H₂ Storage in Microporous Carbons from PEEK Precursors

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Large surface area (524–3275 m²/g) microporous carbons (MPCs) derived from poly(etheretherketone), or PEEK, have been synthesized and categorized for their roles as H₂ storage materials. It was found that, because of their very large surface areas (≥ 3000 m²/g), large cumulative pore volumes (~ 1.7 cm³/g), and small pore sizes (predominantly ≤ 3 nm), these materials displayed impressive H₂ sorption properties, including excess gravimetric and volumetric H₂ storage capacities of approximately 5 wt % and 35 g/L, respectively, at 77 K and 20 bar.

1. Introduction

Recent increases in gas and oil prices are reminders of the need to develop cleaner, more reliable, and renewable fuels with which to power our society. Of the alternative fuel sources under development, perhaps the most promising is H₂.¹ It is safe to handle and produce and creates only harmless byproducts upon combustion. Also, H₂ is the lightest molecule and thus has a profound advantage over other fuel sources, having approximately 3 times the gravimetric energy density of petrol.² As a result, much interest has been focused on the development of efficient and applicable H₂-powered devices. However, many issues have inhibited the use of H₂ as an energy source in mainstream applications. Presently, the biggest problem standing in the way of such widespread use of H₂ is its storage. A great deal of effort has been focused on meeting the current Department of Energy (DOE) 2015 system H₂ storage capacity target of 5.5 wt % (40 g/L). Several materials have shown varying degrees of promise for meeting these goals; among these are chemical hydrides, compression cylinders, and porous materials. However, each has its own limitations. Metal hydrides store H₂ well but run into problems with heat management and low net H₂ capacities in on-board systems. Essentially, desorbing H₂ from metal hydrides for use as fuel requires large amounts of energy and is not an efficient process. Compression cylinders and similar storage media are dangerous and difficult to transport. Furthermore, they have issues with very high pressures and low volumetric densities. Sorbents, such as metal organic frameworks (MOFs) and porous carbons, demonstrate improvements in heat management and transportation safety concerns. Unfortunately, such materials have encountered problems of low surface areas and unstable or inaccessible pores, all of which limit the amount of H₂ able to be stored in such media. However,

recent improvements in the production of porous carbons have helped to distinguish them as a leading candidate for use as H₂ storage media. Among this class of materials, it is thought that microporous carbons have the pore diameters best suited for H₂ storage.³ However, it has proven nontrivial to achieve both the large surface areas and the micropore diameters necessary for optimized H₂ storage.⁴ Many methods, such as activation⁵ and inorganic⁶ or organic⁷ templating, have been utilized to achieve such porous materials; however, no material has mastered both a large surface area and a small pore diameter. Additionally, most of the templating procedures suffer from dangerous template removal conditions⁶ and very narrow production conditions, making large-scale production impractical.^{7,8} Initial results indicated that CO₂ treatments of poly(etheretherketone), or PEEK (Figure 1), may produce a porous carbon with attributes desirable for H₂ storage, as indicated by Cansado et. al.⁹ This method is simple, robust, and does not require the removal of any template or the use of any dangerous chemicals. It relies on oxidation of the PEEK structure to create well-defined pores. However, more work needed to be done to appropriately characterize this method and explore its versatility. Most significantly, the H₂ storage capabilities of its porous carbon products needed to be investigated.

Here, we describe two methods of producing large surface area porous carbons derived from Cansado's method and explore the H₂ storage capabilities of the resulting products. Using these scalable production methods, we were able to produce samples with large surface areas (>3000 m²/g), small pore diameter distributions (predominantly ≤ 3 nm), and large cumulative pore volumes (~ 1.7 cm³/g). Thus, these methods can be used to engineer a porous carbon with the optimal balance of surface area and microporosity for the storage of H₂. If these materials are ultimately successful, the methods outlined herein will aid in the production of tailored porous carbon materials for H₂ storage purposes and ultimately aid in the replacement of conventional nonrenewable fuel sources with H₂.

