Article

Direct Utilization of Elemental Sulfur in the Synthesis of Microporous Polymers for Natural Gas Sweetening



Coskun and colleagues describe the direct utilization of elemental sulfur in the synthesis of ultramicroporous benzothiazole polymers without the use of any solvent or catalyst under environmentally benign conditions in quantitative yields. Remarkably, the resulting material was found to be highly porous and showed exceptional thermal stability. The authors observed sulfur loadings up to 24 wt %, which naturally increased CO_2 affinity while limiting CH_4 diffusion, thus offering a very unique porous material for the purification of CH_4 from natural gas and landfill gas streams.



Sang Hyun Je, Onur Buyukcakir, Daeok Kim, Ali Coskun

coskun@kaist.ac.kr

HIGHLIGHTS Sulfur in porous polymer synthesis

Solvent- and catalyst-free approach

Exceptional CO₂ separation

High-value application for sulfur

Je et al., Chem 1, 482–493 September 8, 2016 © 2016 Elsevier Inc. http://dx.doi.org/10.1016/j.chempr.2016.08.003





Article

Direct Utilization of Elemental Sulfur in the Synthesis of Microporous Polymers for Natural Gas Sweetening

Sang Hyun Je,¹ Onur Buyukcakir,¹ Daeok Kim,¹ and Ali Coskun^{1,2,3,*}

SUMMARY

Elemental sulfur, which is produced by a process called hydrodesulfurization mainly as a byproduct of the purification of natural gas, is one of the most abundant elements in the world. Herein, we describe solvent- and catalyst-free synthesis of ultramicroporous benzothiazole polymers (BTAPs) in the presence of elemental sulfur in quantitative yields. BTAPs were found to be highly porous and showed exceptional physiochemical stability. Moreover, in situ chemical impregnation of sulfur within the micropores increased CO₂ affinity of the sorbent while limiting diffusion of CH₄. As low-cost, scalable solid sorbents, BTAPs showed promising CO₂ separation ability and high regenerability under vacuum swing adsorption for the simulated flue gas, natural gas, and landfill gas conditions. The fact that elemental sulfur can be directly utilized in the synthesis of BTAPs means that it can be recycled back to the natural gas sweetening process for efficient CO_2/CH_4 separation, thus offering a high-value, scalable, large-scale application for elemental sulfur.

INTRODUCTION

Sulfur is one of the world's most versatile and common elements.¹ However, unlike that of other chemical commodities, production of sulfur is mostly "involuntary" in that it mainly arises from petroleum refineries and natural gas processing, thus creating a global surplus of sulfur.² Currently, elemental sulfur is mainly used in the production of sulfuric acid, which is a main commodity in the preparation of fertilizers.¹ In addition, it has been also investigated as a concrete additive.³ More recently, lithium-sulfur batteries,^{4–6} polymeric materials^{7–10} synthesized via copolymerization of sulfur, and various organic transformations have also emerged as important, high-value, yet relatively small-scale applications for elemental sulfur. Therefore, it is still highly desirable to develop synthetic strategies that could enable direct large-scale utilization of sulfur for high-value applications.

Petroleum- and natural-gas-producing regions now account for the majority of elemental sulfur production. Methane, as the primary component of natural gas, has emerged as an important energy source in recent years mainly as a result its abundance and clean nature in comparison with other fossil fuels. In order to use natural gas as a fuel, however, it should be processed by a procedure called hydrode-sulfurization or natural gas sweetening. Natural gas containing varying amounts of CO_2 and H_2S is called sour natural gas, and it is generally treated with amine solutions, followed by regeneration of these solutions at increased temperatures to release captured H_2S and CO_2 . This acid gas is then further treated by the Claus process¹¹ to produce elemental sulfur. However, high CO_2 levels significantly decrease

The Bigger Picture

Elemental sulfur, mainly produced as a byproduct of natural gas purification, is one of the most abundant elements in the world but is utilized in a relatively limited number of large-scale applications, such as gunpowder and sulfuric acid production. Herein, we report on a high-value and scalable application for this low-value commodity, that is, using elemental sulfur and organic linkers to synthesize highly porous polymers with ultrafine pores. These polymers showed high affinity toward CO₂, a known primary greenhouse gas, thus allowing us to capture and separate CO₂ from large point sources such as flue gas and natural gas streams. Elemental sulfur can therefore be directly utilized in the synthesis of porous polymers and recycled back for an efficient, sustainable CO₂ separation process. These polymeric materials offer new possibilities for directly utilizing elemental sulfur to provide sustainable solutions for challenging environmental issues.



the efficiency of the sulfur recovery process in the Claus plant. Moreover, the absorption of CO_2 from the gas mixture is more complicated with amine solutions because it involves two pathways, namely bicarbonate and carbamate formation.¹² Thus, a two-step separation in which H₂S is first removed with tertiary amine solutions and then CO_2 is separated from CH₄ with either amine solutions or porous sorbents such as microporous polymers has been proposed.^{13,14}

