

remarkable pH-dependent hydrophily. The observed essential integrity of the SWNT frames renders this method appealing in order to achieve functionalized and biocompatible nanostructures, practical for both nano-composite material and biochemical applications.

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Activated carbon cryogels for low pressure methane storage

Aaron Feaver *, Guozhong Cao

University of Washington, Materials Science and Engineering, Seattle, WA 98195-2120, USA

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Enhancements in methane storage must be achieved before natural gas vehicles can be widely adopted. There are problems with highly compressed natural gas (CNG) and cryogenic liquid natural gas [1]. Using activated carbon to store adsorbed methane may enable storage perfor-

mance competitive with CNG but at pressures as low as 3.45 MPa [2] (as opposed to 15.17 MPa for CNG) thus eliminating many pressure related logistical problems. Thus far, the search for an ideal activated carbon has sought to find the best existing or naturally occurring carbonaceous precursors, and subsequent tuning by pyrolysis and/or activation parameters. The following work presents carbon cryogels as an activated carbon derived from a

* Corresponding author. Fax: +1 206 543 3100.

E-mail address: feaver@u.washington.edu (A. Feaver).

tunable precursor. This demonstration that precursor design alone can result in high methane capacity, represents a significant step in the field of methane storage on activated carbons.

Carbon cryogels were first reported by Tamon et al. [3] and are very similar to the carbon aerogels developed by Pekala from resorcinol-formaldehyde (RF) aerogels [4,5]. This work and others [6–9] demonstrated the ability to control the surface area and pores size of both carbon cryogels and aerogels by manipulating the catalyst ratio (R/C) and sol concentration (resorcinol/water—R/W ratios). Bock et al. [10] specifically demonstrated by comparing BET vs. SAXS surface area data that carbon aerogels contained a high degree of concealed micropores. This work utilizes R/C and R/W to tune carbon cryogels for methane storage and accesses the micropores for gas adsorption by activating the surface of the carbon cryogels.

The chemicals utilized in this work are resorcinol {99+%, Sigma–Aldrich, $C_6H_4(OH)_2$ }, formaldehyde solution {37% stabilized with methanol (C_2H_5OH), Fisher Scientific, COH_2 }, sodium carbonate {99.5%, Sigma–Aldrich, $NaCO_3$ }, trifluoroacetic acid {99%, Aldrich, $C_2HF_3O_2$ }, and *tert*-butyl-alcohol (*tert*-butanol) {99.8%, J.T. Baker, $(CH_3)_3COH$ }. These were used as received without further treatment. A series of carbon cryogels with initial composition listed in Table 1 were fabricated using the Pekala method [4] and modified by Tamon [3]. The molar ratio of resorcinol to formaldehyde was maintained at 1:2 for all sols, while the molar ratio of resorcinol to sodium carbonate catalyst (R/C) and the mass or molar ratio of resorcinol to water (R/W) were varied systematically. The sols were prepared by admixing resorcinol and formaldehyde in stirred DI water then adding catalyst at room temperature. The resulting sols were sealed in glass ampoules or vials and gelled at 90 °C for at least 24 h or until gelation was complete (as long as 7 days). The resulting RF hydrogels underwent solvent exchange to replace water with *tert*-butanol by rinsing three times in fresh *tert*-butanol for 24 h each time, followed by subsequent freeze drying for 3 days. The resulting RF cryogels were pyrolyzed at 1050 °C in N_2 for 4 h

then activated at 900 °C in CO_2 with a flow rate of 400 SCCM for various durations. The methane storage capacity was measured with a Sievert's apparatus [11], and porous structures were characterized by nitrogen sorption at 77 K.

Fig. 1 shows that the gravimetric storage capacity varies as a function of R/C ratio. Increasing the R/C value from 10 to 25 resulted in a significant increase in methane storage capacity (~4 times), which reaches its maximum of 13 mmol/g at R/C = 50, and then decreases as the R/C ratio increases further to 75. Total pore volume and BET surface area are also plotted in Fig. 1 showing a close correlation between all three metrics.

An R/C value either too high or too low drastically decreases the storage performance of the material. Pekala [12] has shown by SAXS analysis that in the RF system, the length scale of the solid and solvent phases in the gelling RF polymer network are equal and dependant on R/C. At low R/C ratios, the width of both the pores and solid phases are very small whereas high R/C ratio results in an open structure with large pores and correspondingly large solid

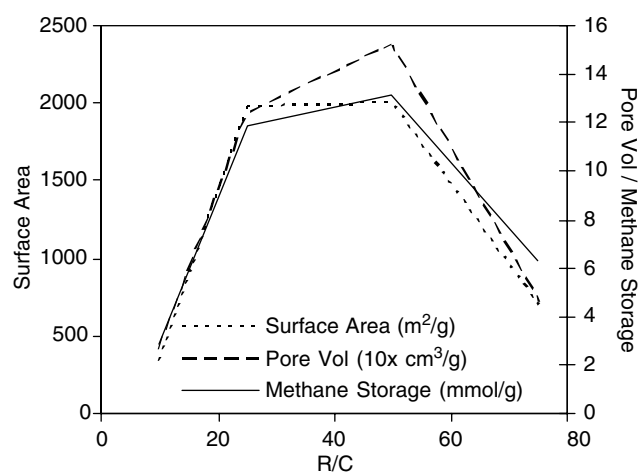


Fig. 1. Gravimetric (mmol/g) methane storage performance, surface area (m^2/g), and total pore volume ($10 \times cm^3/g$) as a function of R/C for carbon cryogels with R/W of 0.25 and activation levels from 67% to 75%, samples 1–4.