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Figure 1. PEEK in an alumina combustion boat (A) before and (B) after thermal treatment under CO₂. It should be noted that the products after thermal treatment were similar in appearance when treated with steam. (C) The chemical structure of one subunit of PEEK. (D) After thermal treatment, the porous products were analyzed using TEM. Here, PEEK-CO₂-9-80 is used to display a typical TEM image in which small diameter pores are evident. The scale bar in this image is 10 nm.

2. Experimental Section

Detailed experimental procedures can be found in the Supporting Information. Briefly, PEEK was loaded into a 1 in. quartz tube furnace and flushed with Ar. The temperature was raised from room temperature to the reaction temperature (900 °C) at a rate of 10 °C/min and allowed to carbonize at 900 °C for 30 min. After carbonization, the gas was changed to either CO₂ or steam and allowed to react for a predetermined amount of time. After completion, the gas was changed back to Ar and the system was allowed to cool back to room temperature. Excess H₂ adsorption isotherms were measured at NREL and Caltech at 77 K. Density functional theory was used to calculate cumulative pore volumes and diameter distributions.

3. Results and Discussion

After thermally treating PEEK under different environments, a blackened and highly porous powder product was formed. TEM and N₂ sorption isotherm analysis shows that these porous products have a relatively narrow distribution of small pores at a low percent burn-off (BO), while higher BO products have a slightly broader diameter range. Figure 1D displays one such example of a high BO product (PEEK-CO₂-9-80). It is evident that there is a significant portion of pores with diameters at and around 1 nm; however, it is also apparent that larger diameter pores are present throughout the structure (diameter ≥ 4 nm). It is generally thought that steam provides a gentler oxidation environment than CO₂. Thus, in this study, steam was used to limit pore diameter widening and, therefore, investigate the relative importance of the diameter distribution and pore volume to H₂ storage in microporous carbons. Accordingly, characterization of the pore diameter distributions as well as pore volume distributions was integral. Perhaps most importantly, an understanding of the evolutions of each was paramount to appropriately categorize these methods. Such an understanding is

necessary for the successful application of these methods and their tailored porous carbon products, especially to H₂ storage aims.

One of the most important factors for H₂ storage by porous materials is surface area. In general, at 77 K, graphitic slit pore materials typically have excess adsorption capacities of ~1 wt % for every 500 m²/g of surface area.¹⁰ As such, achieving a large surface area is extremely important. Here, we have demonstrated that both CO₂ and steam (ST) can be utilized to produce porous carbons with very large surface areas, in both cases, reaching ~3000 m²/g or more. It is critical to note that the samples consist almost entirely of pure carbon, as determined by X-ray photoelectron spectrometry (XPS). XPS data indicated that the surface chemistries of the pores were largely graphitic. This was true even after extended treatment and thus at large surface areas (Figure S1, Supporting Information). Therefore, direct comparison of these CO₂- and steam-derived products can be utilized to compare not only these products but also the importance of pore diameter and volume to H₂ sorption.

Figure 2 shows the evolution of the Brunauer–Emmett–Teller (BET) surface area with BO and demonstrates the large surface area (ca. ≥ 3000 m²/g) achievable using both methods. It is evident that the surface area increases with increasing BO in both cases. This is in line with the proposed pore formation mechanism in which pores are oxidatively etched from the carbonized PEEK structure. However, CO₂ produces a much more regular and linear increase in BET surface area with BO. Steam-produced samples appear to suffer from a significant amount of pore collapse. This could be due to differences in the mechanism of oxidation by CO₂ as compared with steam. If steam did conserve the pore diameter distribution better and increase the pore volume with surface area more than CO₂, this could cause structural collapse at certain periods during the extended thermal treatment process. Essentially, the etching

Figure 2. Plot showing the evolution of the Brunauer–Emmett–Teller (BET) surface area with burn-off. Large surface area (ca. ≥ 3000 m²/g) products were achieved using both CO₂ and steam thermal treatments.

