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Mesoporous carbons with self-assembled surfaces of defined crystal orientation

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Abstract

The design of carbon sorbents traditionally focuses on the control of pore structure and the number and type of surface functional groups. The present paper explores the potential of also controlling the carbon crystal structure, or graphene layer orientation, in the immediate vicinity of the internal surfaces. We hypothesize that this crystal structure influences the properties of the carbon surfaces and affects the number and type of active sites for functionalization. Here a series of mesoporous carbons are fabricated by capillary infiltration of mesophase pitch (naphthalene homopolymer) into a series of controlled pore glass templates of different characteristic pore size followed by carbonization and template etching. The liquid crystalline mesogens are known to adopt perpendicular alignment (anchoring) at liquid/silica interfaces, which after carbonization lead to a high concentration of graphene edge sites at the inner surfaces. These surfaces are shown to have elevated chemical reactivity, and the pore structures are shown to be consistent with predictions of a quantitative model based on the negative replica concept. Overall, the use of mesophase pitch for templated mesoporous carbons allows systematic and simultaneous control of both pore structure and interfacial crystal structure through the well-defined rules of liquid crystal surface anchoring.

Keywords

templating; crystal structure; interfacial engineering; liquid crystal; functionalization

1. Introduction

There is great interest in the development of improved mesoporous carbons as sorbents,^{1–3} catalyst supports,^{4–6} capacitors,^{7–9} and electrodes.^{10–12} The optimization of mesoporous carbons typically focuses on the control of pore structure, surface area, and the number and type of surface functional groups. A porous carbon property that is often overlooked is the crystal structure of the carbon in the immediate vicinity of the internal surfaces. This interfacial structure provides the carbon “platform” for subsequent surface treatment and can thus determine the number of potential active sites for functionalization and influence the final polarity, surface charge density, and/or chemisorptive activity of the carbon material.

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It is now becoming possible to control the spatial arrangement of graphene layers through molecular engineering, especially in near-surface regions, through liquid crystal templating using mesophase pitch or related polyaromatic precursors.^{13–15} Liquid crystal templating techniques have been used to fabricate platelet-symmetry carbon nanofibers,^{15–17} and nanotubes,^{14, 18–19} all-edge carbon thin films,²⁰ and porous carbons.^{21–25} Previous work has established surface anchoring rules for the discotic mesogens in mesophase pitch, which prefer edge-on anchoring onto most (but not all) substrates.^{13,26} In confined spaces the discotic molecules form unique supramolecular configurations that are often predictable from liquid crystal theory. Figure 1 shows selected configurations that have been reported from previous studies. The further carbonization process can covalently capture the supramolecular assembly order, leading to carbons with controllable physical shape, graphene layer orientation, and in many cases abundant edge sites at surfaces.

Many (but not all) of the new mesophase-derived nanomaterials have surfaces composed solely of graphene edges. Carbon edge sites are generally more active than the atoms in basal planes in a variety of chemical reactions,^{28–30} and it is reasonable to expect that the edge-rich carbon surfaces would offer advantages for high-density functionalization, heterogeneous electron transfer, or rapid lithium intercalation and de-intercalation. Recently, it has been reported that graphene edge plane surfaces can have high hydrophilicity,^{16,31} which could be valuable for nanomaterial dispersion and functionalization in biomedical applications. There is need for more work focused on the quantitative surface property analysis of these all-graphene-edge surfaces.

The goal of the current research is to synthesize and characterize a set of new mesoporous carbons in which both the pore structure and the interfacial graphene layer structure have been systematically controlled by liquid crystal templating. We focus on silica templates that cause edge-on discotic anchoring and yield carbons with inner surfaces rich in graphene edge sites. We hypothesize that these all-edge surfaces will have high chemical reactivity, and a second goal of the research is to assess that hypothesis through quantitative measurements of the surface functionalization density following treatment with nitric acid and molecular oxygen. Showing high reactivity on all-edge-site surfaces is key to the applications of a number of new carbon forms whose outer or inner surfaces have high concentrations of exposed edge sites due to perpendicular or tilted graphene layer order.

