[33] BINOL network **4** shows ~3 times as much adsorbed water as BPL carbon, presumably as a result of its more hydrophilic nature.

Postcombustion carbon capture in coal-fired power plants produces a gas composition of up to 15% CO_2 in nitrogen. The gas uptake in network **4** was therefore also measured in a stream of 15% CO_2 in nitrogen (Figure 2a). The uptake dropped to 0.72 mmol/g under dry conditions, while under humidified conditions, the uptake was only 0.40 mmol/g.

These uptakes are greater than corresponding measurements for the tetraphenylmethane-based network (Figure S8), illustrating that sorbent polarity may still “win out” overall when dealing with diluted CO_2 streams under wet conditions.

In summary, we have shown that polymerization of alcohol-containing monomers using Friedel–Crafts alkylation produces microporous networks with surface areas of up to 1015 m^2/g. It is also possible to produce chiral networks with high surface areas without any complex monomer syntheses. The BINOL network, **4**, has one the highest CO_2 uptakes reported to date for a MOP as a result of high and persistent isosteric heats of sorption. However, despite this high CO_2 uptake under dry conditions, the performance of **4** under more realistic “wet” conditions is substantially decreased (by 50%) because these more polar MOPs also adsorb water. In contrast, more hydrophobic MOPs show a much smaller drop in CO_2 capacity of just 5%. This result, as well as physicochemical stability and cost, is an important point to consider in the future design of sorbents for CO_2 capture, not only for polymers but also for materials such as MOFs, zeolitic imidazolate frameworks (ZIFs), covalent organic frameworks (COFs), and zeolites. To date, most of the literature on MOPs has focused on idealized conditions—that is, using dry, pure CO_2—but as these new results show, materials that perform well in such tests may not always be the most promising materials under more practical conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and detailed characterization, including FTIR, SEM, elemental analysis, and gas sorption data. 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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