

Synthesis and Characterization of New Covalent Triazine Frameworks

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Abstract

Objective: The purpose of the synthesis was the preparation of porous materials with capacity for adsorption of gases, such as CO_2 and CH_4 , in order to contribute to the search for temporary solutions to the energy needs and pollution problems in nowadays.

Methodology: We used an experimental modification of the previously reported ionothermal methodology for the polymerization of the monomers, which were 2,3-dicyanohydroquinone, 2,3-dicyanopyrazine, and 4,5 dicyanoimidazole. We used data from Scanning Electron Microscopy (SEM), Fourier Transformed Infrared Spectroscopy (FT-IR), Raman spectroscopy; X-Ray Diffraction (XRD), Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (CP-MAS-NMR), and gas adsorption experiments for characterization of the materials.

Results: Three Covalent Triazine-Based Polymers (CTFs) were synthesized and characterized, the adsorption experiments of the polymers showed a very small pore size (230 pm), compared to the kinetic diameter of the gases: CO_2 (330 pm), N_2 (370 pm), and CH_4 (380 pm).

Conclusion: The pore sizes of the synthesized polymers were too small in order to adsorb the intended gases; nevertheless, we have improved the methodology for the ionothermal synthesis of CTFs; these materials, by modeling and selection of appropriate monomers could be prepared with improved adsorption capacity.

Keywords: Ionothermal polymerization; Polycyanide monomers; Adsorption of gases; Triazine based polymers; X-ray diffraction; Raman spectroscopy; Structure refining

Introduction

Storing methane in porous materials, with high adsorbent capacity (i.e. 263 cm³/cm³), at reliable pressure and temperature (DOE target: 298 K, 64 atm.) has been described as an intermediate alternative to circumvent the fuel needs in the near future [1]. Metal-Organic Frameworks (MOFs), Covalent Organic Frameworks (COFs) and Covalent Triazine Frameworks (CTFs) all pertain to the assayed porous materials investigated to date for several purposes, including catalysis, capacitors enhancement, drug delivery, gas separation, electrochemical catalysis, cathodic counterparts in lithium batteries, photocatalyst for water splitting, and gas storage [2-24]. Previous work in the field of Covalent Organic Frameworks (COFs) from theory and experiments have suggested that Covalent Triazine Frameworks (CTFs) are reliable candidates for preparing microporous polymers with high pore volumes, which would enable them for high gas storage capacity [5]. The most reliable molecules suggested for the synthesis of triazine-based polymers are those cyano derivatized, containing aromatic rigid systems [3,25-27]. Recent efforts in the synthesis of triazine based microporous materials include the work by Saleh and coworkers, who reported the oxidative coupling polymerization of carbazole-derivative porous polymers as a suitable methodology to prepare porous polymers possessing some advantages over the commonly used ionothermal polymerization of polyamide-containing

molecules, including milder conditions such as room temperature and less contamination problem [10]. Using FeCl₃ as a catalyst for oxidative coupling, Zhang et al. utilized bulky dendritic building blocks with high connectivity to develop carbazole-derivative porous materials with enhanced porosity; these materials were shown to possess high surface areas and gas uptake capacity among the highest reported to date at 77 K [12].

They used that class of building blocks strategically to overcome network interpenetration, which reduces the pore size [12-15]. Additional findings about the influence of heteroatoms in the particular case of triazine frameworks are those of Sekizkardes et al. [13], who synthesized porous materials by condensation of 2,4,6-tris(4formylphenyl)-1,3,5-triazine with 1,2,4,5 benzenetetramine and with 2,3,6,7,14,15-hexaaminotriptycene; these materials were shown to possess exceptionally high selectivity for CO₂ over N₂ at 298 K [17]. The presence of the imidazole N atoms was evoked to be a factor influencing the high CO₂ uptake of these materials. We here report the synthesis and characterization of three Covalent Triazine Frameworks (CTFs) based on additional heteroatom-containing precursors, namely, 2,3-dicyanohydroquinone; 2,3dicyanopyrazine; and 4.5dicyanoimidazole and using an experimental modification of the afore reported ionothermal methodology [27].

