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Preparation of tailored carbons with meso- and micro- porosity via template synthesis route

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A low cost templating approach to making non-ordered carbons with a tailored meso/micropore structure is described. A series of mesoporous carbons was prepared from polyfurfuryl alcohol and phenolic resin precursors by a templating route, using a variety of commercially available silica gels as the template material. Carbons were produced with mesopore volumes up to $1 \text{ cm}^3 \text{ g}^{-1}$, mesopore sizes in the range of 4 nm to 8 nm and surface areas in the range of 300 to 700 $\text{m}^2 \text{ g}^{-1}$. These mesoporous carbons were subsequently activated in CO_2 to add controlled amounts of microporosity to produce carbons with both a micro and mesoporous structure. Significantly, the activation process did not appreciably change the mesopore size distribution of the carbons. By altering the activation time, it was possible to tailor the micropore: mesopore volume ratios within wide limits.

1. Introduction :

Carbons are widely used as adsorbents in both the gas and liquid phases due to their high surface areas, large adsorptive capacity and chemical stability. Most of these carbons are microporous (pore widths < 2 nm), but there is a need to prepare carbons with larger pore sizes in the mesopore size range (2 – 50 nm) for applications such as double layer capacitors [1], catalyst supports for liquid phase work [2] and the ability to adsorb larger molecules than conventional microporous carbons [3]. Also required are adsorbents with a bi-modal pore size distribution; micropores for gas/vapour adsorption and larger mesopores for reduced pressure drop and better mass transfer and [4].

Traditionally, mesoporous carbons have been difficult to prepare but recently a templating method has been adopted to produce carbons with different mesopore sizes. The technique involves infiltrating a porous inorganic template material with a precursor carbon solution or vapour, a polymerisation stage followed by a carbonisation step and, finally, the leaching out of the template material. This produces a carbon which is a negative replica of the template. A number of different precursor carbon materials have been used, including phenolic resins [5], polyfurfuryl alcohol [6], sucrose [7] and acetonitrile [8]. These materials give high carbon yields on carbonisation and have the added benefit of producing ‘clean’ materials, as carbons prepared from natural sources can contain unwanted trace

amounts of metals and other contaminants.

The template needs to have a well defined pore structure, a reasonably high pore volume and be easily removed after carbonisation. However, a very highly ordered carbon is not necessarily required for all potential uses of mesoporous carbons, such as the adsorption of vapours or catalysis. A variety of different templating materials have been used previously to prepare porous carbons. These include zeolites (to prepare microporous carbons) [9], MCM materials [10], clays [11] and meso-structured silicas such as SBA-15 [12]. These materials tend not to be readily available commercially in bulk and often need to be specially prepared prior to infiltration, or are expensive to purchase. Only a small amount of work has been reported using commercially available silica templates [13, 14]. The advantage of these materials is that they are widely available with a range of different pore structures and are relatively inexpensive.

A number of different pore size distributions have been obtained by using various template materials. Templating using silica gel was first reported by Knox et al [15, 16], who used a silica gel with a pore size of 15 nm, but little work on this material has been reported since, possibly due to the interest in using template materials with a highly ordered structure. Petro et al. [13] used a 6 nm silica gel and saccharose as the precursor to prepare a carbon for

chromatographic applications but did not report on the resulting porosity of the carbon. The SBA-15 template has been used to prepare carbons with a mesopore size between 3 and 5.2 nm [17]. MCM-48 template produced carbons from sucrose with a pore size of around 3 nm [7] and 2.3 nm for a phenol-formaldehyde precursor [18].

Most, if not all, of the work with templated carbons has not involved any subsequent treatment of the carbons. However, it is possible to introduce micropores into these materials by a subsequent activation stage where the microporosity is developed, by high temperature treatment in CO₂ or steam, and is superimposed on the existing mesopore structure. This method yields carbons with a range of pore sizes, allowing a wide range of molecules to be adsorbed.

We have previously reported the vapour adsorption properties of these materials [19]; this paper presents the preparative methods used to make mesopore carbons with a variety of mesopore sizes and their subsequent activation to give a range of tailored meso/micropore structures.