Microporous polymers have emerged as promising candidates for CO₂ capture and separation as a result of (1) the modularity of their synthesis, which enables structural tunability for the desired application, 15-19 (2) their high thermal and water stability, and (3) their lower heat of adsorption of CO_2 than that of amine solutions, ^{20,21} which reduces the energy penalty for the regeneration process. To date, several crystalline and amorphous microporous polymers incorporating various polar functional groups to tailor their affinity for CO₂ gas have been prepared.^{22–32} Most of these polymers, however, require either expensive rare-earth metals or stoichiometric amounts of catalysts for their synthesis, which significantly limits their scalability. In addition, post-washing steps have to be applied in order to remove unreacted monomers, by-products, and high-boiling-point solvents. Thus, the development of polymerization strategies to address these issues is critical to ensuring the low cost and scalability of the resulting microporous polymers. Here, we introduce a catalyst- and solvent-free polymerization strategy that enables direct utilization of elemental sulfur in the synthesis of highly microporous benzothiazole polymers (BTAPs) with Brunauer-Emmett-Teller (BET) surface areas up to 750 m² g⁻¹. We synthesized BTAPs in quantitative yields by mixing two-dimensional (2D) or threedimensional (3D) organic linkers incorporating p-tolyl and 4-aminophenyl moieties with elemental sulfur at 275°C under an Ar atmosphere. Subsequent heating at 400°C was applied to remove excess sulfur and to activate the pores, thus eliminating the post-washing step. BTAPs showed exceptional thermal stability up to 550°C under nitrogen and 500°C under air conditions, which are some of the highest values reported to date. Although BTAPs showed high affinity toward CO₂, we observed very low affinity toward CH₄, presumably because of its limited diffusion in the presence of a high concentration of polar functional groups within the micropores. These results prompted us to carry out breakthrough experiments to test the performance of real gas separation. BTAPs showed excellent CO₂/CH₄ separation performance and high regenerability values for the vacuum swing adsorption (VSA) process. Thus, BTAPs as low-cost, microporous, highly stable porous solid sorbents could be ideal candidates for large-scale utilization of elemental sulfur; they can then be fully recycled back to the natural gas sweeting process to separate CO₂ from CH₄ and to capture CO₂ from a flue gas mixture.

RESULTS AND DISCUSSION

Design and Synthesis of the BTAP Series

Benzothiazole is an aromatic heterocyclic compound incorporating S and N atoms in its structure. Although there are various synthetic routes for its synthesis, we followed a catalyst- and solvent-free synthetic route involving the reaction of methyland amine-substituted aromatic rings in the presence of elemental sulfur.^{33,34} We first synthesized (Figure S1) 2-phenylbenzothiazole as a model compound under these reaction conditions. In order to test this approach for the preparation of BTAPs, we synthesized (Figure 1; Supplemental Experimental Procedures and Figure S2) 2D organic linkers, 1,3,5-tris(4-tolyl)benzene (M1) and 1,3,5-tris(4-aminophenyl)benzene (A1), and 3D organic linkers, tetrakis(4-methylphenyl)methane (M2) and tetrakis(4-aminophenyl)methane (A2), and reacted them in the presence

¹Graduate School of Energy, Environment, Water, and Sustainability (EEWS)

²Department of Chemistry Korea Advanced Institute of Science and Technology (KAIST), Yuseong-Gu, Daejeon 305-701, Republic of Korea

³Lead Contact

*Correspondence: coskun@kaist.ac.kr http://dx.doi.org/10.1016/j.chempr.2016.08.003





Figure 1. Synthetic Scheme for the Preparation of BTAPs

The synthetic approach for making ultramicroporous benzothiazole polymers (BTAPs) through environmentally benign conditions without using any solvent or catalyst. BTAPs were synthesized by simply reacting aromatic methyl- (M1 or M2) and amine-substituted monomers (A1 or A2) and elemental sulfur, S₈, at 275°C in quantitative yields, followed by a heating step at 400°C for pore activation and sulfur impregnation. See also Figures S1 and S2.

of elemental sulfur. To determine the optimal amount of sulfur for the polymerization reaction, we reacted (Figure 1) M1 and A1 in the presence of varying amounts (20, 40, 100, 200 equiv with respect to amine) of elemental sulfur to synthesize BTAP-1 at 275°C for 5 hr under an Ar atmosphere and subsequently at 400°C for 5 hr to remove excess sulfur. We carried out BET surface-area analyses for BTAPs by Ar adsorption at 87 K. On the basis of these results, 100 equiv of elemental sulfur loading was identified as the optimal condition for the polymerization reaction for the preparation of BTAPs with high surface area and the control polymers (cBTAPs), which were obtained without the additional thermal treatment at 400°C.

Structural Characterization of BTAPs

To verify the formation of BTAPs, we carried out elemental analysis (EA), energydispersive spectroscopy (EDS), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), solid-state UV-visible spectroscopy (UV-Vis), cross-polarization magnetic-angle spinning (CP/MAS) ¹³C nuclear magnetic resonance (NMR), powder X-ray diffraction (PXRD), and scanning electron microscopy (SEM) analyses. We carried out EA to verify the sulfur content in BTAPs and cBTAPs, (Supplemental Experimental Procedures). BTAP-1, BTAP-2, and BTAP-3 showed 8, 11, and 10 wt % more sulfur content, respectively, than the calculated values, and the sulfur loading amounts reached up to 20.93, 24.94, and 24.27 wt %, respectively. We attribute this additional sulfur loading to the C-H insertion reaction of sulfur radicals during the synthesis of BTAPs^{35-39} given that elemental sulfur can be transformed into its radical linear chain form at high temperatures (>160°C) and is simultaneously inserted on the aromatic rings. During the polymer synthesis process at 275°C and subsequently at 400°C, inserted sulfur chains can be broken by a process called inverse vulcanization,⁶ which can lead to the formation of short sulfur chains (S_2-S_4) and thiol groups. We observed