2. Experimental

2.1 Preparation and structural analysis of mesoporous carbons

The preparation of mesoporous carbons through templating consists of three basic steps: (a) infiltration of porous templates by the carbon precursor, (b) non-catalytic carbonization of the template/precursor composites, and (c) chemical etching of the templates. As a carbon precursor we use HP grade AR-mesophase pitch (Mitsubishi Gas Chemical) made from catalytic polymerization of naphthalene. The templates are controlled pore glass (CPG) from CPG Inc. and silica gel from Aldrich. CPG samples are available in a variety of pore sizes for a range of applications including enzyme immobilization and chromatography. For this study we used CPG templates with mean pore size of about 12 nm, 25 nm, 45 nm, 70 nm, and 100 nm, and silica gel templates with mean pore size of about 6 nm and 15 nm. Both template materials are used as <100 μm powders to facilitate infiltration. The CPG templates show uniform and regular pore structures, while silica gels are more irregular. The templates are labeled as CPG-12, CPG-25, CPG-45, CPG-70, CPG-100, SG-6, and SG-15 with respect to the template type and mean template pore size.

A physical mixture of template powder and lightly ground solid AR-mesophase pitch was heated at 300 °C for 2 hours in a tube furnace under nitrogen atmosphere, during which the

AR precursor exhibits a homogeneous discotic nematic liquid crystalline phase,^{13,26} and infiltrates into the template spontaneously by capillary flow. The temperature was then slowly raised to 700 °C with a heating rate of 4 °C/min and held for 1 hour to fully carbonize the AR precursor. After cooling to room temperature, the template was removed¹⁵ by washing in 4 M NaOH at 70 – 80 °C. The resulting carbon product had a similar particles size as the template and was washed thoroughly with distilled water and oven dried. Some of the carbons were further annealed at temperatures up to 2500 °C in nitrogen. AR mesophase precursors were also carbonized separately under the same condition without templates. The non-templated carbon was served as the blank reference for the internal porosity test. Non-isothermal thermogravimetric analysis (TGA) up to 1000 °C in air was applied to monitor the complete removal of templates. The asproduced porous carbons are labeled as CPG-12-C, CPG-25-C, CPG-45-C, CPG-70-C, CPG-100-C, SG-6-C, and SG-15-C with respect to their template names. The structures of mesoporous carbons were examined by SEM, TEM, HRTEM, XRD, and nitrogen vapor adsorption techniques. The isotherms (20-points) were analyzed by the BET theory to estimate total surface area and the BJH theory on the desorption branch for pore size distribution.

2.2 Surface treatment and characterization of surface activity

To characterize carbon surface activity, selected carbon samples were treated with nitric acid and the total acid site density determined by base titration.^{32–34} Two mesoporous carbons (CPG-25-C and CPG-70-C) were treated with 10 wt-% and 70 wt-% HNO₃ solutions for 24 hours at room temperature, then washed thoroughly using distilled/deionized water, and dried in the oven. For the titration, 50 mg of HNO₃-treated carbon powder was added to a vial containing 20 ml freshly prepared NaOH solution with pH value approximately 11 measured by a Vernier (Beaverton, OR) pH electrode. The pH values of the NaOH/carbon mixture solutions were measured after 18 hours. The pH values of blank NaOH solutions were also measured initially and after 18 hours as a control. The quantities of acidic sites (pK_a < 11) were calculated from titrant stoichiometry.

The carbon surface activity can also be characterized for active surface area (ASA) analysis, which is based on the concept of active sites,^{35–36} available for oxygen chemisorption.^{37–38} Specifically, two mesoporous carbons (CPG-25-C and CPG-100-C) were heated to 950 °C under vacuum to a pressure below 10^{−6} Pa to clean the surface. The sample was then cooled to a pre-selected adsorption temperature and a known pressure of gas was admitted. For most carbon materials the active surface area is determined by measuring the amount of oxygen chemisorbed at 300 °C in 24 hours with a starting pressure of 66 Pa. Because chemisorption can be slow, it is more accurate to determine the number of active sites by measuring the amount of gas desorbed. Thus, after evacuation at adsorption temperature, the oxygen complex that forms during adsorption was removed as carbon monoxide and carbon dioxide by heating the sample to 950 °C in a closed system of known volume. The relative amounts of the two gases formed were measured by trapping out the CO₂ in a liquid nitrogen bath to prevent back reaction and then measuring the pressure of each gas separately after the completion of desorption. The amounts of CO and CO₂ were then converted to an equivalent oxygen concentration to calculate the ASA covered by the surface complex, based on three assumptions: (1) the chemisorption occurs on the prismatic planes, i.e. the atoms on the edges of the basal planes, which the pioneering work of Hennig²⁸ and Thomas²⁹ had identified as the sites of attack by molecular oxygen; (2) the complex consists of one oxygen atom per carbon atom; and (3) each carbon atom occupies an area of 0.083 nm².