2. Experimental :

A variety of commercial silica gels with different pore sizes and pore volumes was used as the template material and their properties are summarised in table (1). The silicas were dried in air at 120 °C prior to use to remove adsorbed water.

Two carbon precursor polymers were used for infiltration of the silica gel templates, a phenolic resin and polyfurfuryl alcohol. The phenolic resin solution was prepared by dissolving resin (SMD 3027, Schenectady Europe Ltd.), mixed with hexamethylenetetramine (hexamine, 99 % Aldrich) in a ratio of 10:1 by mass, in methanol (in a 1:1 ratio by mass of resin to solvent). Polyfurfuryl alcohol was prepared by adding approximately 0.05 cm³ of 2M HCl to 10 cm³ of furfuryl alcohol (99 %, Aldrich) and stirring for 4 hours at room temperature.

The phenolic resin solution was added to the silica gels in excess, i.e. more solution was added than was necessary just to fill the pores of the template. The solution was added slowly and the mixture was stirred vigorously during the impregnation process. The solvent was allowed to evaporate off and the infiltration process repeated. The polyfurfuryl alcohol precursor materials were prepared in a similar way but were only given one infiltration step as the solution had lower viscosity and hence filled the pores more readily.

The phenolic resin infiltrated samples were crosslinked, in air, at 200 °C and the polyfurfuryl alcohol samples at 85 °C and 140 °C, under N₂. The materials were then carbonised at 500 °C under flowing N₂. The silica template was removed by dissolution in hot concentrated NaOH solution (5M). The latter process was carried out three times and XRF measurements (Spectro x-lab 2000) on the resulting carbon powders showed silicon levels were less than 0.5 %. To remove any remaining sodium ions, which might affect the subsequent activation process, the carbons were washed with 2M HCl and then with hot water followed by cold water until the pH was 7. Absence of Na was confirmed by XRF and EDX (INCA, Oxford Instruments). The resulting mesoporous carbons (1 g) were

subsequently activated at 900 °C for between 2 and 7 hours in flowing CO₂ (50 cm³ min⁻¹).

The surface area and pore size distributions were measured by nitrogen adsorption at – 196 °C using an automated instrument (Omnisorp 100CX, Beckman Coulter). The samples were outgassed for at least 6 hours at 200 °C prior to measurement. Surface areas were calculated using the BET method (p/p₀ range of 0.05 to 0.2). Mesopore size distributions were calculated from the desorption isotherms using the BJH model [20] and micropore volumes were calculated using t-plot analysis.

Silica gel code	Pore size / nm	Pore volume / cm ³ g ⁻¹	Supplier	Particle size / μm
40 Å	4	0.68	Aldrich	210 - 500
60 Å	6	0.75	Aldrich	63 - 210
100 Å	10	1.0	Aldrich	63 - 210
150 Å	15	1.15	Alfa Aesar	10 – 500 ^b
'large pore'	19 ^a	1.6	Alfa Aesar	50 – 150 ^b
SD1503	12	1.25 ^a	Crosfield ^c	106 - 150
SD1502	22	1.89 ^a	Crosfield ^c	< 200 ^b
SD2335	22	1.24	Crosfield ^c	< 20 ^b
SD2336	35	1.7	Crosfield ^c	< 50 ^b
SD2337	15	0.9	Crosfield ^c	< 70 ^b

Table 1. Summary of the properties of the silicas used as template materials. All the values are from the suppliers unless marked with an ^a, where they were measured by N₂ adsorption or ^b by SEM observation. ^c now INEOS Silicas.

3. Results :

3.1 Phenolic resin-derived carbons prior to activation :

When non-templated phenolic resin-derived carbon was carbonised under the same conditions, the carbon produced had a BET surface area in the region of 80 m² g⁻¹, with a small amount of microporosity present (micropore volume of 0.03 cm³ g⁻¹) and no mesoporosity. The carbon yield was around 65 % of the starting material in terms of mass.