higher sulfur contents of 29.79, 39.64, and 40.90 wt % for cBTAP-1, cBTAP-2, and cBTAP-3, respectively, as a result of the presence of elemental sulfur within the pores. The sulfur content of the BTAP particles was also verified (Figure S3) with EDS analysis, the results of which show that sulfur atoms were mostly located within the BTAP particles. To further verify the form of sulfur within the frameworks and analyze thermal stability of BTAPs and cBTAPs, we carried out TGA analysis (Figure 2A). BTAPs were found to be stable up to 550°C under N_2 and 500°C under air conditions (Figure S4), indicating that residual sulfurs were chemically impregnated in the framework. These values are comparable with, if not better than, those of the all-carbon frameworks, such as PPN-6²² (520°C in air) and PPN-5⁴⁰ (450°C in N₂). In contrast, cBTAPs showed (Figures 2B and S5) significant weight loss in the temperature range of 150°C-400°C, pointing to the fact that sulfur is mainly trapped in the pores in its elemental form. We carried out PXRD analysis (Figure 2C) to evaluate the crystallinity of BTAPs, which were found to be amorphous. We performed XPS analysis (Figures 2D-2F) to further elucidate the form of sulfur within the BTAP structures. The strong S 2p peak at 164.0 eV indicates the presence of sulfur in a thiophenyl form,⁴¹ which suggests successful formation of benzothiazole moieties in BTAPs. The peak at 165 eV was assigned to the formation of S-S bonds between polymer chains, which could originate from the dimerization thiol groups generated by the cleavage of sulfur chains at increased temperatures by a process called inverse vulcanization.⁶ We believe that the 3D interpenetrated framework structure favors the formation of disulfide bonds. We also observed (Figures 2D and S6) two additional peaks in BTAP-1 around 168.0 and 169.2 eV, which we attributed to the short sulfur chains (S_2-S_4) , which is in good agreement with the recently reported 2D sulfur-embedded covalent triazine frameworks.³⁸ Formation of benzothiazole linkages in BTAPs and cBTAPs was also evaluated (Figures S7-S9) by FT-IR analysis. We observed characteristic benzothiazole -C=N- and -C-S- stretching bands and an -N=C-S vibration band at 1,480, 1,390, and 667 cm⁻¹, respectively, in the FT-IR spectra of the model compound, cBTAPs, and BTAPs, indicating the successful formation of benzothiazole linkages.⁴² Moreover, the complete disappearance of free N–H stretching bands at 3,400, 3,300, and 3,200 cm^{-1} for the A1 and A2 monomers also supports quantitative formation of cBTAPs and BTAPs. We also carried out solid-state UV-Vis analysis (Figures S10 and S11); all BTAPs showed a characteristic benzothiazole absorption peak at 290 nm.⁴³ Moreover, BTAPs also showed broad absorption in the visible range, which could be attributed to the formation of polycyclic thiophenes during the formation of networks, as described previously by White et al.³⁹ and verified (Figures 2D-2F) by the XPS analysis. These observations point to the fact that BTAPs can also be promising candidates for lightharvesting applications. The molecular connectivity of BTAPs was elucidated (Figure S12) by solid-state CP/MAS ¹³C NMR spectroscopy. The CP/MAS ¹³C NMR spectra of BTAPs were found to be in a perfect agreement with that of the model compound. In particular, the carbon atom of the benzothiazole ring, which resonated at 179.0 ppm, provides clear evidence of the formation of benzothiazole rings. Additional aromatic carbon peaks located at 167.3, 158.1, and 152.3 ppm in the model compound were also observed in BTAPs. Moreover, the carbon peak located at 90.2 ppm in the CP/MAS ¹³C NMR spectra of BTAP-2, -3 was ascribed to the quaternary carbon core of tetraphenylmethane. In order to evaluate bulk-scale morphology of BTAPs, we have carried out (see Figure S13) SEM analysis. BTAPs formed spherical particles with an average particle size of 500, 650, and 800 nm for BTAP-1, BTAP-2, and BTAP-3, respectively. We also observed the formation of film-like superstructures in the case of BTAP-2 and BTAP-3, which could explain their relatively lower surface areas (Figure 3) than that of BTAP-1, presumably as a result of the decreased accessibility of micropores.

CellPress



Figure 2. Thermal Stability Analyses and Structural Characterization of BTAPs

(A) Thermogravimetric analysis (TGA) revealed that BTAPs are very stable up to 500° C under air without any mass loss.

(B) TGA of cBTAP (control polymer), which was obtained without thermal treatment at 400° C,

revealed that sulfur remained in its elemental form within the framework.

(C) PXRD patterns of BTAPs indicate the amorphous nature of these porous polymers.

(D-F) XPS analyses indicate the formation of thiophene and disulfide (S–S) functionalities, along with short sulfur chains in the case of BTAP-1.

See also Figures S3-S13.

Gas Sorption, Selectivity Studies, and Breakthrough Experiments

The porosity of BTAPs and cBTAPs (Figures S14 and S15) was investigated by Ar adsorption-desorption isotherms measured at 87 K (Figure 3). All Ar isotherms showed a typical type I adsorption profile. The rapid uptake observed at the low relative pressure range, below 0.03 (P/P_{o}), and the lack of desorption hysteresis suggest the permanent microporous nature of BTAPs. The BET surface areas of BTAPs were calculated from Ar adsorption isotherms over a valid relative pressure range of 0.01-0.12, which was determined from the Rouquerol plots (Figures S16 and S17). It is important to note that the loading amount of sulfur plays a crucial role in the determination of network porosity. We observed (Figure 3A) increasing surface area with increasing amounts of sulfur up to 100 equiv and observed a slight decrease in the BET surface area when sulfur was further increased up to 200 equiv. The BET surface areas of the BTAP-1 series in the presence of 20, 40, 100, and 200 equiv of elemental sulfur were 0, 545.3, 750.9, and 702.7 $m^2 g^{-1}$, respectively. Because the singlet state of sulfur can undergo a C-H insertion reaction,⁴⁴ the accessibility of the micropores could be reduced at high sulfur loading amounts. The BET surface areas of BTAP-1, BTAP-2, and BTAP-3 synthesized in the presence of 100 equiv of sulfur were found to be 750.9, 445.6, and 419.9 m² g⁻¹, respectively. We attribute the lower surface areas of BTAP-2 and BTAP-3 to the interpenetration of the framework structure because they both involve 3D organic linkers in their synthesis. We also carried out (Figure \$18) Soxhlet extraction on BTAP-1 and analyzed its gas sorption properties. Notably, we did not observe any significant change in its surface area or CO₂ uptake



Figure 3. Analysis of the Textural Properties of BTAPs

(A) The effect of the amount of elemental sulfur on the surface area of BTAP-1. For the synthesis of BTAPs, 100 equiv of sulfur was identified as the ideal condition because it showed the highest surface area.