Table 1

The initial molar resorcinol to catalyst ratio (R/C), resorcinol to water ratio by weight (R/W), molar resorcinol to water ratio, level of activation (% activation—expressed in % of original material removed), gravimetric methane storage capacity in mmol/g (mmol of methane per gram of carbon), gravimetric methane storage capacity in gravimetric % (grams of methane per 100 g of carbon), and powder density

Sample number	R/C	R/W by weight	R/W molar	% Activation	mmol/g	% Gravimetric	Density
1	10	0.250	0.041	67	2.9	4.63	0.75
2	25	0.250	0.041	75	11.9	19.08	0.38
3	50	0.250	0.041	68	13.1	21.05	0.29
4	75	0.250	0.041	70	6.3	10.18	0.75
5	75	0.125	0.020	33	9.6	15.36	0.30
6	75	0.250	0.041	36	6.7	10.75	0.63
7	75	0.500	0.082	24	4.1	6.62	0.82
8	75	1.000	0.164	14	5.5	8.80	0.69
9	75	2.000	0.327	26	4.9	7.90	0.74
10	75	0.250	0.041	7	5.0	8.07	0.74
11	75	0.250	0.041	16	5.6	8.93	0.76
12	75	0.250	0.041	78	5.6	9.03	0.73

portions. Hence a high R/C carbon cryogel exhibits poor methane storage capacity because the material consists of large solid chords of carbon separated by pores of an equal size—larger than that which is beneficial. Poor performance in low R/C cryogels may be explained by drying or pyrolysis induced collapse of the very small pores that result from the highest catalyst concentrations. Related behavior such as reduced micropore volume and surface area at high or low R/C ratio has been noted in the literature [13].

Fig. 2 shows pore size distribution acquired from nitrogen sorption for the same carbon cryogels noted in Fig. 1. Activated carbon cryogels have either bimodal or trimodal pore size distribution. The mesoporous peak at 7–8 nm is typical of unactivated carbon cryogels and aerogels, whereas the microporous peak (<2 nm) has probably evolved from exposure of new micropores by CO₂ activation. The third ~3 nm peak may represent preexisting pores or could be due to activation induced widening of preexisting micropores. Although all samples contain noticeable amounts of micropores (diameter <2 nm), carbon cryogels with R/C = 25 and 50 possess appreciably higher micropore volumes than that of samples with R/C = 10 and 75.

Fig. 3 relates R/W to nominal powder density and storage performance. Increasing the powder density increases the amount of storage material per unit volume which should allow for smaller methane storage devices. However, for carbon cryogels, increased R/W improves density, but also corresponds to lower gravimetric storage capacity. Increasing the density of the final activated carbon by increasing R/W is not an efficient way to improve the volumetric performance. The reduced gravimetric performance implies that the extra precursor/unit volume (higher R/W) is reducing in terms of its storage efficiency in the final carbon material.

The reduction in gravimetric performance may be explained in terms of the rapid gelation that was observed at high R/W. As with very high catalyst concentrations, at higher ratios of reactants to water, a limit may be reached

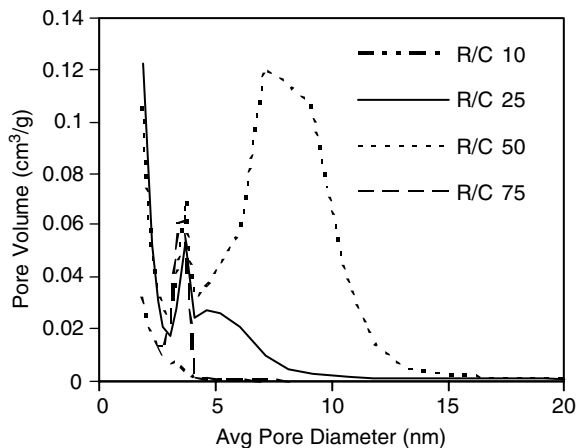


Fig. 2. Pore size distribution for carbon cryogels with R/C of: 10, 25, 50, 75 and activation levels held between 67% and 75% and R/W held at 0.25, samples 1–4.