would eventually cause the pore walls that separate individual pores to break down. This fact is supported by NMR investigations of steam products. These investigations show that the peaks of H₂ in micro/mesopores become indistinguishable from those of H₂ in large voids at very high BO. This indicates that most of the pores are connected to each other and to the voids, allowing free exchange of H₂ (Figure S2, Supporting Information). Thus, steam-derived samples reaching 3000 m²/g are not ideal for H₂ storage and, therefore, were not analyzed beyond surface area measurements in this work. Therefore, CO₂ is better for achieving stable, large surface area products. However, which method produced the samples with the smallest pore diameters and, therefore, largest pore volumes? Also, how important are these factors to storing H₂?

To determine this, differential pore volume measurements were taken to analyze and compare the products of each method. Figure 3A shows that the sample with the largest pore volume is PEEK-CO₂-9-80, which has the largest surface area of all the samples whose diameters were analyzed (3103 m²/g). However, along with the large surface area and pore volumes, the diameter distribution is evidently higher than that of the other samples with smaller surface areas. This sample has pores of approximately 1.2, 1.35, 1.8, and 2.5 nm with the largest pore volume (0.1 cm³/Å/g) at a diameter of 1.35 nm. However, the pores at 1.8 and 2.5 nm also have relatively large pore volumes of approximately 0.06–0.07 cm³/Å/g. Although the volume of all pores increases with increasing BO, it is apparent from Figure 3B,C that the larger pores develop “later” than smaller pores. Again, this agrees well with the theory of pore formation because the etching of the pore walls continues for the entire duration of the treatment, as would pore nucleation. Thus, pores would both widen in diameter and increase in volume as BO progresses. Figure 3B displays this evolution for samples produced using CO₂. From Figure 3B, it is evident that PEEK-CO₂-9-26 is dominated by pores with diameters <1.5 nm. Also, as BO continues, the volume of pores with diameters of ~1.35 to 2.5 nm increases most noticeably, as demonstrated in PEEK-CO₂-9-59. This represents an increase in BET surface area from ~1000 to 2000 m²/g, respectively, between the samples. Increasing the BET SA further to ~3000 m²/g in PEEK-CO₂-9-80 demonstrates a drastic increase in all pore volumes, with the largest increase in pores with diameters of 1.2 and 1.35 nm. Figure 3C shows the same evolution for steam-

derived samples. This graph shows that, unlike the CO₂-derived samples, increasing the surface area from ~1000 to 2000 m²/g in steam-treated samples (PEEK-ST-9-35 and PEEK-ST-9-70, respectively) causes the most dramatic pore volume increase in pores with diameters of ~1.2 nm. The second most dramatic increase is in pores with diameters of ~2.5 nm; however, the pore volume of the 1.2 nm pores increases approximately twice as much as the pore diameter at ~2.5 nm. This seems to indicate that steam treatment may indeed help conserve the pore diameters while successfully expanding the pore volumes, particularly of the crucial pores with diameters around 1 nm. If steam is favorable to CO₂ in this regard, this should be reflected in a comparison of the differential pore volume distributions of steam- and CO₂-derived samples normalized to BET surface area. Figure 3D,E displays these comparisons between steam- and CO₂-derived samples. Figure 3D displays that, at 1000 m²/g, the volume of all pore diameters is notably larger for the steam-treated product as compared with the CO₂-treated product. Also, the pore with the largest volume for this steam sample has a diameter of ~1.35 nm, indicating a predominantly microporous product. The difference in pore volumes is even more pronounced when analyzing the differential pore volume distributions normalized at 2000 m²/g (Figure 3E). Here, it is evident that the pores with diameters of 1.2 and 1.35 nm in the steam-treated sample have significantly larger volumes than in the CO₂-treated samples. This does support that steam can be utilized to help conserve small pore diameters while increasing the pore volumes of porous carbon products.