(B) Ar uptake isotherms of BTAPs at 87 K; filled and empty symbols represent adsorption and desorption, respectively.

(C) Calculated pore-size distribution of BTAPs according to the non-local density functional theory.

See also Figures S14-S20.

capacity after Soxhlet extraction, thus proving that our synthetic strategy can eliminate the post-washing steps for sorbent activation. cBTAP-1, cBTAP-2, and cBTAP-3 showed much lower surface areas of 328.9, 147.6, and 20.7 m² g⁻¹, respectively, along with pore volumes of 0.07, 0.04, and 0.003 cm³ g⁻¹, respectively. We attribute the lower surface areas and pore volumes of cBTAPs to the elemental sulfur trapped within the pores because it blocks the accessibility of micropores to the gas molecules. The pore-size distributions of BTAPs were calculated from Ar adsorption isotherms via non-local density functional theory. BTAPs exhibited a very narrow pore-size distribution in the microporous region (Figure 3C and see also Figures S19 and S20). Specifically, a pore width below 0.7 nm is credited as ultramicroporosity,⁴⁵ and BTAP pore-width maxima centered between 0.5 and 0.7 nm clearly showed their ultramicroporous nature. The micropore volumes were obtained (Figure S21) by the t-plot method and determined to be 0.242, 0.137, and 0.131 cm³ g⁻¹ for BTAP-1, BTAP-2, and BTAP-3, respectively.

The permanent porosity of BTAPs prompted us to explore their affinity toward small gases such as CO_2 , CH_4 , and N_2 (Figure 4). Single-component isotherms were collected up to 1 bar at 273 and 298 K. BTAP-1 showed CO₂ uptake of 3.26 and 1.78 mmol g^{-1} at 273 and 298 K, respectively. BTAP-2 and BTAP-3 revealed CO₂ uptake capacities of 2.55 and 2.23 mmol g^{-1} , respectively, at 273 K and 1.58 and 1.41 mmol g^{-1} , respectively, at 298 K as a result of their lower surface areas. The isosteric heats of adsorption (Q_{st}) for CO_2 were calculated from CO_2 isotherms collected at 273, 288, and 298 K. The Q_{st} for CO₂ was found to be in the range of 31.7 and 33.8 kJ mol⁻¹ at zero coverage. These Q_{st} values could be attributed to the ultramicroporosity and polar and highly basic⁴⁶ benzothiazole moieties and sulfur chains within BTAPs. Although the relatively high Q_{st} values indicate the CO₂-philic nature of BTAPs, the completely reversible CO_2 adsorption-desorption isotherms without any hysteresis suggest (Figure S22) a physiosorptive mechanism rather than chemisorption. This is highly important for the regeneration of BTAPs by CO₂ evacuation by only lowering pressure without any heat treatment because the thermal swiping process leads to a high-energy penalty. We also investigated the sorption

CellPress



Figure 4. Pure-Gas Isotherms of BTAPs and the Isosteric Heat of Adsorption for CO₂ and CH₄ (A) Single-component CO₂, CH₄, and N₂ uptake isotherms of BTAPs at 273 K and 1 bar. The isotherms are presented without desorption for clarity.

(B) Single-component CO_2 , CH_4 , and N_2 uptake isotherms of BTAPs at 298 K and 1 bar. The isotherms are presented without desorption for clarity.

(C) The isosteric heat of adsorption for CO_2 and CH_4 , calculated with pure-gas uptake isotherms at 273, 288, and 298 K in the Clausius-Clapeyron equation.

See also Figures S21 and S22.

behavior of BTAPs for CH₄ (Figures 4A and 4B). The low-pressure pure-component isotherms were collected at 273 and 298 K. All BTAPs demonstrated relatively low uptake capacities for CH₄. BTAP-2 showed CH₄ uptake of 0.72 and 0.48 mmol g⁻¹ at 273 and 298 K, respectively. The $O_{\rm st}$ values for CH₄ were found to be in the range of 17.8–21.6 kJ mol⁻¹ (at zero coverage). Although all isotherms revealed a steep rise and complete reversibility, we observed little hysteresis in the adsorption-desorption isotherm as a result of the ultramicroporosity of BTAPs and limited diffusion of CH₄.

In order to investigate the CO₂ selectivity of BTAPs over N₂ and CH₄ for flue gas and natural gas purification, we calculated (see Figures S23–S25) CO₂/N₂ and CO₂/CH₄ selectivities according to the ideal adsorbed solution theory (IAST). To simulate flue gas conditions, the CO_2/N_2 selectivities were calculated with single-component isotherms for a CO₂/N₂ binary gas mixture in the ratio of 20:80 as a function of pressure at 273 and 298 K. All BTAPs displayed similar CO₂ selectivities in the range of 36–58 at 273 K. These comparably high selectivity values can be attributed to the CO₂-philic nature of polar benzothiazole functional moieties and the ultramicroporous nature of BTAPs. The increase in temperature led to a decrease in selectivity to 24 at 298 K because of the loss of binding affinity of gas molecules toward the sorbent. Although BTAPs did not show the highest selectivity performance for CO₂ separation from the CO_2/N_2 binary gas mixture, these selectivity values are still higher than those of most common sorbents, such as porous polymers (COF-300,⁴⁷ conjugated microporous polymers,⁴⁸ hypercrosslinked polymers,⁴⁹ porous aromatic frameworks,²² and azo-linked polymers [ALPs]⁵⁰), zeolites (4A and 13X), and activated carbons. To demonstrate the performance of BTAPs for CH₄ purification, we evaluated the selectivity of BTAPs for CO2/CH4 with the IAST method under two different CO_2/CH_4 gas feed compositions: 5:95 for natural gas sweeting and 50:50 for landfill gas purification. In particular, compared with the previously synthesized porous polymers,^{12,51–53} BTAP-3 exhibited one of the highest selectivities for gas composition ratios 12 (5:95) and 20 (50:50) at 273 K. Although IAST is an important tool for predicting mixed-gas selectivities from pure-gas isotherms, these selectivities should be verified (Table S1 and Supplemental Experimental Procedures) by breakthrough experiments. In order to elucidate the real CO₂ separation

