

THQ Synthesis, Formation of Aerogels for CO₂ Capture

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Abstract:

This project's goal is to formulate new materials for high capacity and selective CO₂-sorption. The material of focus is polymerized from the newly synthesized tetrahydroquinazoline (THQ) monomer. THQ is prepared in a four-step synthesis and polymerized through an acid catalyzed ring-opening mechanism. The PTHQ wet gels are then supercritically dried in an autoclave using CO₂. The resulting aerogels are aromatized at 240°C under O₂ then carbonized at high temperatures under inert gas to yield carbon aerogels. Lastly, the aerogels are etched at 1000°C under CO₂ flow to increase the micropore volume dramatically. The etched carbon aerogels show very high CO₂-sorption (11.2 ± 0.9 mmol/g) at atmospheric pressure (1 bar) and 273K, as well as high selectivity towards CO₂ in comparison to H₂, CH₄, and N₂ gases. Overall, the PTHQ carbon aerogels show promise as future candidates for carbon dioxide capture.

Introduction:

The accelerated increase of carbon dioxide concentration in the atmosphere over the modern era damages natural ecosystems through ocean acidification and global warming. Ocean acidification is caused by CO₂ in the atmosphere being absorbed by seawater (Kroeker et al, 2013). This, in turn, increases carbonate ion concentration in the ocean and leads to a continuing decrease in pH overall. This

acidification harms marine life and is only getting worse.¹ Global warming is also caused by CO₂ in the atmosphere. This time, the gas reflects escaping heat back towards the Earth, termed the "Greenhouse Effect." This also has devastating consequences for the entire world. As such, carbon capture is an essential tool for regulating CO₂ levels from rising further, or, ideally, decreasing the carbon footprint overall.²

Currently, carbon capture is primarily being achieved using solid sorbents. Many of these have low CO₂-sorption and these materials are primarily powders, leading to inconvenience in using them industrially. Lastly, a project aimed at sustainability should prioritize reusability of the product.

The PTHQ aerogels of our study retain their monolithic shape throughout the characterization. This upgrade in usability and transport is complemented by its reusability. PTHQ aerogels capture CO₂ in a low-energy bonding to the molecule. Due to its small energy difference, application of a vacuum allows for the sequestration of CO₂ and reuse of the same sample for further carbon capture. Lastly, the overall CO₂-sorption of PTHQ is much higher than previous materials. This is due to the absorption of CO₂ into its micropores, as well as the adsorption of CO₂ on its surface. Overall, PTHQ shows large improvements over its predecessors.

Experimental Theory and Design:

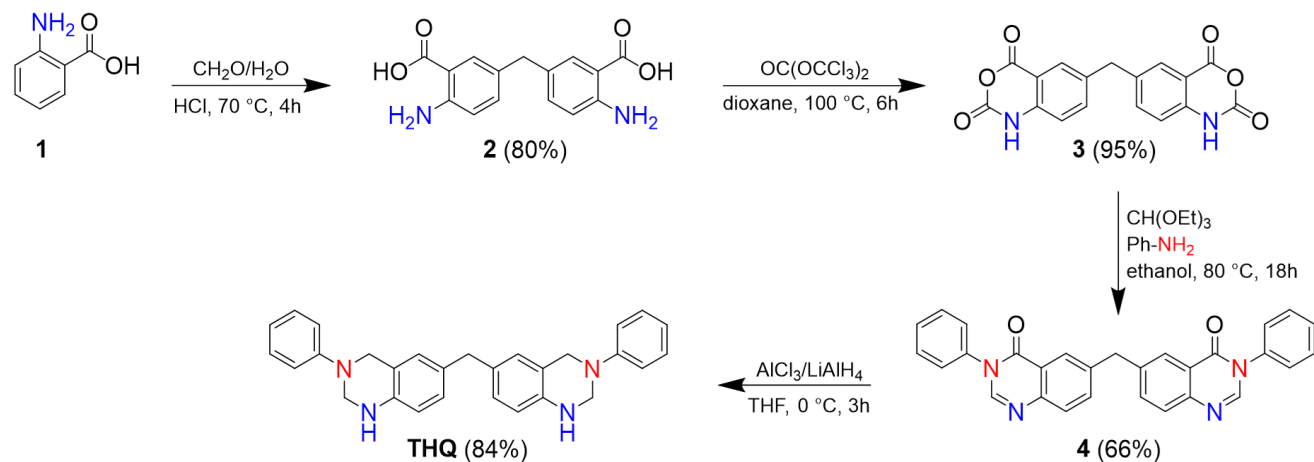


Figure 1: Synthesis of THQ monomer

Preliminary Design:

To design the desired monomer, we started with a literature analog. The THQ monomer is based on Ishida's benzoxazine (BO) monomer.³ Both molecules are shown in Figure 2. More nitrogen in the polymer increases affinity for CO₂ overall. As such, the departure from benzoxazine is the replacement of the ether group with that of an amine. With the monomer goal in mind, the experimental reactions will now be outlined. The rest of the reaction design was adapted from literature procedures.