3. Results and discussion

3.1 Morphology, pore structure, and crystal structure of mesoporous carbons

Typical morphologies of the mesoporous carbons derived from CPG templates are shown in Figure 2. Although the CPG templates vary widely in pore size (from 12 nm to 100 nm), all the carbons show a similar morphology – they are uniform, bi-continuous solid/gas phases with monodisperse pore size (Figure 2A,B,C) suggesting that the carbons are accurate negative replicas of the original templates (which have a similar appearance). The continuous, interconnected nature of the silica template aids in complete template removal (no template encapsulation) and high-purity carbons. Both thermogravimetric and elemental analysis indicate that the carbon is essentially free of residual template. Figure 2D shows that the mesoporous carbons possess an abundance of exposed edge-site-rich surfaces, reflecting the preferred edge-on anchoring state of the discotic AR liquid on glass.^{13,26}

Figure 3 shows the morphologies of silica gel templates and the corresponding porous carbons. Silica gel (see Figure 3A) shows a more irregular pore structure (with pore size ranges from several nm to hundreds of nm) compared with CPG templates. The resulting carbons show irregularity (see Figure 3B) due to the negative replica templating of the irregular silica gels. Although silica gel templates exhibit irregular pore structure, they are much less expensive than CPG templates and are thus good alternative candidate templates for achieving practical high-surface-area mesoporous carbons.

Selected porous carbons were post-synthesis annealed at high temperature. Figure 4 shows the XRD spectra of the as-produced 700 °C mesoporous carbons and the 2500 °C annealed carbons. Comparing with the broad 002 peak for 700 °C sample, the sharp 002 peak and its shifting to higher diffraction angles of 2500 °C annealed sample indicate a much higher degree of crystallinity.

All the templates and resulting mesoporous carbons were subjected to standard nitrogen vapor adsorption/desorption characterization. Table 1 and Figure 5 show the resulting pore structures of the templates and corresponding carbons, including BET (Brunauer, Emmett, and Teller) surface area³⁹, total pore volume, and pore size distribution (PSD). Figures 5 (a)–(f) present the pore size distributions of the carbons using BJH (Barrett, Joyner, and Halenda) method⁴⁰. The results show the strong influence of the templates (both uniform CPG and irregular silica gel templates) on the dominant pore size of the carbons, which ranges from several to 100 nanometers.

Table 1 shows some correlation between the mesoporous carbon surface area and the area of the original template. Careful consideration of the inverse replica concept, however, indicates that this should not be a complete and correct fundamental relationship. Other parameters, such as total pore volume of template and carbon yield (which together determine carbon mass) along with possible carbonization shrinkage together govern the mass-specific surface area of the resultant carbon. The next section proposes a more complete model that provides a better description of the surface area of mesoporous carbons.

Model development—Here we develop a quantitative model of the negative replica process assuming: (1) complete infiltration of all pores, (2) negligible development of intrinsic (non-templated) microporosity, (3) a carbonization yield approximately equal to the bulk (unconfined) value for AR, 85 wt-%, (4) negligible template shrinkage or structural collapse during carbonization or cooling. All the templates we used have pore size ranging from several to hundreds of nanometers. In this range, AR molecules (1–2 nm disk-like molecules) are able to infiltrate into most of these pores by capillary forces. Separate BET surface area experiment for carbonized AR mesophase (produced without using any template) shows almost zero

surface area for the sample, indicating very limited intrinsic microporosity development. In the absence of porosity development, the organic phase must, by unavoidable geometric constraints, shrink locally within the template by a factor of $(Y \cdot \rho_p / \rho_c)^{1/3}$, where Y is the carbon yield upon heating. In an unconstrained body, shrinkage reduces area, but within a fixed template the effect of local shrinkage depends on curvatures leading either to a decrease in area (convex surfaces as in a spherical solid grain), or an increase in area (concave surfaces, as in a spherical pore). The complex pore shapes in this study should exhibit both types of curvature, so we assume that area is approximately independent of local shrinkage, and based on the negative replica concept that the absorption surface area of the two phases (carbon/inorganic) is identical but their masses are different, leading to the following geometric relation we derived for carbon area:

$$\left(\frac{A}{m}\right)_c = \frac{\left(\frac{A}{m}\right)_t}{V_{\text{pores},t} \cdot \rho_p \cdot Y} \quad (1)$$

where $(A/m)_c$ is the total carbon area per unit mass, $(A/m)_t$ is the total template area per unit mass, $V_{\text{pores},t}$ is the total pore volume of the template per unit mass, $\rho_p = 1.23 \text{ gm/cm}^3$, which is the typical density of AR mesophase pitch, and $Y = 85 \text{ wt-\%}$, which is the bulk carbon yield for AR. The predicted values are shown in Table 1 and Figure 6. The measured surface area and predicted surface area, as shown in Figure 6, match well providing support for the quantitative negative replica concept.

3.2. Characterization of surface activity

Two complementary techniques were used to assess the activity of the edge-rich surfaces selected mesophase-derived carbons.

3.2.1. Total acid site determination following nitric acid treatment—Table 2 shows the base titration data of HNO_3 -treated mesoporous carbons. The data show that acidic site density ranges from around 2.5 to 5.9 $\mu\text{mol/m}^2$, equivalent to 1.5 to 3.6 acid-sites/(nm)². In principle the calculated fractional coverage strictly depends on whether the underlying carbon edge is the zigzag or armchair plane. The theoretical edge site density on the zigzag and armchair surfaces of graphite is 12.0 and 13.8 carbon-edge-sites/(nm)² respectively. The functional groups on the carbon surface after HNO_3 treatment are believed to be complex, including a variety of groups such as carboxyl, phenolic hydroxyl, carbonyl, lactone and ester groups; nitro groups are also possible due to the nitration.⁴¹ It is difficult to determine all the functional groups quantitatively and qualitatively, and the NaOH base titration here is used to determine the total amount of acidic groups including carboxyl, hydroxyl and possibly lactone groups available on the surfaces.³⁴

Table 2 reveals several interesting trends. First, the acid site coverage for mesoporous carbons is higher for concentrated (70 wt-%) HNO_3 treatment than dilute (10 wt-%). Secondly, the acid site coverage is higher for mesoporous carbons with larger pore size. This effect may be due to the more uniform edge-on anchoring state seen in larger pore (larger carbon domain) materials. As domain size (and pore size) decrease, it becomes increasingly difficult for the discotic molecules to adopt strictly edge-on orientation at all surfaces as this requires director curvature over ever finer length scales. Finally, although higher temperature may cause carbon surface reconstruction in the form of loops or arches,^{16,42} changing the annealing temperatures from 700 °C to 1000 °C has little effect on the surface properties after HNO_3 treatment. The possible reason is that HNO_3 is a strong oxidant and it will open the reconstructed surface loops or arches, and thus makes the 1000 °C carbons indistinguishable from 700 °C carbons under

HNO₃ treatment. It has been reported that HNO₃ can effectively remove the surface loops on carbon nanofibers.⁴³

It is valuable to compare the present data on surface activity with published results for other materials. Li et al.⁴⁴ report the acidic site density of activated carbons treated with a series of HNO₃ solutions (0.5–67 wt-%) at 93 °C. The total acidic groups per BET area ranges from 0.21–3.7 μmol/m² (equivalently 0.37–3.69 mmol/g), of which about half of the acidic sites are carboxylic groups. The reported density of surface acidic groups on multi-walled carbon nanotubes (MWNTs) treated with nitric acid ranges from 0.2–0.5 a.t.%.^{45–46} Hu et al.⁴⁷ report the density of carboxylic functionality and total acidic functionality of 1–2% and 1–3% respectively for purified single-walled carbon nanotubes (SWNTs) treated under severe HNO₃/H₂SO₄ conditions. The much higher values here (2.48–5.9 μmol/m², 10–30% see Table 2) reflect higher surface defect densities due to the combination of low temperature synthesis and uniformly exposed edge sites due to the liquid crystal origin of these carbons. Overall there is evidence that the edge-rich surfaces on the mesophase-derived porous carbons in this study have a higher activity to nitric acid than activated carbons and multi-wall or single-wall nanotubes, both conventional carbon forms that do not possess ordered molecular architecture with all-edge surfaces.