Templated carbons prepared from silica gels that had a pore size of less than 10 nm produced carbons which had low mesopore volumes and no defined mesopore structure. This is probably due to the low initial pore volumes of these silica gels and the viscosity of the phenolic resin solution being too high for their pores to be fully infiltrated by the solution.

However, carbons prepared from silica gel templates with a pore size ≥ 10 nm, produced materials with a well defined mesopore structure. The results are summarised in table (2). Two infiltration steps of resin solution were found to be necessary, as carbons prepared from just one impregnation stage produced a bimodal mesopore size distribution with the larger sized pores having a very broad size distribution (figure 1). It was also found that if the solution added to the template silicas was just sufficient to fill the pores (as calculated from pore volume of silica

template), even after two infiltration steps a bimodal mesopore distribution was obtained.

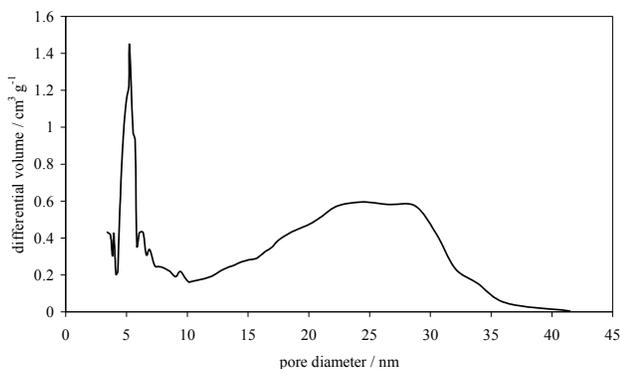


Figure (1) : Mesopore size distribution of phenolic resin-derived carbon prepared using 150 Å silica gel with one impregnation step, prior to activation.

Silica gel template	S_{BET} ($m^2 g^{-1}$)	V_{mes} ($cm^3 g^{-1}$)	V_{mic} ($cm^3 g^{-1}$)	d_{mes} (nm)
100 Å	680	0.44	0.08	5
150 Å	630	0.43	0.12	5.8
'large pore'	590	0.31	0.14	5
SD1503	620	0.45	0.14	8-9
SD1502	580	0.31	0.12	4.8
SD2335	633	0.40	0.13	5.2
SD2336	620	0.31	0.16	5.5
SD2337	595	0.49	0.1	5.5

Table (2) : Summary of N_2 adsorption isotherm results for the different silica gel templated carbons prepared from phenolic resin.

The carbons produced were all mesoporous but with a small amount of microporosity also present. The mean pore size was related to that of the silica gels used as the template material. However, mesopore volumes were in the order of 0.3 - 0.5 $cm^3 g^{-1}$ and did not vary greatly with the template silica. Pore size distributions were narrow and the mean pore size varied between 5 nm and 8.5 nm depending on the template used.

3.2 Polyfurfuryl alcohol derived carbons prior to activation :

PFFA-derived carbon prepared under the same conditions, but without silica templating, had no significant surface area. The carbon yield was around 50 % of the starting mass. As with the phenolic resin, PFFA-derived carbons prepared from templates with pore sizes < 10 nm did not produce carbons with significant mesoporosity. A summary of the results for templates with pore sizes ≥ 10 nm is shown in table (3). However, as noted above, only one coating of PFFA solution was required to prepare carbons with a mono-modal mesopore size distribution, as the PFFA solution was less viscous than the phenolic resin solution. Pre-activation micropore levels were lower than for phenolic resin-derived carbons, but the mesopore volumes were generally higher with a greater variation.

This could be due to either fewer blocked pores, as the templates only received one coating of solution, and/or to the lower viscosity of the PFFA solution used for impregnation, allowing for more effective pore penetration. The mesopore size distributions were similar to those obtained from phenolic resin-derived carbons using the same template material.