CellPress





(A–C) Calculated IAST selectivity values of BTAPs for three different gas-mixture compositions: flue gas (CO₂/N₂, 20:80) (A), natural gas (CO₂/CH₄, 5:95) (B), and landfill gas (CO₂/CH₄, 50:50) (C) at 273 K. (D–F) Calculated IAST selectivity values of BTAPs for three different gas-mixture compositions: flue gas (CO₂/N₂, 20:80) (D), natural gas (CO₂/CH₄, 5:95) (E), and landfill gas (CO₂/CH₄, 50:50) (F) at 298 K. (G–I) Column-breakthrough measurements for CO₂-containing binary gas-mixture streams with different feed gas compositions to investigate the CO₂ capture capacity of BTAPs for large-scale applications under simulated conditions of flue gas (CO₂/N₂, 20:80) (G), natural gas (CO₂/CH₄, 50:50) (I) at 298 K. See also Figures S23–S27.

performance of BTAPs, we conducted column-breakthrough separation experiments (Figures S26 and S27). BTAPs were analyzed with three different binary gasmixture compositions, CO_2/N_2 (20:80), CO_2/CH_4 (5:95), and CO_2/CH_4 (50:50), for flue gas, natural gas, and landfill gas purification, respectively. BTAPs showed remarkable CO_2 separation performance for all the binary gas mixtures tested. For the CO_2/N_2 (20:80) gas mixture at 298 K (Figure 5G), N₂ immediately appeared in the detector, whereas CO_2 was adsorbed until the breakthrough time of 1.8 min. The total CO_2 storage capacities of BTAP-1, BTAP-2, and BTAP-3 were found to be 0.59, 0.49, and 0.36 mmol g⁻¹, respectively. To simulate natural gas (Figure 5H) and landfill gas (Figure 5I) conditions at 298 K, we also tested the performance of

BTAPs for the separation of these CO_2/CH_4 binary gas mixtures. CO_2 was quantitatively adsorbed in the column until the breakthrough time of 2.8, 1.1, and 0.7 min under landfill gas conditions for BTAP-1, BTAP-2, and BTAP-3, respectively, and CH₄ gas appeared in the stream and returned back to feed the gas stream levels just after breakthrough. BTAP-1 showed high CO_2 storage capacities of 0.17 and 1.34 mmol g⁻¹ for CO_2/CH_4 (5:95) and CO_2/CH_4 (50:50), respectively. These findings are in good agreement with the results observed for single-component isotherms and further verify BTAPs' potential for use in real gas streams.

We also evaluated BTAPs under VSA conditions according to five adsorbent evaluation criteria (Table S2): (1) N_1^{ads} , CO₂ uptake under adsorption conditions; (2) ΔN_1 , the working capacity; (3) R, regenerability; (4) α_{12}^{ads} , selectivity under adsorption conditions; and (5) S, sorbent selection parameter.⁵⁴⁻⁵⁶ To compare the performance of BTAPs with other porous sorbents that have been evaluated according to these criteria, we evaluated the BTAPs for CO_2 separation from a CO_2/N_2 (10:90) mixture under VSA conditions. BTAP-1 showed one of the highest regenerability values (88%) among all the porous sorbents analyzed. On the other hand, BTAP-2 and BTAP-3 demonstrated comparatively high CO₂ uptake (N_1^{ads}) and working capacities because of their high Q_{st} values. It is noteworthy to mention that the $Q_{\rm st}$ of sorbents plays a more important role than their surface area in obtaining a higher working capacity for flue gas separation under VSA conditions because this value is obtained from the lower-pressure (0.1 bar) CO_2 uptake. BTAPs were also evaluated according to the criteria for landfill gas (CO₂/CH₄, 50:50) separation under VSA conditions. BTAPs exhibited excellent regenerability values in the range of 78-86. In fact, BTAP-1 exhibited one of the highest regenerability values reported to date and exceeded all the porous polymers (Table S2), including ALPs, benzimidazole-linked polymers, porous organic polymers, SNU-C1-va, zeolites, and activated carbons. In addition to showing incredible regenerability, BTAPs showed remarkable sorbent-selection parameters and selectivity values along with moderate working and CO₂ uptake capacities in comparison with other porous materials. Unlike these porous materials, however, BTAPs have several other advantages, such as solvent- and catalyst-free synthesis, high thermal and water stability, elimination of post-washing steps, and high gas selectivity and regenerability.

In summary, we have presented a simple, efficient, and scalable approach for the direct utilization of elemental sulfur in the synthesis of ultramicroporous benzothiazole polymers with high surface areas without any solvent or catalyst. These polymers showed excellent breakthrough CO_2 separation performance under flue gas, natural gas, and landfill gas conditions. The fact that elemental sulfur mediates the formation of these polymers, and it can be effectively recycled back to the natural gas purification process, thus offers the potential for a high-value, large-scale application for a low-value commodity such as elemental sulfur. Although we focused primarily on gas separation, this approach can be extended to the capture and removal of toxic metals, such as mercury, and to energy-storage applications and can be utilized as a support for catalytically active nanoparticles. More importantly, it will open up new material possibilities for the utilization of elemental sulfur to provide sustainable solutions for challenging environmental issues.