Materials and Methods

2,3-dicyanohydroquinone; 2,3-dicyanopyrazine; 4,5dicyanoimidazole, and zinc chloride (Sigma Aldrich) were used as received. The ionothermal reaction was carried out in a stainless steel mini reactor designed to overcome some inconvenience with the quartz ampule used by Katecomol et al. [27]. The procedure here used introduced the use of an inert material reactor to increase yield and safety. The reactor is made of a 316 chromium-nickel inert material. The mixture of 1:1 ratio of monomer and desiccated ZnCl₂ (13 mmol each) was placed into the stainless-steel 316 mini reactor and dried in vacuum at 100°C for 12 h. After completion of the drying cycle, the furnace automatically was switched to reach the heat treatment at 400°C for 40 hours. After automatic switching to the cooling phase, the reactor reached the room temperature, it was opened, and the solid black monolith obtained was ground thoroughly. The powder was washed with hot water (90°C), with vigorous stirring for 12 hours in a 50 mL vial. The washing solution was exchanged for 0.1 M HCl, and the powder was further washed at 90°C for another 12 hours with vigorous stirring. The solid was finally washed with water, Dimethyl sulfoxide (DMSO), and distilled acetone, and completely dried, for 12 hours in vacuum at 150°C. Powder X-ray diffraction (PXRD), Raman Spectroscopy (RS), Fourier Transform Infrared Spectroscopy (FTIR), Autosorb (AS) and Scanning Electron Microscopy (SEM) were analytical techniques used for characterization experiments. The XRD profiles were gathered with a Bruker D8 Advance system in Bragg-Brentano vertical goniometer configuration.



Figure 1: X-ray diffraction profiles of the COFs LH004, LH006, and LH008.

The 2θ angular measurements were made by applying steps of 0.01 degree. The X-ray radiation source was a ceramic Cu anode tube. Variable Soller slits were included, and a Ni filter was placed, before the detector [20-23]. Additionally, a LynxEye[®] one-dimensional detector was used to produce large counting that resulted in high-quality XRD profiles. In adsorption, the exchange of materials between the sample and the immediate surroundings was possible either opening or covering the sample using a lid with a hole. The measurements were performed with a dynamic temperature program at rates between 0.5 and 50 K/min, often at 20 K/min. A starting temperature of 25°C to 30°C was used to detect possible drying of the sample. Organic samples were pyrolyzed under nitrogen. Purge balance protection gas

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was used for all measurements. The nitrogen (Praxair, 99.99 %) adsorption was investigated at 77 K in the pressure range from 0 up to 1 bar on samples degassed at 373 K for four hours in high vacuum (10^{-6} Torr) in a Quantachrome AS-1 automatic sorption analyzer [24-27]. The Raman spectra were taken over a predetermined sample surface area in a set sequence and with a defined point interval (spatial resolution). It was acquired a visible image survey of the sample using the built-in video camera and motorized stage.

The Raman spectra were recorded in backscattering geometry using a triplemate equipped with a microscope and a charge-coupled device detection system; 514.5 nm line of an Innova argon laser was used as an excitation source. The Infrared Fourier transformed spectra were gathered using a Thermo Scientific Nicolet iS10 FTIR spectrometer; data were collected at a resolution of 4 cm⁻¹ running 100 scans per sample at room temperature under N₂ flow (Praxair, 99.99%) at a rate of 50 cc/min [28-32]. Materials for SEM analysis were "bulk" material. It was typically 1-3 cm in diameter and often requires little preparation. The material was mounted on stubs with silica that are 1 inch (2.5 cm) in diameter. Cross Polarization Magic Angle Spinning (CP-MAS) spectra of the samples were taken using an AEON 400 MHz Bruker NMR Spectrometer. We used a JEOL JSM 6360 microscope for the SEM analysis. For this study, the SEM was used in secondary electron mode at an accelerating voltage of 25 kV to image the surface of the CTFs powders. The powders adhered to the sample-holder with an adhesive tape. The average grain size was estimated from SEM images, once the surface morphology was revealed.

Results and Discussion

Polymeric materials identified as LH004; LH006; and LH008, for 2,3-dicyanohydroquinone; 4,5 dicyanoimidazole; and 2,3-dicyanopyrazine, respectively were obtained using the reactor described above. The experimental yields were excellent, ranging 95-97%, as compared to those expected from theoretical calculations. X-ray diffraction pattern of the synthesized materials: By definition, diffraction=scattering+interference; then, using the Bragg law: $2d_{hkl}sin\theta = \lambda$, d is the distance between the (hkl) lattice planes, Θ , the angle between the planes where the sample lies and λ , the X-ray wavelength; it is possible the calculation of the inter-planar distances using the wavelengths, as shown in the table (Table 1).

