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Carbon Aerogels for High Capacity Adsorption of CO2

Samuel Hackett
Missouri University of Science and Technology

Carbon Aerogels for High Capacity and Selective Adsorption of Carbon Dioxide

Samuel Hackett

Faculty Advisor: Chariklia Sotiriou-Leventis

Department: Chemistry

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Abstract:

Carbon aerogels are light, highly porous materials with high surface areas. Their applications have been demonstrated in a wide range of areas, one of which is CO_2 capturing. We have attempted to form a carbon aerogel that specializes in the selective absorption of CO_2, which we created from a previously-synthesized tetrahydroquinazoline (THQ) monomer. This monomer was polymerized to form a PTHQ aerogel, which was then oxidized, carbonized, and etched to form a carbon aerogel. This transformation process has variable steps, which affect the characteristics of the derived aerogel. This carbon aerogel exhibits porosity favorable for high capacity of carbon dioxide, and for the selective adsorption of carbon dioxide versus other common gases. High uptake of CO_2 (11.2 ± 0.9 mmol g^{-1} at 273 K, 1 bar) was observed for etched PTHQ carbon aerogels, and the selectivity towards CO_2/H_2 (407 ± 104) and CO_2/N_2 (52 ± 18) was observed.

Introduction:

Global warming has been a major issue during the last few decades. CO_2, CH_4, and NO_2, as the main greenhouse gases in the atmosphere, are the major cause of global warming and atmospheric climate change. Their concentrations in the atmosphere are still increasing due to human activities such as burning of fossil fuels.[1-5] Consequently, the atmospheric CO_2 concentration has exceeded from the pre-industrial value of 280 ppm to over 415 ppm in 2020, and that of CH_4 has also doubled.[6,7] Due to COVID-19, there is significant reduction in anthropogenic CO_2 emission[8] but, a pandemic is not a solution for reducing the concentration of greenhouse gases in atmosphere. Thus, carbon capture and sequestration (CCS) has been considered as an optional approach to reduce CO_2 concentration, which contributes to global warming. CCS refers to capturing CO_2 emission from large scale sources, such as power plants, transferring to a storage and disposing it so that it will not return to the atmosphere.[9,10]

One method of CCS is through CO_2 absorption in carbon aerogels. Carbon aerogels are microporous carbons which are chemically inert, physiochemically stable with wide pore size distribution and high surface area.[11,12] They are carbonizable polymeric aerogels synthesized via typical sol-gel chemistry and pyrolyzed to yield carbon aerogel.[13-15] Chemical transformation during pyrolytic carbonization are responsible for the rigidity and porosity of the carbon aerogel. Surface properties of the carbon aerogels can be modified by doping heteroatom in the polymeric system (e.g., oxygen and nitrogen) to increase interaction with CO_2. Thus, they are viable candidates for CCS due to their template-free synthesis, high thermal stability, tunable surface chemistry, weak physical interaction with CO_2, and high selectivity toward other gases. They are additionally stable at room temperature.

For these reasons, we are creating carbon aerogels with the maximization of absorption of CO_2 along with selective adsorption of carbon dioxide versus other common gases (notably hydrogen, methane, and nitrogen) so that an effective and efficient CCS mechanism may be found, which can then be used to reduce CO_2 emissions into the atmosphere.

Experimental:

Preparation of PTHQ Carbon Aerogels:

Scheme 1 summarizes the synthesis of PTHQ carbon aerogels. The THQ monomer was synthesized by using the process from our previous work. The synthesis of polymeric PTHQ aerogels was carried out via HCl catalyzed ring opening polymerization. Gelation was carried out at 100 °C for 3 days. The concentration of THQ monomer in DMF solution was 20% w/w. Gelation solvent was exchanged with acetone, and wet gels were dried into aerogels supercritically using liquid CO_2 in an autoclave which was further vented off as a gas. The aerogels obtained after drying were referred to as PTHQ-100. PTHQ-100 aerogels were subjected to oxidation at 240 °C under flowing oxygen for 24 h and the aerogels obtained were referred to as PTHQ-240. The ring fusion aromatization during oxidation via well-established oxygen/ superoxide/ hydroperoxyl radical chemistry is prerequisite for obtaining sturdy carbons after carbonization. The carbonization of PTHQ-240 aerogels was conducted at 800 °C under flowing high-purity argon and referred to as PTHQ-C-800. The carbonization yield was found to be 61%. Reactive etching of PTHQ-C-800 carbon aerogels was conducted at 1000 °C under flowing CO_2 and referred to as PTHQ-EC-1000 with the etching yield of 35%. Reactive etching removed more than half the mass of carbonized aerogel but it is responsible for the development of high surface area and the formation of micropores.