Silica gel template	S_{BET} ($m^2 g^{-1}$)	V_{mes} ($cm^3 g^{-1}$)	V_{mic} ($cm^3 g^{-1}$)	d_{mes} (nm)
100 Å	663	0.63	0.04	4.8
150 Å	711	0.79	0.05	5.9
'large pore'	487	0.37	0.08	5
SD1503	824	0.88	0.07	8-9
SD1502	523	0.33	0.12	5.5
SD2335	857	1.19	0.05	5-6
SD2336	542	0.32	0.08	4.5

Table (3) : Summary of N_2 adsorption isotherm results for the different silica gel templated carbons prepared from polyfurfuryl alcohol.

Template material	Activation time (min)	S_{BET} ($m^2 g^{-1}$)	V_{mes} ($cm^3 g^{-1}$)	V_{mic} ($cm^3 g^{-1}$)	d_{mes} (nm)
100 Å	0	683	0.44	0.08	5
100 Å	120	974	0.47	0.20	5
100 Å	330	1317	0.56	0.31	5
100 Å	430	1510	0.59	0.39	5
'large pore (LP)'	0	594	0.3	0.14	5.1
LP	120	830	0.31	0.24	4.9
LP	330	1168	0.39	0.36	4.9
LP	430	1443	0.44	0.45	5
SD1502	0	580	0.31	0.12	4.8
SD1502	120	775	0.36	0.23	4.7
SD1502	330	1063	0.42	0.42	4.7
SD1503	0	622	0.39	0.13	8 - 9
SD1503	120	772	0.44	0.24	8 - 9
SD1503	330	1013	0.50	0.33	8 - 9
SD2335	0	633	0.39	0.13	5.2
SD2335	120	820	0.39	0.23	5.1
SD2335	330	1039	0.44	0.32	5.1
SD2336	0	620	0.28	0.13	5.5
SD2336	120	747	0.28	0.25	5
SD2336	330	989	0.32	0.34	5
SD2337	0	595	0.49	0.1	5.4
SD2337	120	810	0.45	0.22	5.1

Table (4) : Summary of N_2 adsorption isotherm results for the different silica gel templated phenolic resin-derived carbons activated in CO_2 .

3.3 Activation of phenolic resin-derived templated carbons :

On activation at 900 °C in flowing CO_2 the carbons lost mass and, as expected, micropores were formed. A number

of different activation times were used to vary the amounts of microporosity. The N₂ adsorption isotherm results are summarised in table 4. On activation, the micropore volumes and surface areas increased as activation time was extended, again as expected. The mesopore volumes also increased on activation but the mesopore size did not alter significantly. Mesopore size distributions remained narrow. Figure 2 shows the mesopore size distribution for carbon prepared from the ‘large pore’ silica gel template and Figure 3 shows the corresponding N₂ isotherms.

It should be noted that the bimodal mesopore size distribution obtained when one infiltration step was used could be utilised to give a bimodal-mesopore distribution in carbons and then activated to introduce microporosity. However this possibility was not investigated further at this stage.

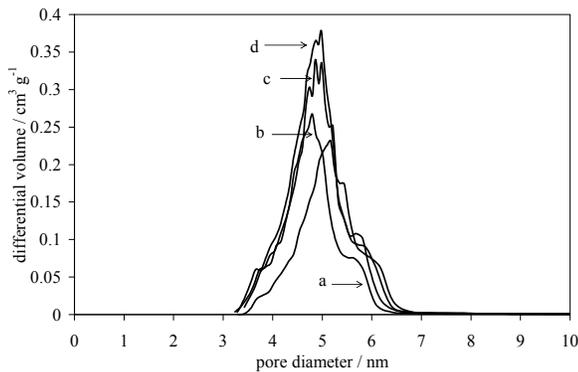


Figure (2) : Mesopore size distribution of phenolic resin-derived carbon prepared using the ‘large pore’ silica gel template (with 2 impregnation steps) and subsequently activated in CO₂, at 900 °C, for a) 0 minutes, b) 120 minutes, c) 330 minutes and d) 450 minutes.