Sample	d1(Å)	d1(Å)
LH004	6.82	3.40
LH006	6.01	3.52
LH008	6.95	3.25

Table	1:	From	XRD	data:	Interplanar	distance	as	calculated	using
equati	on	2 (Sch	errer e	quatic	on).				

These are reasonable data since the distance of the plane No. 1 approximately duplicates the distance of plane No. 2. These results indicate that the unit cell is consistent with the tetragonal system. Furthermore, calculations made for the determination of the cell parameters "a" and "c" for the LH004, LH006, and LH008 COFs, using the interplanar distances of both angles were calculated using equation 1,

$$\frac{1}{d^2} = \left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right]^{-1/2} \tag{1}$$

given for tetragonal systems. Table below is an example of the calculation of the angles (Θ 1 and Θ 2), and the a, d, and c parameters from peaks 1 (Θ 1), and peak 2 (Θ 2) for sample LH004, and using peaks 1 and 2 shown in figure also (Table 2 and Figure 2).

λ =2dsin	d(Å)	hkl	a(Å)	c(Å)
θ_1 =12.998	6. 816	1,0,0	6.82	-
θ ₁ =26.260	3.934	0,0,1	-	3.4

Table 2: Parameters a and c calculated using peaks from X-ray diffraction pattern for sample LH004.



Figure 2: Representation of 2,3-dicyanohydroquinone, 4,5dicyanoimidazole and 2,3-dicyanopyrrzine, the building blocks corresponding to the LH004, LH006 and LH008 COFs respectively.

Approximate crystallite Size Calculation: The crystallite size is calculated with the Scherrer equation (Equation 2) [31]:

$$\delta = \frac{K}{FWHM} \left(\frac{\lambda}{\cos \theta} \right) \tag{2}$$

Where: δ , is the crystallite size, K≈0.9, is a shape factor, λ (K-alpha Cu)=1.5418 Å, is the X-rays wavelength and average FWHM= $\Delta(2\Theta)=6$ degrees=0.104 radians, which is the line width at half maximum intensity calculated from the first peak of the chromatogram. The angle θ was calculated from the average of the angle within the three samples (LH004, LH006, LH008). The average 2θ =12.71, therefore, the θ =6.35. Thereafter, we can estimate that the three CTFs have a crystallite size, $\delta \approx 1.3$ nm, a promising size for the potential use of these materials in dynamic adsorption flow reactors. Crystallography-Crystalline Structure Determination: The unit cell is the repeating pattern on the crystal lattice and is described using three vectors. Table 3 summarizes the shape of the unit cell. Scanning Electron Microscopy (SEM) Analysis revealed images based on two types of electrons: One indicates the topography and other indicating the atomic mass distribution of the sample. Those indicating the topography are the secondary electrons from the sample, which have been excited due to a collision with an incident electron from the electron beam. We can see a very fine particle size of the synthesized triazines, composed basically of particles of sizes approximately between 10-50 nm that come together to form larger assemblies (Figure 3).

We believe that mesoporous particles are responsible for the good absorptive activity of these obtained materials. These mesopores between particles contribute greatly to a large surface area. From FT-IR Spectroscopic data, All CTFs showed the Aromatic hetero rings (Triazine) peak around 1550 cm⁻¹ to 1650 cm⁻¹. For C=C aromatic, the peak can be observed between 1400 cm⁻¹to 1600 cm⁻¹. The peak belonging to nitrile, near 2220 cm⁻¹-2280 cm⁻¹ is absent on any of the spectra. It demonstrates that the monomer reacted to completion to form the polymer; in the CTF LH004 spectrum, the peak belonging to O-H at 2800 cm⁻¹-3500 cm⁻¹ is present. The given figure is an example of an FT-IR spectrum for LH004 (Figure 4). To corroborate the spectroscopy is useful, as shown in the figure for LH006 as an example (Figure 5). To further verify the disappearance of the nitrile band the CP-MAS NMR spectrum of one of the samples (LH004). From adsorption of N₂ at 77 K experiments, and using the Dubinin equation [32], the synthesized CTFs were shown to possess pores sizes of approximately 2.3 Å; this is not large enough to fit the nitrogen molecule, as N₂ kinetic diameter is about 3.70 Å.





disappearance nitrile band from the monomer to the polymer, Raman

WD10mmSS30 x27.000 0.5µm 10kV del Turabo Figure 3: Scanning electron micrograph of LH004.