Synthesis of THQ monomer:

The synthesis of THQ monomer is outlined above in Figure 1. The starting material is anthranilic acid. Upon addition of formaldehyde and an acid catalyst, two moles of anthranilic acid nucleophilically attack the electrophilic carbon of formaldehyde para to the amino group. This creates two units of anthranilic acid bridged by the formaldehyde. Upon removal of water, compound 2 is created. It is collected through washing with hot water and filtered out to dry.

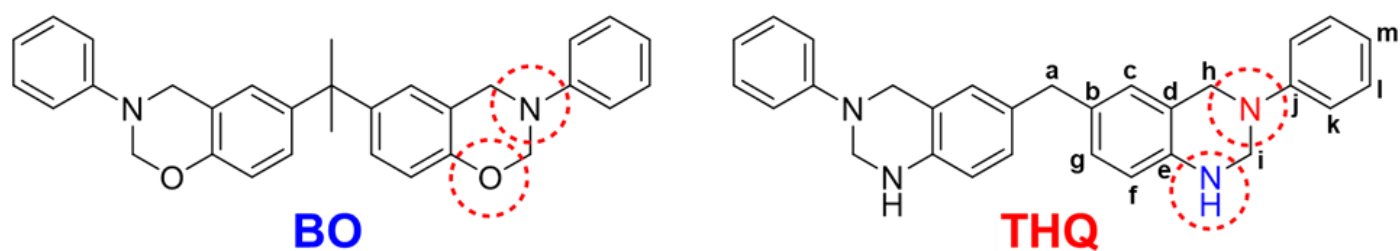


Figure 2: Ishida's Benzoxazine and THQ

Upon addition of triphosgene and dioxane solvent, the nitrogens of compound **2** nucleophilically attack the electrophilic carbon of triphosgene's carbonyl group. This reaction is stabilized through loss of HOCCl_3 in triphosgene. The carboxylic acid groups of compound **2** then attack the same carbon center as the nitrogens had. Upon another removal of HOCCl_3 , the product was washed with hot dioxane and dried in a vacuum oven; resulting in compound **3**.

Upon addition of aniline and triethyl orthoformate in ethanol solvent, aniline nucleophilically attacks the carbonyl carbon para to the amino group of compound **3**. At the same time, the amine's nitrogen attacks the central carbon of triethyl orthoformate. Upon removal of CO_2 and ethanol, the attached aniline's nitrogen attacks the same carbon center as the amine, resulting in another removal of ethanol. The last ethanol is removed, which creates the imine group ($\text{C}=\text{N}$) shown in compound **4**. Upon washing with ethanol and drying in a vacuum oven, compound **4** is isolated.

Lastly, lithium aluminum hydride and aluminum chloride in THF were reacted with compound **4**. The aluminum hydride bonds to the carbonyl's oxygen, and the OAlH_3 leaves. The carbonium is stabilized through a nitrogen double bond. This double bond leaves nitrogen with an unstable positive charge which is reduced by more aluminum hydride. The aluminum hydride also reduces the other nitrogen double bond, hydrating the nitrogen. The product is finally washed with THF and isolated through rotary evaporation in a few parts. Lastly, the THQ monomer is refluxed in hot methanol to filter out any unreacted

chemicals and washed to give the final pure product.

Preparation of Etched Carbon Aerogels:

To create the sol, THQ was dissolved in dimethylformamide and HCl was added as a catalyst. The gel monolith molds were created by elongating Pyrex™ test tubes under propane torch flame. The sol was pipetted into the molds and each tube was attached to a vacuum. The tubes were purged with argon. The liquid bath was filled with liquid nitrogen. The setup was slowly lowered into the bath, allowing the samples to freeze. Once frozen, the vacuum was turned on and allowed to purge the air. The samples were removed from liquid nitrogen and allowed to re-liquify. This cycle of freeze, vacuum, and re-liquify (freeze-drying) was repeated twice. Finally, the tubes were sealed off by application of heat, and the tubes were pulled so the glass seals into an ampoule. This is important as any exposure to air can mess with the gel creation. Gelation takes place at 100°C for 3 days in an oven.

To harvest the gels, the tubes were broken open and gels collected. They were then put into a DMF bath and gently swirled for 4 hours. The wash liquid was discarded and the DMF wash was repeated seven more times. The same process was repeated six more times with acetone, with all wash liquids being discarded at the end. This process removes unreacted compound, leaving the pure wet-gel behind.