EXPERIMENTAL PROCEDURES

General Synthetic Procedure for the Syntheses of BTAPs

Aryl amine (1.0 equiv), arene (1.0 equiv), and elemental sulfur (100.0 equiv) were mixed and transferred into a crucible. After the crucible was placed in a tube furnace,

the atmosphere was replaced with argon. The temperature was gradually increased to 275°C over 1 hr, and this temperature was maintained for 5 hr. Then, the temperature was increased to 400°C over 1 hr, and this temperature was maintained for an additional 5 hr. The resulting powder was cooled down to room temperature to afford BTAPs in quantitative yields.

General Synthetic Procedure for the Syntheses of cBTAPs

Aryl amines (1.0 equiv), arenes (1.0 equiv), and elemental sulfur (100.0 equiv) were mixed and transferred to crucibles. After the crucible was placed in a tube furnace, the atmosphere was replaced with argon. The temperature was gradually increased to 275°C over 1 hr, and this temperature was maintained for 5 hr. After the temperature was reduced to room temperature, the resulting solid was dried under a vacuum to yield cBTAPs.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 27 figures, and 2 tables and can be found with this article online at http://dx.doi.org/10. 1016/j.chempr.2016.08.003.

AUTHOR CONTRIBUTIONS

A.C. conceived the project and prepared the manuscript. S.-H.J. and O.B. synthesized and characterized the monomers. S.-H.J. synthesized and characterized the polymers. S.-H.J. and O.B. carried out the gas adsorption analyses and analyzed the corresponding data. D.K. carried out the breakthrough experiments. All authors commented on and contributed to the writing of the manuscript.

ACKNOWLEDGMENTS

This work was supported by the Energy Efficiency & Resources Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), which is granted financial resources from the Ministry of Trade, Industry, and Energy of the Republic of Korea (20152020104870). This work was also partially supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST; NRF-2014R1A4A1003712) and the BK21 PLUS program.

Received: June 17, 2016 Revised: August 2, 2016 Accepted: August 11, 2016 Published: September 8, 2016

REFERENCES AND NOTES

- 1. Nehb, W., and Vydra, K. (2006). Sulfur (Wiley).
- 2. Rauchfuss, T. (2011). Under sulfur's spell. Nat. Chem. 3, 648.
- Mohamed, A.-M.O., and El-Gamal, M. (2010). Sulfur Concrete for the Construction Industry: A Sustainable Development Approach (J. Ross Publishing).
- Lim, J., Pyun, J., and Char, K. (2015). Recent approaches for the direct use of elemental sulfur in the synthesis and processing of advanced materials. Angew. Chem. Int. Ed. Engl. 54, 3249–3258.
- 5. Ji, X., Lee, K.T., and Nazar, L.F. (2009). A highly ordered nanostructured carbon-sulphur

cathode for lithium-sulphur batteries. Nat. Mater. *8*, 500–506.

- Chung, W.J., Griebel, J.J., Kim, E.T., Yoon, H., Simmonds, A.G., Ji, H.J., Dirlam, P.T., Glass, R.S., Wie, J.J., Nguyen, N.A., et al. (2013). The use of elemental sulfur as an alternative feedstock for polymeric materials. Nat. Chem. 5, 518–524.
- 7. Steudel, R. (2002). The chemistry of organic polysulfanes R-Sn-R (n>2). Chem. Rev. 102, 3905–3945.
- Guntreddi, T., Vanjari, R., and Singh, K.N. (2015). Elemental sulfur mediated decarboxylative redox cyclization reaction of

o-chloronitroarenes and arylacetic acids. Org. Lett. 17, 976–978.

- 9. Nguyen, T.B., Ermolenko, L., Retailleau, P., and Al-Mourabit, A. (2014). Elemental sulfur disproportionation in the redox condensation reaction between o-halonitrobenzenes and benzylamines. Angew. Chem. Int. Ed. Engl. 53, 13808–13812.
- Xu, J.X., Cao, S.W., Brenner, T., Yang, X.F., Yu, J.G., Antonietti, M., and Shalom, M. (2015). Supramolecular chemistry in molten sulfur: preorganization effects leading to marked enhancement of carbon nitride photoelectrochemistry. Adv. Funct. Mater. 25, 6265–6271.