If indeed steam is favorable to CO₂ in maintaining small pore diameters while increasing pore volume, this would indicate that, as steam samples increased in surface area, so would their total pore volume as compared with CO₂-derived samples. In essence, per unit surface area, steam-produced samples would have larger cumulative pore volumes than samples produced using CO₂. Such a comparison is made in Figure 4. It is clear from these data that, per unit surface area, steam-derived samples do have larger cumulative pore volumes than those produced using CO₂. This fact only becomes more pronounced as the surface area increases; however, as was mentioned previously, steam-derived samples with very large surface areas (~3000 m²/g) suffer from pore breakdown and were, therefore, not analyzed further. As such, the largest cumulative pore volumes (~1.7 cm³/g) were achieved by the high surface area CO₂-derived products (PEEK-CO₂-9-80,85). Still, it is apparent that steam is favorable compared with CO₂ with regard to maintaining small diameter pores.

However, it should also be noted that, in all samples, the major pore population was predominantly below a diameter of ~3 nm. Furthermore, several samples have significant pore populations dominated by pores with diameters ≤ 1.5 nm, which is well within the ideal microporous diameter range that is so crucial for optimized H₂ storage. This is further supported in Figure 5, which represents a graph mapping the NMR shift corresponding to H₂ in micro/mesopores versus changing pressure. From previous work,¹¹ we know that a shift that does not change with evolving pressure indicates pores with diameters ≤ 1.2 nm. Such shifts can be seen in PEEK-CO₂-9-1,26 and PEEK-ST-9-20 (Figure 5). This means that the pore diameters of these samples are primarily at or below ~1.2 nm. This is supported by the fact that, as was previously stated, steam appears to conserve smaller pore diameters than CO₂ at higher BO. Again, this likely results from the differences in the mechanism of pore formation between these two methods.

Figure 3. Plot of differential pore volume measurements at 77K for several CO₂- and steam-derived samples. (A) PEEK-CO₂-9-80 has the largest pore volumes and the largest surface area of all the samples whose diameters were analyzed (3103 m²/g). All samples have pores with diameters centered around 1.2, 1.35, 1.8, and 2.5 nm. Panels B and C show the evolution of the differential pore volumes of CO₂- and steam-derived samples, respectively. These data indicate that steam treatment may be best at conserving the pore diameters while successfully expanding the pore volumes as compared with CO₂. This is especially important and prominent in pores with diameters from 1 to 2 nm, which are important for H₂ storage concerns. (D) At 1000 m²/g, the volume of all pores is notably larger for the steam-treated product as compared with the CO₂-treated product. This difference in pore volumes is even more pronounced when analyzing (E), the differential pore volume distributions normalized at 2000 m²/g. It should be noted that the density field theory analysis of these data below 1 nm is unreliable. As such, interpretation of pore diameters around 1 nm is supported by NMR data.

Regardless, both methods are able to produce large surface area samples with pore diameters at or below 1.2 nm.

The small diameters, large pore volumes, and large surface areas of these samples are very impressive among porous carbon

Figure 4. Plot of cumulative pore volume versus BET surface area. Data were taken such that comparisons could be made at ~ 1000 , 2000 , and $3000 \text{ m}^2/\text{g}$. However, as was mentioned previously, the pore structure of steam-derived samples is compromised above $\sim 2000 \text{ m}^2/\text{g}$, making comparison at $3000 \text{ m}^2/\text{g}$ impossible. From the available data, it is apparent that, per unit surface area, steam-derived samples do have larger cumulative pore volumes than those produced using CO_2 . However, because of pore collapse in steam-derived samples, the largest cumulative pore volumes were achieved by the high surface area CO_2 -derived products (PEEK- CO_2 -9-80,85).