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Figure 5: Raman spectrum for LH006, as in Figure 4, the circle indicates the absence of a peak due to the cyanide group.

Adsorption study

Porous materials have found application as catalysts, adsorbents, separation materials, and others; moreover, gas adsorption is a characterization method for these materials. Concretely, gas adsorption measurements are widely used for the determination of the surface area, pore size distribution and pore volume of porous materials. To be definite, the IUPAC classifies pores by their inner pore width being microporous materials those with pores sizes less than 2 nm, while the mesopore pores are those with internal width between 2, and 50 nm, consequently, the framework indicates (Figure 6) that the produced COFs are microporous materials.

Therefore, to make the analysis of the adsorption data, we used the Dubinin adsorption isotherm equation; expressed in the following form [32]:



$$n_a = N_a \exp\left(-\frac{RT}{E} \ln\left[\frac{P_0}{P}\right]\right)^n \qquad (3)$$

Which in linear form is given by:

$$y = \ln(n_a) = \ln(N_a) - \left(\frac{RT}{E}\right)^n \ln\left(\frac{P_0}{P}\right)^n = b - mx$$
 (4)

Where:
$$y = 1n(n_a)$$
, $b = 1n(N_a)$, $m = \left(\frac{RT}{E}\right)^n$ and $x = 1n\left(\frac{P_0}{P}\right)^n$ being, n_a

the magnitude of adsorption, in mole adsorbed/mass of dehydrated adsorbent, $E,\ is\ a\ parameter\ named\ the\ characteristic\ energy\ of$

adsorption, N_a , is the maximum amount adsorbed in the volume of the micropore, and, n (1<n<5), is an empirical parameter. The below figure shows the Dubinin plots corresponding to the adsorption isotherm of N₂, at 77 K, in the tested COFs (Figure 7).

The fitting process of the Dubinin equation for n=2 allowed the calculation of the best fitting parameter, i.e. N_a . E, the regression coefficient, and the standard errors along with, W, the micropore volume, calculated with the following expression: W=b N_a ; Where, b=0.0289 mole/cc, is the molar volume of liquid nitrogen at 77 K; data in Table 3, demonstrate that the pore size of all the synthesized COFs is not enough to let the nitrogen molecule get into the porosity of the produced COFs. W≈0 as seen in the table (Table 3); because the kinetic diameter of the nitrogen molecule, $d(N_2)$, is 3.64 Å, while the pore size of the framework is D=2.3 Å. More studies are in progress looking for larger pore sized polymers.



Triazine Frameworks, J Pollut 2: 114.



Figure 7: Nitrogen adsorption at 77 K data, fitted to the Dubinin isotherm equation in linear form.

Sample	Regression Equation	Na (mmol/g)	E (kJ/mol)
LH004	y=-0.0293 × -3.96, R2=0.87	0.019	0.26
LH006	y=-0.0301 × -6.12, R2=0.62	0.02	0.27
LH008	y=-0.0392 × -1.93, R2=0.99	0.145	0.28

Table 3: Results obtained with the Dubinin fitting of Nitrogen at 77 K adsorption data.

Conclusion

Citation:

We resynthesized three Covalent Triazine-Based Polymers (CTFs) using an experimental modification of the previously reported ionothermal methodology, the yields obtained were substantially improved. The selected monomers for the synthesis considered the presence of additional heteroatoms, compared to most previously reported synthesis of CTFs; theoretically, the presence of additional heteroatoms should improve the electronic interactions of the polymers with adsorbed gases, affording better gas adsorption capacity. Characterization process of the CTFs used SEM, FT-IR, and Raman Spectroscopy, X-ray diffraction, CP-MAS NMR and gas adsorption experiments. The purposes of the synthesis were to obtain porous materials with capacity for adsorption of gases, such as CO2 and CH4 in order to contribute to the search for temporary solutions to the energy needs and pollution in nowadays. The adsorption experiments of the polymers showed a very small size (230 pm), compared to the kinetic diameter of the gases, CO2 (330 pm), N2 (370 pm), and CH4 (380 pm). Nevertheless, we have improved the methodology for the ionothermal synthesis of CTFs, and by modeling and selecting other monomers, polymers of larger pore size, and therefore, with better adsorption capacity can be synthesized.

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