CellPress

- Eow, J.S. (2002). Recovery of sulfur from sour acid gas: a review of the technology. Environ. Prog. 21, 143–162.
- D'Alessandro, D.M., Smit, B., and Long, J.R. (2010). Carbon dioxide capture: prospects for new materials. Angew. Chem. Int. Ed. Engl. 49, 6058–6082.
- McKeown, N.B., and Budd, P.M. (2006). Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage. Chem. Soc. Rev. 35, 675–683.
- Carta, M., Malpass-Evans, R., Croad, M., Rogan, Y., Jansen, J.C., Bernardo, P., Bazzarelli, F., and McKeown, N.B. (2013). An efficient polymer molecular sieve for membrane gas separations. Science 339, 303–307.
- Farha, O.K., Yazaydin, A.O., Eryazici, I., Malliakas, C.D., Hauser, B.G., Kanatzidis, M.G., Nguyen, S.T., Snurr, R.Q., and Hupp, J.T. (2010). De novo synthesis of a metal-organic framework material featuring ultrahigh surface area and gas storage capacities. Nat. Chem. 2, 944–948.
- Nugent, P., Belmabkhout, Y., Burd, S.D., Cairns, A.J., Luebke, R., Forrest, K., Pham, T., Ma, S., Space, B., Wojtas, L., et al. (2013). Porous materials with optimal adsorption thermodynamics and kinetics for co2 separation. Nature 495, 80–84.
- Xu, Y., Jin, S., Xu, H., Nagai, A., and Jiang, D. (2013). Conjugated microporous polymers: design, synthesis and application. Chem. Soc. Rev. 42, 8012–8031.
- Li, J.R., Yu, J., Lu, W., Sun, L.B., Sculley, J., Balbuena, P.B., and Zhou, H.C. (2013). Porous materials with pre-designed single-molecule traps for CO₂ selective adsorption. Nat. Commun. 4, 1538.
- Thomas, A. (2010). Functional materials: from hard to soft porous frameworks. Angew. Chem. Int. Ed. Engl. 49, 8328–8344.
- Keskin, S., van Heest, T.M., and Sholl, D.S. (2010). Can metal-organic framework materials play a useful role in large-scale carbon dioxide separations? ChemSusChem 3, 879–891.
- Yang, S., Lin, X., Lewis, W., Suyetin, M., Bichoutskaia, E., Parker, J.E., Tang, C.C., Allan, D.R., Rizkallah, P.J., Hubberstey, P., et al. (2012). A partially interpenetrated metalorganic framework for selective hysteretic sorption of carbon dioxide. Nat. Mater. 11, 710–716.
- Ben, T., Ren, H., Ma, S., Cao, D., Lan, J., Jing, X., Wang, W., Xu, J., Deng, F., Simmons, J.M., et al. (2009). Targeted synthesis of a porous aromatic framework with high stability and exceptionally high surface area. Angew. Chem. Int. Ed. Engl. 48, 9457–9460.
- Dawson, R., Stockel, E., Holst, J.R., Adams, D.J., and Cooper, A.I. (2011). Microporous organic polymers for carbon dioxide capture. Energy. Environ. Sci. 4, 4239–4245.
- El-Kaderi, H.M., Hunt, J.R., Mendoza-Cortes, J.L., Cote, A.P., Taylor, R.E., O'Keeffe, M., and Yaghi, O.M. (2007). Designed synthesis of 3D covalent organic frameworks. Science 316, 268–272.

- 25. Shimomura, S., Higuchi, M., Matsuda, R., Yoneda, K., Hijikata, Y., Kubota, Y., Mita, Y., Kim, J., Takata, M., and Kitagawa, S. (2010). Selective sorption of oxygen and nitric oxide by an electron-donating flexible porous coordination polymer. Nat. Chem. 2, 633–637.
- 26. Gadipelli, S., Patel, H.A., and Guo, Z. (2015). An ultrahigh pore volume drives up the amine stability and cyclic CO₂ capacity of a solidamine@carbon sorbent. Adv. Mater. 27, 4903– 4909.
- McDonald, T.M., Mason, J.A., Kong, X., Bloch, E.D., Gygi, D., Dani, A., Crocella, V., Giordanino, F., Odoh, S.O., Drisdell, W.S., et al. (2015). Cooperative insertion of CO₂ in diamine-appended metal-organic frameworks. Nature 519, 303–308.
- 28. Zhu, X., Tian, C., Mahurin, S.M., Chai, S.H., Wang, C., Brown, S., Veith, G.M., Luo, H., Liu, H., and Dai, S. (2012). A superacid-catalyzed synthesis of porous membranes based on triazine frameworks for CO₂ separation. J. Am. Chem. Soc. 134, 10478–10484.
- Patel, H.A., Je, S.H., Park, J., Chen, D.P., Jung, Y., Yavuz, C.T., and Coskun, A. (2013). Unprecedented high-temperature CO₂ selectivity in N₂-phobic nanoporous covalent organic polymers. Nat. Commun. 4, 1357.
- Zhu, X., Tian, C., Jin, T., Wang, J., Mahurin, S.M., Mei, W., Xiong, Y., Hu, J., Feng, X., Liu, H., et al. (2014). Thiazolothiazole-linked porous organic polymers. Chem. Commun. 50, 15055– 15058.
- 31. Farha, O.K., Spokoyny, A.M., Hauser, B.G., Bae, Y.-S., Brown, S.E., Snurr, R.Q., Mirkin, C.A., and Hupp, J.T. (2009). Synthesis, properties, and gas separation studies of a robust diimidebased microporous organic polymer. Chem. Mater. 21, 3033–3035.
- 32. Islamoglu, T., Behera, S., Kahveci, Z., Tessema, T.D., Jena, P., and El-Kaderi, H.M. (2016). Enhanced carbon dioxide capture from landfill gas using bifunctionalized benzimidazolelinked polymers. ACS Appl. Mater. Inter. 8, 14648–14655.
- Zhang, L.F., Ni, Z.H., Li, D.Y., Qin, Z.H., and Wei, X.Y. (2012). Convenient synthesis of 2arylbenzothiazoles and 2-arylnaphthothiazoles. Chin. Chem. Lett. 23, 281–284.
- Nguyen, T.B., Ermolenko, L., Dean, W.A., and Al-Mourabit, A. (2012). Benzazoles from aliphatic amines and o-amino/mercaptan/ hydroxyanilines: elemental sulfur as a highly efficient and traceless oxidizing agent. Org. Lett. 14, 5948–5951.
- Hwang, T.H., Jung, D.S., Kim, J.S., Kim, B.G., and Choi, J.W. (2013). One-dimensional carbon-sulfur composite fibers for Na-S rechargeable batteries operating at room temperature. Nano Lett. 13, 4532–4538.
- 36. Fanous, J., Wegner, M., Grimminger, J., Andresen, A., and Buchmeiser, M.R. (2011). Structure-related electrochemistry of sulfurpoly(acrylonitrile) composite cathode materials for rechargeable lithium batteries. Chem. Mater. 23, 5024–5028.
- Wang, J., Yang, J., Xie, J., and Xu, N. (2002). A novel conductive polymer-sulfur composite cathode material for rechargeable lithium batteries. Adv. Mater. 14, 963–965.