Figure 5. Plot of the NMR shift corresponding to H_2 in micro/mesopores versus changing pressure. Shifts that do not change with pressure indicate samples having pores with diameters $\leq 1.2 \text{ nm}$ (as in PEEK- CO_2 -9-1,26 and PEEK-ST-9-20). The positive slope from PEEK- CO_2 -9-59 and PEEK-ST-9-35,47 indicates the presence of pores with diameters $> 1.2 \text{ nm}$. Data were taken at 100 K , and the estimated error for the NMR shifts is $\pm 0.2 \text{ ppm}$.

materials. Additionally, having both small pores and large surface areas is extremely beneficial for H_2 storage applications. Figure 6 shows the H_2 gravimetric uptake at 77 K and 2 bar as it evolves with surface area for samples produced using both steam and CO_2 . It should be noted that both methods suffer from a certain degree of pore collapse and pore restructuring during the extended reaction. This is why many of the trends, including H_2 uptake, are not linearly related to surface area. The H_2 sorption profiles of the materials produced using both methods are very similar at surface areas up to approximately $1500 \text{ m}^2/\text{g}$. However, at $\sim 2000 \text{ m}^2/\text{g}$, the steam-derived product displays an obvious advantage compared with the material produced using CO_2 . As was discussed previously, the main difference between these two samples is that the pore volumes

Figure 6. Excess H_2 gravimetric uptake versus BET surface area at 77 K and 2 bar . The H_2 sorption profiles of materials produced using steam and CO_2 are very similar at surface areas up to approximately $1500 \text{ m}^2/\text{g}$. However, at $\sim 2000 \text{ m}^2/\text{g}$, the steam-derived product displays an obvious advantage compared with the material produced using CO_2 . Ultimately, the best gravimetric uptake is demonstrated by PEEK- CO_2 -9-80, which achieves $3.7 \text{ wt } \%$ at a surface area of $3103 \text{ m}^2/\text{g}$.

of the smaller diameter pores (1.2 and 1.35 nm) are notably larger for steam products as compared with CO_2 products. The larger pore volumes, particularly of these smaller diameter pores, seem to play a noteworthy role in the H_2 storage capabilities of these materials. However, the ability of CO_2 to produce stable samples with large surface areas ultimately overshadows this fact in these samples. Here, these large surface areas ($> 3000 \text{ m}^2/\text{g}$) and relatively large pore volumes and small pore diameters combine to produce a sample that has very impressive H_2 sorption capabilities; specifically, PEEK- CO_2 -9-80, which achieves $3.7 \text{ wt } \%$ at 77 K and 2 bar . Table 1 compares the materials produced here with several other doped and undoped porous carbon products presently being investigated within and outside of the DOE Hydrogen Sorption Center of Excellence. It is apparent from this comparison that the materials investigated in this work are among the most impressive and exciting candidates for H_2 storage media. One trend that is particularly interesting is that the gravimetric uptake of these materials outperforms other materials with larger surface areas in many cases. Surface area is a key factor involved in H_2 storage; however, in the case of these PEEK-derived materials, it is obvious that other factors are contributing significantly to their H_2 sorption profiles. For example, PEEK- CO_2 -9-80 has a larger H_2 gravimetric uptake compared with AX-21 at the same temperature and pressure.

Additionally, high-pressure excess H_2 adsorption isotherms were achieved for PEEK- CO_2 -9-80 (Figure 7). As has been stated previously, this material has an extremely large surface area ($3103 \text{ m}^2/\text{g}$), which is particularly beneficial for achieving large excess H_2 gravimetric uptake values. Furthermore, this material has a large cumulative pore volume ($> 1 \text{ cm}^3$) and small pore diameters (predominantly $\leq 3 \text{ nm}$). Both of these characteristics are ideal for creating a material optimized for H_2 storage. As such, this material demonstrates an exceptionally large gravimetric uptake, ranging to $\sim 5 \text{ wt } \%$ at 77 K and 20 bar (Figure 7). Furthermore, this corresponds to a H_2 volumetric uptake of $\sim 35 \text{ g/L}$ using the unaltered porous carbon density of $\sim 0.7 \text{ g/mL}$. However, it should be noted that, upon compression of 15 t , the density of this material was effectively raised to $\sim 1 \text{ g/mL}$; this density corresponds to a H_2 volumetric