3.2.2. Active surface area by oxygen chemisorption—Table 3 shows the calculated active surface area (ASA) and surface active site coverage (ASA/TSA); i.e. the portion of total surface area (TSA) that is active for chemisorption. In general the active sites include the edges of the basal plane, twin boundaries, imperfections such as vacancies, dislocations, and impurity sites, steps in the basal plane, etc. ASA is calculated as the product of carbon active site cross-sectional area (0.083 nm²)³⁵ and the total number of accessible active sites, which is derived from the amount of CO and CO₂ that is desorbed. The calculated ASA/TSA of the mesoporous carbons is about 5%. For comparison, Ehrburger et al.⁴⁸ report similar ASA/TSA ratios (3–6%) for phenolic carbon fibers, which are disordered materials. The more ordered carbon fibers from mesophase or PAN precursors have an ASA/TSA ratio of 4–5%⁴⁹, that remains relatively constant with burnoff.⁴⁸ The ordered carbon, Graphon, is reported to have an initial ASA/TSA ratio of 0.29% that rises with partial gasification to an asymptotic maximum of 3.1%.³⁵ Thus many different carbon materials show similar maximum ASA/TSA ratios to the ordered-self-assembled carbons in this study. We also note that the active site coverage is higher for mesoporous carbons with larger pore size, and possess different CO/CO₂ ratios. This suggests that the surfaces have different proportions of sites that form functional groups that decompose to form CO and those that decompose to form CO₂.

An important fundamental question is why these mesoporous carbon surfaces, which by crystal orientation should be populated by only graphene edge sites, cannot be functionalized at densities approaching 100%. One explanation is the tendency of the graphene edge plane to undergo spontaneous reconstruction to reduce surface energy and cap exposed carbon active sites.^{16,42} Figure 7 shows typical surface reconstructions observed in various edge-carbon surfaces from the Brown laboratories. These surface reconstruction features have been observed to form at temperatures as low as 600 °C¹⁶ and are quite common at higher annealing temperatures^{16,42,43}.

These reconstruction features are expected to limit functionalization density on edge planes. They may also be responsible for the lower surface coverage determined by the oxygen chemisorption technique (~ 4–5% ASA/TSA) relative to the total acid site titration on HNO₃ treated surfaces (as high as 30%) by the following argument. The chemisorption technique involves vacuum thermal desorption of oxides to produce the bare unfunctionalized surface, which is then cooled for the next oxygen chemisorption cycle. Applied to our all-edge surfaces, this treatment would produce continuous arrays of neighboring active sites that would impart

an extremely high energy to the freshly desorbed surface and a correspondingly high driving force for reconstruction. We imagine that single active sites on conventional carbon surfaces may be metastably trapped (and thus observable) while pairs or clusters of immediately adjacent active sites on our self-assembled surfaces may readily undergo small-scale collective rearrangements to reduce what would be a very high local surface energy. The present data (4–5 % ASA/TS) suggest that such bare all-edge planes are too energetic to be realized in practice. The HNO₃ treatment on the other hand can attack reconstruction films, arches, or interstitial amorphous carbon atoms and lead to new active sites on the underlying (unreconstructed) edge plane that are immediately functionalized and thus stabilized with oxygen groups. Unlike the chemisorption/thermal-desorption-cycle, the HNO₃ treatment never requires formation of the bare, all-edge surface, but rather uses progressive functionalization to minimize surface energy continuously during the reactive treatment, which occurs isothermally, not in chemisorption/desorption cycles. The higher apparent functionalization densities with nitric acid may also be due to the formation of complex product films on inner surfaces that are stable to washing.

4. Conclusions

The use of liquid crystalline precursors for templated mesoporous carbons allows simultaneous control of both pore structure and interfacial crystal structure through the well-defined rules of liquid crystal surface anchoring. AR mesophase is a particularly advantageous precursor for the synthesis of "designer" mesoporous carbons. It exhibits a high carbon yield with almost no intrinsic porosity, so the pore structure can be completely controlled by template selection and can be approximately predicted by quantitative application of the geometric negative replica concept. When silica or other oxide templates are used the favored anchoring state is edge-on, yielding inner surfaces rich in active edge sites. There is evidence that these surfaces have higher chemical activity than conventional carbon surfaces and show total acid site densities as high as 30% following nitric acid treatment. Mesophase-derived templated porous carbons may find applications where a controlled mesopore size is required in combination with high surface activity or functional group density.

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Figure 1.