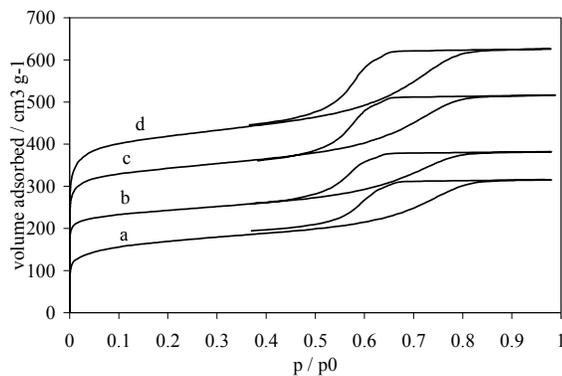


Figure (3) : Nitrogen isotherms of phenolic resin-derived carbon prepared using the ‘large pore’ silica gel template and subsequently activated in CO₂, at 900 °C, for a) 0 minutes, b) 120 minutes, c) 330 minutes and d) 450 minutes showing the development of microporosity.

3.4 Activation of polyfurfuryl alcohol derived templated carbons :

A summary of the nitrogen isotherm results is given in table 5. The results show the same trend as was seen with

the phenolic resin-derived templated carbons, with the level of microporosity increasing with CO₂ activation time, as expected. Figure 4 shows the mesopore size distribution of carbon prepared from the SD1503 silica gel and figure 5 the nitrogen isotherms. Generally the micropore volumes are lower than those seen with the phenolic resin-derived carbon.

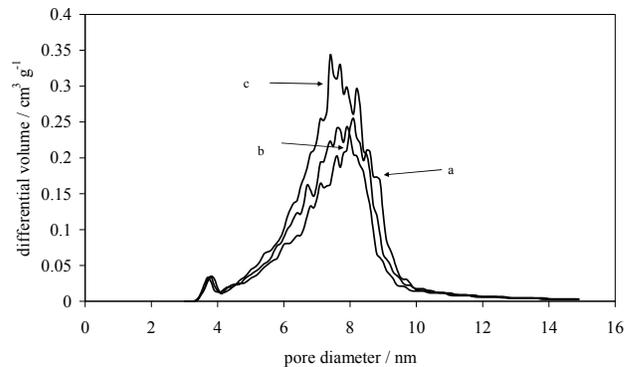


Figure (4) : Mesopore size distribution of PFFA-derived-carbon prepared using the SD1503 silica gel template and subsequently activated in CO₂, at 900 °C, for a) 0 minutes, b) 120 minutes and c) 330 minutes.

Template material	Activation time (min)	S _{BET} (m ² g ⁻¹)	V _{mes} (cm ³ g ⁻¹)	V _{mic} (cm ³ g ⁻¹)	d _{mes} (nm)
100 Å	0	681	0.63	0.04	4.8
100 Å	120	844	0.68	0.17	4.5 - 5.0
100 Å	330	1400	0.79	0.30	4.5 - 5.0
100 Å	430	1830	0.90	0.32	4.5 - 5.0
‘large pore (LP) ‘LP’	0	478	0.37	0.08	5
‘LP’	120	743	0.39	0.21	5
‘LP’	330	1205	0.51	0.37	5
SD1502	0	492	0.29	0.08	4.6
SD1502	120	720	0.31	0.20	4.3
SD1502	330	1050	0.35	0.32	4.6
SD1502	430	1380	0.48	0.41	4.6
SD1503	0	625	0.64	0.14	7 - 8
SD1503	120	716	0.63	0.18	7 - 8
SD1503	330	986	0.80	0.27	7 - 8
SD2335	0	820	0.87	0.07	5.5
SD2335	120	864	0.87	0.12	5.5
SD2335	330	1170	1.06	0.20	5.5
SD2336	0	523	0.30	0.12	5 - 5.5
SD2336	120	605	0.29	0.18	5 - 5.5
SD2336	330	840	0.37	0.26	5 - 5.5
SD2336	430	1044	0.44	0.33	5 - 5.5
SD2337	0	857	1.18	0.05	5.8
SD2337	330	1135	1.17	0.17	5.8

Table (5) : Summary of N₂ adsorption isotherm results for the different silica gel templated PFFA-derived carbons activated in CO₂.