- Talapaneni, S.N., Hwang, T.H., Je, S.H., Buyukcakir, O., Choi, J.W., and Coskun, A. (2016). Elemental-sulfur-mediated facile synthesis of a covalent triazine framework for high-performance lithium-sulfur batteries. Angew. Chem. Int. Ed. Engl. 55, 3106–3111.
- White, C.M., Douglas, L.J., Schmidt, C.E., and Hackett, M. (1988). Formation of polycyclic thiophenes from reaction of selected polycyclic aromatic hydrocarbons with elemental sulfur and/or pyrite under mild conditions. Energy Fuels 2, 220–223.
- 40. Yuan, D., Lu, W., Zhao, D., and Zhou, H.C. (2011). Highly stable porous polymer networks with exceptionally high gas-uptake capacities. Adv. Mater. *23*, 3723–3725.
- Kelemen, S.R., George, G.N., and Gorbaty, M.L. (1990). Direct determination and quantification of sulphur forms in heavy petroleum and coals. Fuel 69, 939–944.
- Klots, T.D., and Collier, W.B. (1995). Heteroatom derivatives of indene. Part 2. Vibrational spectra of benzothiophene and benzothiazole. Spectrochim. Acta Mol. Biomol. Spectrosc. 51, 1273–1290.
- Ellis, B., and Griffiths, P.J.F. (1965). The ultraviolet spectra of thiazole and benzthiazole. Spectrochim. Acta 21, 1881–1892.
- 44. Yin, L., Wang, J., Lin, F., Yang, J., and Nuli, Y. (2012). Polyacrylonitrile/graphene composite as a precursor to a sulfur-based cathode material for high-rate rechargeable Li-S batteries. Energy. Environ. Sci. 5, 6966–6972.
- 45. Swaidan, R., Al-Saeedi, M., Ghanem, B., Litwiller, E., and Pinnau, I. (2014). Rational design of intrinsically ultramicroporous polyimides containing bridgehead-substituted triptycene for highly selective and permeable gas separation membranes. Macromolecules 47, 5104–5114.
- 46. Notario, R., Herreros, M., Ballesteros, E., Essefar, M., Abboud, J.L.M., Sadekov, I.D., Minkin, V.I., and Elguero, J. (1994). Gas-phase basicities of 1,3-benzazoles - benzimidazole, benzoxazole, benzothiazole, benzoselenazole and benzotellurazole. J. Chem. Soc. Perkin Trans. 2, 2341–2344.
- Uribe-Romo, F.J., Hunt, J.R., Furukawa, H., Klock, C., O'Keeffe, M., and Yaghi, O.M. (2009). A crystalline imine-linked 3D porous covalent organic framework. J. Am. Chem. Soc. 131, 4570–4571.
- Jiang, J.X., Su, F., Trewin, A., Wood, C.D., Campbell, N.L., Niu, H., Dickinson, C., Ganin, A.Y., Rosseinsky, M.J., Khimyak, Y.Z., et al. (2007). Conjugated microporous poly(aryleneethynylene) networks. Angew. Chem. Int. Ed. Engl. 46, 8574–8578.
- Wood, C.D., Tan, B., Trewin, A., Niu, H.J., Bradshaw, D., Rosseinsky, M.J., Khimyak, Y.Z., Campbell, N.L., Kirk, R., Stockel, E., et al. (2007). Hydrogen storage in microporous hypercrosslinked organic polymer networks. Chem. Mater. 19, 2034–2048.
- 50. Arab, P., Rabbani, M.G., Sekizkardes, A.K., Islamoglu, T., and El-Kaderi, H.M. (2014). Copper(I)-catalyzed synthesis of nanoporous azo-linked polymers: impact of textural properties on gas storage and selective carbon dioxide capture. Chem. Mater. 26, 1385–1392.



- Neti, V.S.P.K., Wu, X.F., Peng, P., Deng, S.G., and Echegoyen, L. (2014). Synthesis of a benzothiazole nanoporous polymer for selective CO₂ adsorption. RSC Adv. 4, 9669–9672.
- 52. Duan, J., Higuchi, M., Horike, S., Foo, M.L., Rao, K.P., Inubushi, Y., Fukushima, T., and Kitagawa, S. (2013). High CO₂/CH₄ and C₂ hydrocarbons/ CH₄ selectivity in a chemically robust porous coordination polymer. Adv. Funct. Mater. 23, 3525–3530.
- 53. Zhu, Y., Long, H., and Zhang, W. (2013). Iminelinked porous polymer frameworks with high small gas (H₂, CO₂, CH₄, C₂H₂) uptake and CO₂/N₂ selectivity. Chem. Mater. 25, 1630– 1635.
- Bae, Y.S., and Snurr, R.Q. (2011). Development and evaluation of porous materials for carbon dioxide separation and capture. Angew. Chem. Int. Ed. Engl. 50, 11586–11596.
- Xie, L.H., and Suh, M.P. (2013). High CO₂capture ability of a porous organic polymer bifunctionalized with carboxy and triazole groups. Chem. Eur. J. 19, 11590–11597.
- Sekizkardes, A.K., İslamoğlu, T., Kahveci, Z., and El-Kaderi, H.M. (2014). Application of pyrene-derived benzimidazole-linked polymers to CO₂ separation under pressure and vacuum swing adsorption settings. J. Mater. Chem. A 2, 12492–12500.