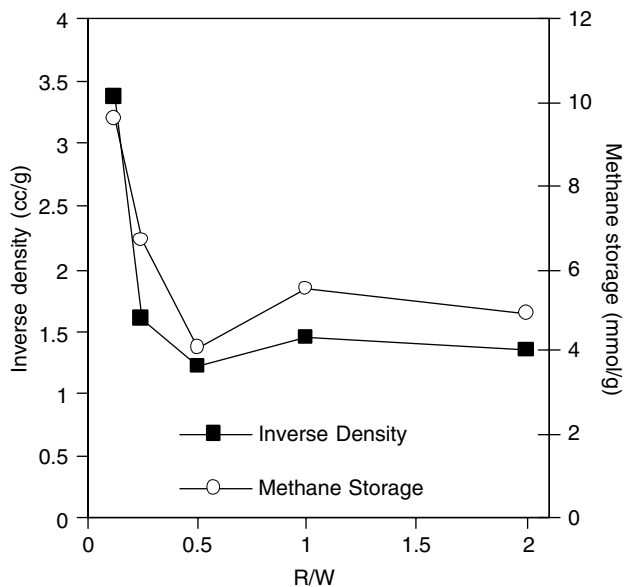


Fig. 3. Gravimetric performance (mmol/g) and inverse density (cm³/g) as a function of R/W on activated carbon cryogel samples with R/C of 75 and activation between 14% and 36%, samples 5–9.

where a significant amount of the final carbon cryogel is rendered non-porous. Once a threshold catalyst concentration is reached (this case of R/C 75 would qualify), the high R/W would enable catalyzed crosslink formation to proceed very rapidly. The close proximity of precursors to one another could result in very dense crosslinking. This may be the same effect that drove pore sizes down in the R/C experiments to the point where they might collapse and hinder the methane storage capacity of the material.

The leveling off of the density curve as R/W increases may be explained by a phenomena that was observed during gelation. In fabricating these materials, it was noted that for materials at R/C 75 and R/W higher than 0.5, the gelation process was very fast (<10 min). A gas was formed during gelation that produced large bubbles in the gel. In a network that forms this rapidly it may be assumed that the formation of large bubbles during gelation might also indicate the presence of smaller undetectable bubbles that would cause a reduction in density. It may be possible to counter this effect by reducing the amount of catalyst to slow down the reaction. Further study involving alternate R/C ratios with high R/W may lead to an ability to maintain high densities and high gravimetric methane storage capacity simultaneously.

Fig. 4 displays an increase in methane storage capacity with increased activation for R/C 75, R/W 0.25 cryogels followed by a decline at higher activation (>70%). This improvement in storage capacity can be attributed to increased micropore volume as activation induces exposure of new micropores. The trend continues up to a point where fewer new micropores are being revealed, the average pore size begins to increase and the surface area decreases. As a result, the gas storage capacity decreases sharply with further increase in activation.

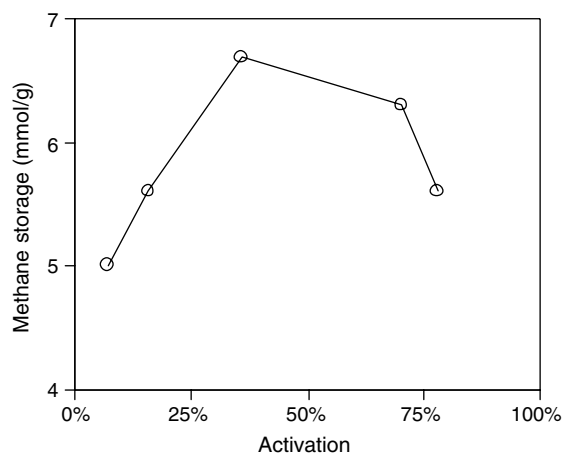


Fig. 4. Methane storage performance (mmol/g) as a function of % activation for R/C 75 R/W 0.25 carbon cryogels, samples 4, 6 and 10–12.

Tunable carbon cryogels that exhibit properties desirable for efficient methane storage have been produced and studied. Carbon cryogels with surface areas exceeding 2000 m²/g and a high volume of pores <2 nm in diameter have been produced and correspond to high methane storage capacities (13.1 mmol/g, 21 wt.%). The R/C ratio plays the most important role in determining the microporous structure and hence the methane storage capacity; R/W ratio and activation percentage also exert a noticeable influence on both micropore structure and methane storage capacity.

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Synthesis of a carbon replica of zeolite Y with large crystallite size

Arnd Garsuch^a, Olaf Klepel^{a,*}, Rita R. Sattler^a, Christine Berger^b,
Roger Gläser^b, Jens Weitkamp^b

^a Universität Leipzig, Institut für Technische Chemie, Linnestr. 3, D-04103 Leipzig, Germany

^b University of Stuttgart, Institute of Chemical Technology, D-70550 Stuttgart, Germany

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* Corresponding author. Tel.: +49 341 973 6310; fax: +49 341 973 6349.
E-mail address: klepel@chemie.uni-leipzig.de (O. Klepel).

The carbon replication of Y-zeolites is a promising method to obtain ordered microporous carbons with narrow pore size distribution and extremely large specific