Scheme 1. Synthetic scheme of PTHQ carbon aerogels.
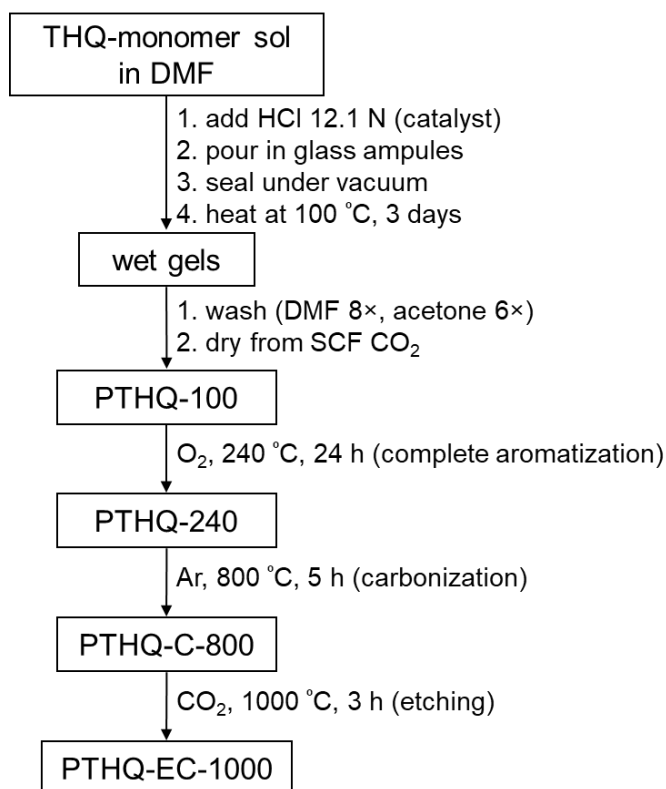
General Material Properties of PTHQ-C-800 and PTHQ-EC-1000:

In terms of materials properties, PTHQ-C-800 shrunk 45% relative to their parent aerogel PTHQ-100 while PTHQ-EC-1000 shrunk 60%. Overall, total shrinkage is 71% and 85% respectively for carbonized and etched samples relative to the molds. The bulk density, ρ_b, of PTHQ-C-800 is (0.225 ± 0.001 g cm^{-1}) which after etching reduced significantly to (0.152 ± 0.021 g cm^{-1}) for PTHQ-EC-1000. Skeletal density, ρ_s, of PTHQ-C-800 (2.197 ± 0.018 g cm^{-1}) is close to the range of expected densities for amorphous carbons (1.8-2.0 g cm^{-1}) while for PTHQ-EC-1000, ρ_s, is (1.843 ± 0.012 g cm^{-1}). The porosity of both the aerogels remained high in the range of 90-92% (Table 1).

Porous Nanostructure of PTHQ-C-800 and PTHQ-EC-1000 Aerogels:

Even though SEM images showed meso- and macroporous nature of the skeletal framework, microporosity is not visible in SEM. The CO_2 adsorption capacity of the material is largely dependent on its micropore volume along with surface functionalities. In order to study the carbons obtained from PTHQ as CO_2 adsorber, quantitative evaluation of pore structure is important. Thus, meso- and macroporosity were evaluated with medium pressure N_2-sorption porosimetry at 77 K. Microporosity was probed with low-pressure N_2-sorption and with CO_2 adsorption at 77 K and 273 K respectively.

Figure 1 shows N_2-sorption isotherms for both PTHQ-C-800 and PTHQ-EC-1000 carbon aerogels. They were Type I isotherms with narrow saturation plateau, signifying micro- and macroporosity. Both carbon and etched carbon aerogels show a rapid rise of the volume of N_2 adsorbed at $P/P_0 \ll 0.1$ indicating microporosity. PTHQ-EC-1000 show dramatic rise in volume of N_2 adsorbed after etching as compared to PTHQ-C-800. In fact, the etching process gave rise to high surface area and microporosity which was further conformed by applying density functional theory (DFT) method to CO_2 adsorption isotherm. The open porosity was evaluated by comparing total pore volumes calculated via $V_{Total} = (1/\rho_b) - (1/\rho_s)$ with V_{max} (the total volume of N_2 uptaken during N_2-sorption porosimetry as $P/P_0 \rightarrow 1$). The data for both the samples are shown in Table 1.

Table 1. Material properties of PTHQ aerogels.