The next step is to dry the gels. All the wet gels were transferred to the autoclave tray and covered with acetone. Just enough acetone was added to cover the gels, as more acetone means longer

dry times. The autoclave was brought to 14°C, and liquid CO₂ was added until pressure reached 50 bar. Once there, the CO₂ flow was turned off and the acetone was vented off. This process is repeated, with CO₂ being added and acetone vented until all of the acetone is gone. Once all the acetone is replaced with liquid CO₂, the temperature of the system was brought to 31°C. The pressure in the system increased to about 75 bar as the liquid CO₂ converts supercritically to gaseous CO₂. Once converted, the CO₂ was vented, leaving behind dried gels; referred to as PTHQ-100.

The next step is to aromatize the gels. The PTHQ-100 gels were put into a tube furnace and the temperature was raised to 240°C at a rate of 2.5°C/min under oxygen flow. This process continued for 24 hours to oxidatively aromatize the gels. The resulting gels are referred to as PTHQ-240.

The PTHQ-240 gels are finally carbonized through pyrolytic conversion. This is done through putting the gels into an oven under inert gas. During my time with the project, different temperatures were tested for this step: 400, 600, and 800°C. This conversion results in blackened monoliths: C-PTHQ-400, C-PTHQ-600, and C-PTHQ-800.

Lastly, the various C-PTHQ gels were put into an oven at 1000°C under inert gas. Once at temperature, the argon was switched to CO₂ for 3 hours. This process allows the CO₂ to make its way into the pores of the gels, increasing micropore size to reflect the size of CO₂ molecules. This step greatly increases the CO₂ absorption and selectivity towards CO₂ over other molecules by increasing microporosity. Once etching is complete, the temperature is slowly decreased back to room temperature

under argon again. This results in the final gels to be characterized: EC-PTHQ-1000.

Results:

The final monoliths were characterized by linear shrinkage, bulk density, skeletal density, porosity, specific pore volume, surface area (BET and micropore), pore diameter, and elemental analysis. All data is reported in the appendix.

Characterization Techniques:

Linear Shrinkage: Linear shrinkage is calculated using the physical dimensions of the gels vs their mold dimensions. The first major shrinkage occurs during aging, PTHQ-100 shrinks about 25% from the size of the tube mold used. No significant shrinkage occurs throughout washes and drying, but oxidation results in an 18% shrinkage from the mold for PTHQ-240. This shrinkage is likely due to higher crosslinking during oxidative aromatization.

Bulk Density: Bulk density is calculated as the mass of the sample over the volume of the gel. As the gels are monolithic, their volumes are calculated as cylinders. All dimensions are found using a scientific caliper.

Skeletal Density: Skeletal densities, or the densities of the crosslinked structures disregarding pores, were measured of the samples using helium pycnometry with a Micromeritics Accupyc II 1340 instrument.

Porosity: Porosity is found through N₂-sorption porosimetry at 77K using Micromeritics Tristar II 3020 after sample

degassing. It is calculated through the skeletal and bulk densities. Porosity= $100 \times (\text{skeletal} - \text{bulk}) / \text{skeletal}$. For aerogels, the higher the porosity, the better. Porosity of our ending material, EC-PTHQ-1000 is 92%, which is ideal for good absorption of CO₂.

BET Surface Area (σ): The Brunauer-Emmett-Teller method (BET) is a measure of the total pore surface area. It is found by using the Micrometrics Tristar II 3020 after degassing the samples. This measure includes micropore (<2nm diameter), mesopore (2-50nm diameter), and macropore (>50nm) combined surface area. The total surface area pre-etching of the C-PTHQ-800 aerogel is 346 m²/g. No significant change in BET surface area is observed by differing pyrolytic carbonization temperatures until below 400°C. This data shows the importance of etching to the pore surface area. Post-etching, the EC-PTHQ-1000 aerogel has a total surface area of 1650 m²/g. As such, etching gives a dramatic increase in porosity and, in turn, the CO₂-sorption of the end product.

Micropore Surface Area: The micropore surface area is calculated by t-plot analysis using the Harkins and Jura method. It shows higher micropore surface area after etching.

Pore Diameter: Pore diameter is calculated using the formula: $4xV/\sigma$. Where V is either pore volume total or pore volume max (both are reported in appendix). Total pore volume is calculated as: $V_{\text{total}} = (1/\text{bulk density}) - (1/\text{skeletal density})$. Max pore volume is the pore volume at max pressure (1 bar), found by adsorption plot analysis.