Known discotic molecular configurations caused by micro- and nano-confinement of mesophase pitch in various geometries: (a) cylindrical,^{15–16} (b) hour-glass,²² (c) laminar,²⁰ and (d) spherical structures, which include Brooks-Taylor mesospheres²⁷ observed at micron length scales, and the homogeneous domains favored at the nanoscale²². These structures are selected by the combination of edge-on anchoring (preferred at most interfaces²⁶, and the avoidance of curvature in the director field which produces elastic strain.

Figure 2.

Morphology of CPG template derived mesoporous carbons. (A) SEM image of carbon CPG-45-C, which shows the interconnected porous nature of the carbon with solid “grains” of about 40 nm in diameter, (B) SEM image of carbon CPG-12-C, with similar morphology, but on a smaller length scale, (C) TEM image of carbon CPG-25-C showing interconnected grains, and (D) High-resolution TEM fringe image of the nanophase carbon derived from 100 nm CPG template revealing the graphene layer orientation perpendicular to the mesoporous carbon grain edges, reflecting the original edge-on anchoring state of the liquid crystalline precursor on glass. The white bars in (D) indicate the dominant orientation of the graphene layers. Exposed edge sites can be directly observed on the surface in this particular image.

Figure 3. Morphologies of original SG-15 silica gel template (A), and the resulting mesoporous carbon (B).

Figure 4.
XRD patterns of mesoporous carbons (CPG-25-C) as a function of post-synthesis annealing temperature.

Figure 5.

Pore size distribution of various mesoporous carbons derived from (a) 12 nm CPG, (b) 25 nm CPG, (c) 45 nm CPG, (d) 70 nm CPG, (e) 6 nm silica gel, and (f) 15 nm silica gel.

Figure 6.
Comparison of model prediction to measured total surface areas for a range of mesoporous carbons.

Figure 7.

Typical reconstruction features observed on the outward facing graphene edge planes in mesophase-derived carbons : (a) closed half-circular loops or half-nanotube arches, 600 °C carbon nanofibers¹⁶, (b) ultrathin films of 1–2 graphene layers covering active edges, 700 °C carbon nanofibers¹⁵, (c) amorphous materials, inner surfaces of mesoporous carbons²², and (d) closed hairpin loops on 2500 °C annealed carbon nanofibers¹⁶. All scale bars are 2 nm.

Table 1

Pore structure characterization* of templates and templated carbons

Template and nominal pore size	BE/T surface area of template (m ² /g)	Total pore volume of template (cc/g)	Measured BE/T surface area of carbon (m ² /g)	Measured Pore volume of carbon (cc/g)	Predicted (from Eq. 1) surface area of carbon (m ² /g)
<i>CPG</i>					
12 nm	116	0.61	247	0.77	182
25 nm	82	0.97	144	0.44	81
45 nm	47	0.77	62	0.40	59
70 nm	39	0.84	44	0.25	44
100 nm	31	1.3	25	0.23	23
<i>Silica Gel</i>					
6 nm	497	0.83	559	0.63	573
15 nm	269	1.15	316	0.44	225

* Based on full 20 point N₂ vapor adsorption isotherms at 77K.

Table 2

Base-titration data of HNO₃ treated mesoporous carbons.

Sample	Annealing temperature (°C)	HNO ₃ (wt-%)	Density of acid sites (μmol/m ²)	Density of acid sites #/(nm) ²	Apparent acid site coverage Zigzag (%)	Apparent acid site coverage Armchair (%)
<i>CPG-25-C</i>						
1	700	10	2.78	1.67	14.0	12.1
2	700	70	3.52	2.12	17.7	15.4
3	1000	10	2.76	1.66	13.9	12.0
4	1000	70	3.10	1.87	15.6	13.5
<i>CPG-70-C</i>						
1	700	10	2.48	1.49	12.5	10.8
2	700	70	5.90	3.55	29.7	25.7
3	1000	10	4.02	2.42	20.2	17.5
4	1000	70	4.49	2.70	22.6	19.6

Note: Density of acid sites = Acidic sites / BET surface area.

Table 3

ASA analysis of mesoporous carbons by oxygen chemisorption

Sample	ASA (m ² /g)	CO/CO ₂	ASA/TSA(%)
CPG-25-C			
Experiment 1	5.87	4.02	4.8
Experiment 2	5.41	3.78	3.8
Experiment 3	5.48	3.88	3.8
CPG-100-C			
Experiment 1	1.35	2.82	5.4
Experiment 2	1.30	2.78	5.2