Sample	Linear shrinkage [%][a,b]	Bulk density, ρ_b [g cm^{-3}][a]	Skeletal density, ρ_s [g cm^{-3}][c]	Porosity Π [% v/v][d]	Specific pore volume [cm^3 g^{-1}]		Surface area [m^2 g^{-1}]		Average pore diam. [nm] via 4 × V/σ[h]	
					V_{Total} [e]	V_{max} [f]	BET, σ	Micropore[g]	$V = V_{Total}$	$V = V_{max}$
PTHQ-100	25.1 ± 2	0.195 ± 0.008	1.575 ± 0.003	88	4.50	0.03	18	3	1136	7.92
PTHQ-240	38.8 ± 0.05	0.236 ± 0.005	1.442 ± 0.009	83	3.54	0.10	42	4	331	9.62
PTHQ-C-800	70.8 ± 1	0.225 ± 0.001	2.197 ± 0.018	90	3.98	0.22	310	257	44.7	2.81
PTHQ-EC-1000	85.60 ± 0.03	0.152 ± 0.012	1.843 ± 0.012	92	6.12	1.02	1650	700	14.6	2.39

a) Average of five samples; b) All values relative to molds; c) Single sample, average of 50 measurements; d) Via $\Pi = 100 \times (\rho_s - \rho_b)/\rho_s$; e) $V_{Total} = (1/\rho_b) - (1/\rho_s)$; f) V_{max}: single point N$_2$ adsorption at 77 K as $P/P_0 \rightarrow 1.0$; g) Via the t-plot method; h) For V_{Total} and V_{max} refer footnotes (e) and (f).
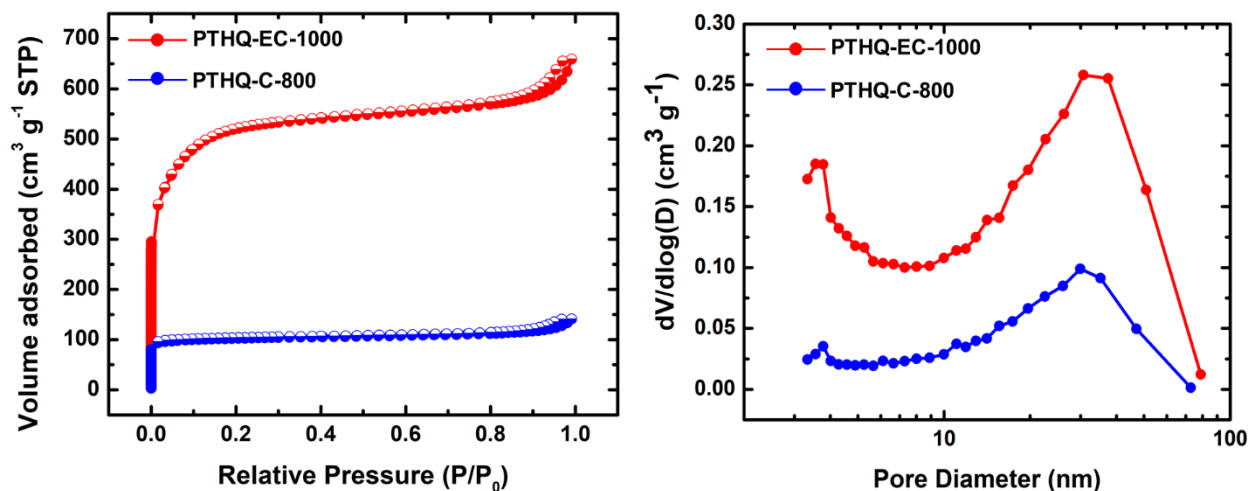
Figure 1. N$_2$-sorption isotherms for both carbon and etched carbon aerogels (left) and their corresponding pore size distribution from BJH method (right).

BET surface area, σ, was calculated from medium pressure N$_2$-sorption followed by *t*-plot analysis of micropore area with the Harkins and Jura method. The surface area of PTHQ-C-800 aerogel is $346 \pm$ m^2 g^{-1} which increases more than 4× to $1650 \pm$ m^2 g^{-1} after etching for PTHQ-EC-1000. BET surface area attributed to micropores was 76% and 42% for C and EC carbon aerogels respectively.