TABLE 1: Materials Produced by Thermally Treating PEEK under Different Chemical Environments Have Impressive H₂ Gravimetric and Volumetric Uptakes Compared with Other Pure and Doped Carbon Materials Presently Being Investigated^a

material	BET SA (m ² /g)	excess H ₂ uptake (wt %) ^b	volumetric capacity (g/L)	cumulative pore volume (cm ³ /g)
PEEK-CO₂-9-1	524	1.6	11	NA
B/C ¹²	780	~1.6 (at 77 K, 1.2 bar)	NA	NA
PEEK-CO₂-9-5	700	2.0	14	NA
CMK-1 ¹³	1788	2.19 (77 K, 1 bar)	NA	NA
PEEK-CO₂-9-26	1027	2.2	15	0.63
<i>PEEK-ST-9-47</i>	<i>1207</i>	<i>2.3</i>	<i>16</i>	<i>NA</i>
<i>PEEK-ST-9-20</i>	<i>1294</i>	<i>2.4</i>	<i>17</i>	<i>NA</i>
<i>PEEK-ST-9-70</i>	<i>1956</i>	<i>3.0</i>	<i>18</i>	<i>0.89</i>
AX-21 ¹⁴	3000	~3.0 (77 K, 2 bar)	NA	NA
PEEK-CO₂-9-80	3103	3.7 (~5 at 77 K, 20 bar)	26 (35 at 77 K, 20 bar)	1.7
Corncob ¹⁵	3500	5 (at 77 K, 20 bar)	NA	NA

^a Materials in bold represent CO₂-derived products, whereas those in italic represent steam-treated products. Materials being used for comparison are in standard font. ^b All H₂ gravimetric uptake measurements were done at 2 bar and 77 K, unless otherwise specified.

uptake of ~50 g/L. Further work needs to be done to fully characterize these products, but it is obvious that these materials

possess outstanding H₂ volumetric adsorption capacities. Furthermore, their large excess gravimetric uptakes (~5 wt %) classify them as one of the best of any materials presently under investigation by the DOE.

Figure 7. Excess H₂ gravimetric uptake isotherm of PEEK-CO₂-9-80 measured at NREL (75.6 K) and Caltech (77 K). Panel A represents this gravimetric uptake isotherm over the full pressure range (0–150 bar), and panel B focuses on the lower-pressure region (0–50 bar). Both show that this material demonstrated an exceptionally large H₂ gravimetric uptake of ~5 wt %. It should be noted that the kinetics of H₂ sorption is assumed to be negligible in these studies. The estimated error of the excess H₂ gravimetric uptakes for the data from Caltech is ±0.1%.

4. Conclusions

It is evident that many factors are very important to the H₂ storage capabilities of these materials. Having a large surface area was known to be advantageous for achieving large H₂ uptake values. However, utilizing the parallel methods discussed in this paper, the importance of having large pore volumes and small pore diameters was shown. As such, it appears that a balance between surface area, pore volume, and pore diameter must be optimized to achieve ideal H₂ storage conditions in porous carbon materials. Both steam and CO₂ treatments were used herein to controllably produce several materials with impressive excess H₂ uptakes, up to ~5 wt % and 35 g/L. These impressive H₂ sorption capacities are thought to be directly related to the balance between large surface area (~2000 to 3000 m²/g), large pore volume (>1 cm³/g), and small pore diameter (predominantly ≤3 nm) achieved in these materials.

Presently, work is being done in our lab to combine these treatments. It is likely that optimized porous carbon for H₂ storage will benefit from both pore formation mechanisms. Namely, combining the relative tendency of CO₂ to nucleate pores with the relative ability of steam to increase surface area by enlarging pore volume should allow for the production of a porous carbon with even more impressive H₂ storage capacity than the already impressive results displayed here. With this in mind, future work investigating reaction mixtures of CO₂ and steam, along with other gases, should be done. It is hoped that these methods will aid in the directed manufacturing of tailored porous carbon materials for H₂ storage applications. Successfully engineering such materials would represent a major step in the effort to replace conventional nonrenewable fuel sources with H₂.

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Supporting Information Available: Further experimental details as well as XPS and NMR data are provided in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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