4. Discussion :

The silica templates are non-ordered and hence, so are the resulting carbons. The precursors both produce high carbon yields, with the phenolic resin being better in this respect. After carbonisation, the templated carbons are predominantly mesoporous, although they do have some microporosity. There was less with the PFFA-derived carbons than the phenolic resin-derived material. This is probably due to the phenolic resins generating some microporosity during the carbonisation process. However, it has been reported by other workers that PFFA carbons are also microporous after carbonisation [21]. It is possible that in this work the micropores were too small to be observed by N₂ adsorption. The silica gels with pore sizes less than 10 nm did not produce porous carbons, possibly because the pore size was too small for the solutions to penetrate them fully and/or the template wall thickness was too thin to produce measurable porosity. The wide range of commercial silicas available means that a large variety of pore sizes and pore volumes can be prepared. The use of silica templates has the valuable advantage that they can be leached out using the relatively easily handled NaOH solution; it is not necessary to use HF as in the case of some other template materials. The similar mesopore sizes obtained with both carbon precursors suggests that both precursor solutions fully infiltrate the template pore structure. The bimodal mesopore size distribution observed with the phenolic resin-derived carbons after one impregnation step was due to incomplete filling of the template pores [22] and can be utilised to prepare materials with this type of pore structure if desired.

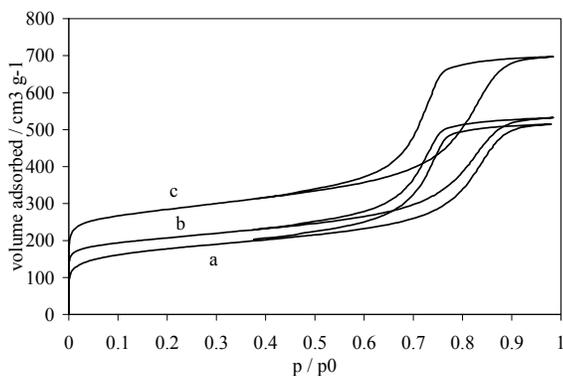


Figure 5. Nitrogen isotherms of PFFA-derived-carbon prepared using the SD1503 silica gel template and subsequently activated in CO₂, at 900 °C, for a) 0 minutes, b) 120 minutes and c) 330 minutes.

As expected and noted above, the subsequent activation of the mesoporous carbons in CO₂ produces micropores without changing the mesopore size distribution. The increase in mesopore volumes after CO₂ activation can be ascribed to the opening up to nitrogen of previously unavailable mesopores that had been blocked by excess precursor material. The higher micropore volumes obtained from the phenolic resin-derived carbons for the same activation times probably arose from there being some microporosity already present in these carbons on pyrolysis. By altering the activation times it is possible to tailor the micropore/mesopore volume ratio within a wide range. The

different shapes of the isotherms of the templated carbons (as seen in figures 3 and 5) indicates how the pore volumes and pore sizes differ between the various templates used. The increasing microporosity with activation time is reflected in the rising amount of N₂ adsorbed at low p/p_0 values, while the broader pore size distribution of the SD1503 PFFA derived carbon results in the wider hysteresis loop. It is reasonable to suppose that greater activation times than reported here would further increase the micropore volumes and surface areas.

No correlation could be found between any of the properties of the starting silica template materials and final properties of the resulting carbons. This could be due to differences in the wall thickness of the silica templates, which would lead to the different pore volumes and pore sizes obtained, and these were not measured in this study.

Most silica templates give similar mesopore sizes for both phenolic resin and PFFA-derived carbons, with two exceptions, i.e. the carbons prepared from the SD1502 and SD2336 templates. For the latter material, the mesopore size was larger when phenolic resin was the precursor, while with the former template, the PFFA-derived carbon had the larger mesopore size. It has been observed previously that phenolic resin and polyfurfuryl alcohol precursors produce carbons with slightly different mesopore sizes. This has been attributed to the fact that the carbon framework expands slightly during silica dissolution [23] due to the relief of the stress of being constrained in the template, and that different carbons expand by different amounts. However, the limitations of the BJH model and normal experimental errors obtained with N₂ adsorption experiments could also explain the small differences found.

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