Elemental Analysis: The CHN chemical composition of each step of

synthesis was monitored using an Exeter Analytical Model CE440 elemental analyzer after calibration with acetanilide, urea, and glycine. The analysis was run three times per sample and the averages are reported in the appendix. This analysis shows the increase in carbon concentration and decrease in nitrogen concentration as the carbonization process continues. The elemental analysis shows results in line with what was expected for each step along the way.

Conclusion:

Based on the problem we set out to achieve, the final aerogels show promise as new materials for carbon capture. EC-PTHQ-1000 is a solid monolith which holds its overall shape well, increasing convenience in distribution and application. This is a big upgrade over the solid sorbents used for carbon capture today which are usually in powder form.

The amount of CO₂ able to be absorbed by EC-PTHQ-1000 is significantly higher than all previous porous sorbents. It has a high uptake of 11.2 ± 0.9 mmol/g. Compared to the unetched C-PTHQ-800 uptake of 4.4 ± 0.3 mmol/g, the etched gels show much higher promise for carbon capture.

The overall effectiveness of EC-PTHQ-1000 at selectively absorbing CO₂ over other common gases is apparent. Selectivity for CO₂ over H₂ is reported up to 407:1. This result is ideal for pre-combustion CO₂ capture. As well, selectivity for CO₂ over N₂ is up to 52:1, which also makes EC-PTHQ-1000 ideal for post-combustion CO₂ capture. These results are exciting as EC-PTHQ-1000 shows promise for all types of CO₂ sequestration.

Overall, EC-PTHQ-1000 is an ideal candidate for CO₂ capture. It is highly selective towards CO₂ over other atmospheric gasses, and it can take in more CO₂ than any other solid sorbent used. On top of that, the CO₂ uptake of EC-PTHQ-1000 is reversible. This is

ideal for reuse of the material. In conclusion, EC-PTHQ-1000 is a perfect next step in carbon capture and can hopefully be implemented to slow the climate change which is threatening the future of the world.

Acknowledgements:

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Appendix:

Table 1: Elemental Analysis of PTHQ Aerogels Pyrolyzed at Different Temperatures

Sample	% C	% H	% N	% O
PTHQ-100	76.92	6.20	11.69	5.91
PTHQ-240	66.62	2.68	10.65	18.24
PTHQ-300	67.51	3.10	10.93	18.45
PTHQ-400	70.69	2.96	11.28	15.06
PTHQ-600	79.83	2.30	10.04	7.83
C-PTHQ-800	84.29	1.01	7.13	7.57
EC-PTHQ-1000	85.72	1.76	3.62	9.20
C-PBO-800	86.00	1.41	5.24	7.35
EC-PBO-1000	88.58	1.17	2.57	7.68

Table 2: 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 $4 \times V/\sigma^i$	
					$V_{\text{Total}}^e)$	$V_{1.7-300\text{ nm}}^f)$	$V_{\text{max}}^g)$	BET, σ	Micropore ^{h)}	$V = V_{\text{Total}}$	$V = V_{\text{max}}$
PTHQ-100	25.1 ± 2	0.195 ± 0.008	1.575 ± 0.003	88	4.50	0.03	0.03	18	3	1136	7.9
PTHQ-240	38.83 ± 0.05	0.236 ± 0.005	1.442 ± 0.009	83	3.54	0.03	0.10	42	4	331	9.6
C-PTHQ-800	70.8 ± 1	0.225 ± 0.001	2.197 ± 0.018	90	3.46	0.09	0.26	346	263	40	3.0
EC-PTHQ-1000	85.60 ± 0.03	0.152 ± 0.02	1.843 ± 0.012	92	6.12	0.21	1.02	1650	700	15	2.4
PTHQ-300	28.6 ± 0.3	0.258 ± 0.005	1.369 ± 0.013	81	3.14	0.04	0.05	23	3	547	8.7
PTHQ-400	29.3 ± 0.6	0.231 ± 0.002	1.394 ± 0.007	83	3.60	0.05	0.07	37	8	385	7.6
PTHQ-600	34.4 ± 0.4	0.216 ± 0.005	1.546 ± 0.012	86	3.98	0.06	0.27	432	342	37	2.5

^aAverage of five samples; ^bAll values relative to molds; ^cSingle sample, average of 50 measurements; ^dVia $\Pi = 100 \times (\rho_s - \rho_b) / \rho_s$; ^e $V_{\text{Total}} = (1 / \rho_b) - (1 / \rho_s)$; ^fBJH-desorption cumulative pore volume; ^g V_{max} : single point N₂ adsorption at 77 K as $P/P_0 \rightarrow 1.0$ ^hVia the *t*-plot method; ⁱFor V_{Total} and V_{max} refer to footnotes e and f.