The quantitative evaluation of average pore size was calculated via 4 *V/σ* method. Two sets of independent data of pore volume was used from independent experiments. Thus, pore sizes were calculated by setting $V = V_{Total}$ or $V = V_{max}$. The pore sizes calculated from two methods diverge significantly from one another. In case of PTHQ carbon and etched carbon aerogels, pore size calculated from $V = V_{Total}$ are much larger for $V = V_{max}$, indicating a higher contribution from larger macropores not probed by N$_2$-sorption (>300 nm).
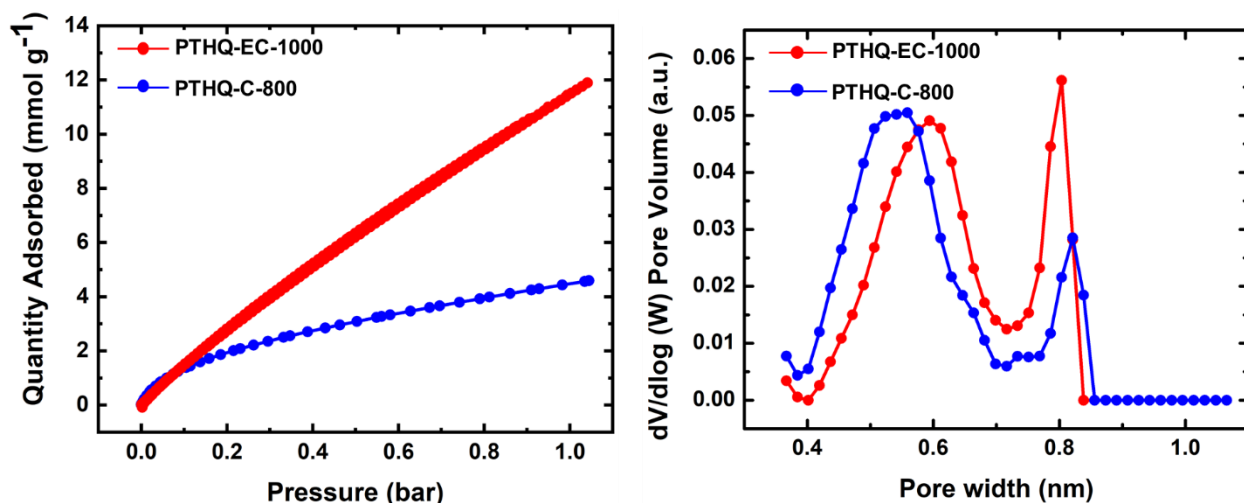
Figure 2. CO_2 adsorption isotherm of PTHQ carbon and etched carbon aerogels at 273 K (left) along with pore size distribution calculated by DFT method assuming slit pore geometry (right).

Micropore size distribution of PTHQ carbon and etched carbon aerogels are shown in Figure 2. The micropore size distribution for both the aerogels looked similar to one another. However, etching process resulted in wider cavities slightly shifting the size distribution towards larger sizes.

PTHQ carbon and etched carbon aerogels as CO_2 adsorbers:

The CO_2 uptake isotherm at 273 K and 1 bar (P/P_0 = 0.03) for PTHQ-C-800 and PTHQ-EC-1000 are shown in Figure 2. Significantly high uptake of CO_2 (11.2 ± 0.9 mmol g^{-1}) was observed for PTHQ etched carbon aerogels. That value is higher than all the porous CO_2 sorbents, microporous polymers, carbon based adsorbers and carbon nanotubes (CNTs) we are aware of in the literature except etched RF while CO_2 uptake value for PTHQ-C-800 (4.4 ± 0.3 mmol g^{-1}) is higher than most of the polymer-based adsorbents and comparable to carbon-based adsorbers.[16] Cleary, etched PTHQ carbon aerogels are more efficient than carbonized aerogels and the uptake amount is significantly large.

Selectivity towards CO_2 relative to other gases:

It is important for CO_2 adsorber to have a high uptake, but just high adsorption capacity is not enough. The material should adsorb CO_2 preferentially competing with other gases. Ideal adsorbent should have high adsorption capacity and good selectivity towards CO_2 as compared to any other gas for practical application. Thus, for pre-combustion capture, selectivity towards CH_4 and H_2 is important while for post-combustion capture, selectivity towards N_2 is desired. Adsorption isotherms of PTHQ-C-800 and PTHQ-EC-1000 for CH_4, N_2, and H_2 at 273 K are shown in Figure 3.
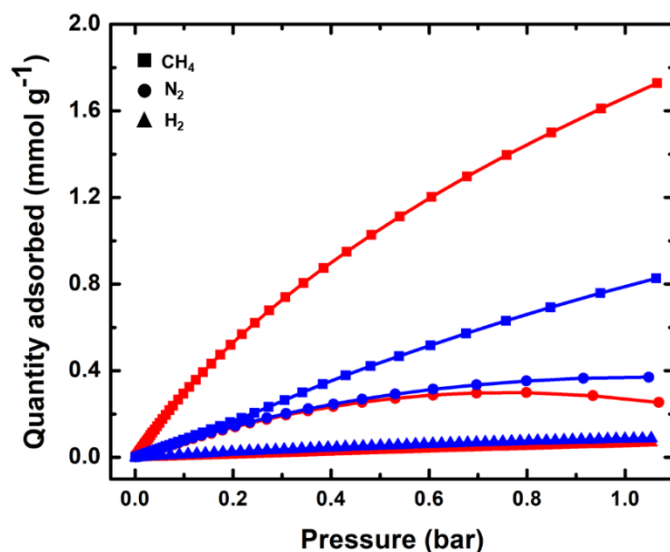
Figure 3. Adsorption isotherm at 273 K up to 1 bar of three gases. Red: PTHQ-EC-1000; Blue: PTHQ-C-800.

Selectivity of both the sample was evaluated by initial slopes of isotherms of two competing gases, assuming that at low coverage the uptake conforms Henry's law. Isotherms at 273 K were fitted with Virial type equation by which Henry's constant K_H was calculated for each gas as described in experimental section. Selectivities were calculated as a ratio of those values and are shown in bar-graph form in Figure 4. Low uptake of N_2 and H_2 at 273 K by both carbonized and etched aerogels resulted in low initial slope from the isotherms leading to high selectivities of CO_2 towards those gases.
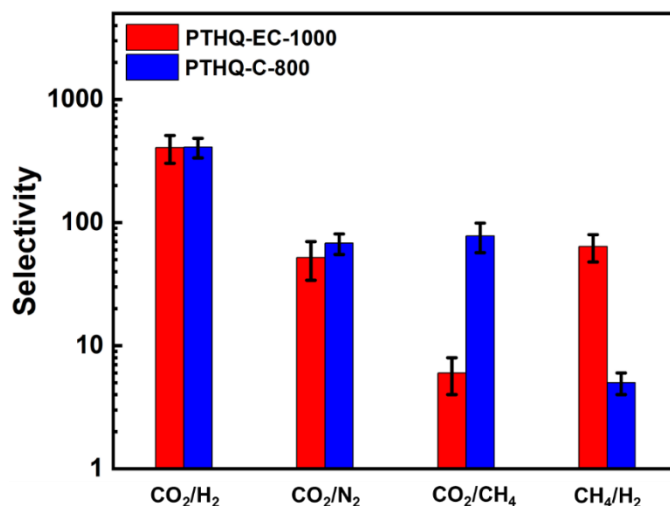

Figure 4. Relative selectivities at 273 K for gases calculated as a ratio of corresponding Henry's constant obtained by virial fitting of the isotherms.

High uptake of CH_4 was observed due to its high polarizability.[17] The adsorption capacity of PTHQ-EC-1000 is higher than PTHQ-C-800 and shows higher selectivity than that of PTHQ-C-800. The trend of high selectivities and low adsorption capacity as in case of CO_2/CH_4 for

PTHQ-C-800 has been observed before with many sorbent systems like MOFs, HPCs, BILPs and carbon aerogels obtained from PA, and PBOs. The selectivities obtained from PTHQ carbon and etched carbon aerogels are far superior to their structurally analogues carbon aerogels derived from PBOs.[18] Thus, PTHQ carbon aerogels with high CO_2 adsorption capacity and no sign of saturation up to 1 bar and high selectivity towards CO_2 makes it a potential candidate for application in CCS. The high selectivity of PTHQ-EC-1000 for CO_2 versus H_2 (up to 407:1) is attractive for pre-combustion capture of CO_2, and the high selectivity of CO_2 versus N_2 (up to 52:1) is attractive for post-combustion CO_2 capture.

Results and Future Research:

PTHQ-C-800 and PTHQ-EC-1000 carbon aerogels show the most promise for effective application in CCS due to their high CO_2 absorption and selectivity of CO_2 versus other common gases. Currently, we are working to gather more information on these carbon aerogels, along with further examining the properties of PTHQ-C-300, PTHQ-C-400, and PTHQ-C-600 aerogels formed from carbonization at different temperatures.

Nomenclature:

THQ: Tetrahydroquinazoline monomer

PTHQ: Polymerized THQ monomer; preceding letters (if any) denote a carbonized polymer ('C') or a carbon-etched polymer ('EC'); subsequent number denotes temperature in Celsius at which the polymer was formed.

Acknowledgements:

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