Synthesis of highly ordered nanoporous carbon molecular sieves from silylated MCM-48 using divinylbenzene as precursor

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Calcined pure silica MCM-48 is modified by silylating its mesopores with trimethylsilyl chloride; such pore modification along with polymerization and carbonization of divinylbenzene as a carbon precursor is found to be a very efficient way of fabricating highly ordered carbon molecular sieves with three-dimensionally interconnected uniform pore arrays, greatly improving structural integrity and thermal stability.

Porous carbons have been greatly studied as adsorbents and electrode materials.[1,2] Since zeolites and other molecular sieves including mesoporous materials possess several attractive characteristics such as high surface area and periodic arrays of uniform pores, they can be used as synthesis templates for carbon with regular pore structures.[3,4] Polymerization and pyrolysis of acrylonitrile were demonstrated in zeolite Y and mordenite channels.[5] The formation of porous carbon by carbonization of poly(acrylonitrile) and poly(furfuryl alcohol) was reported in Y zeolite template.[6] The phenol–formaldehyde polymers and their carbons were also studied in Y, β and L zeolites.[7] However, the pore ordering was not well maintained in the porous carbon structure due to the non-rigidity of the carbon frameworks formed in the narrow pores of zeolites. Most recently, carbon frameworks with ordered pores were reported using mesoporous templates. Ordered porous carbon replicas of the MCM-48 template were reported by converting sucrose in the channels into carbon using an acid catalyst.[8] Mesoporous carbon was also synthesized by acid-catalyzed polymerization of phenol and formaldehyde in Al-implanted MCM-48 followed by carbonization.[9] Here we report the novel synthesis of highly ordered mesoporous carbon materials using a pure silica MCM-48 template with surface-modified pores and divinylbenzene as a carbon precursor. Particularly, this method provides the first example of mesoporous carbon with much improved structural integrity and thermal stability.

High quality silica MCM-48 was prepared using $C_{16}H_{33}N(CH_3)_3Br$ and Brij 30 as surfactants and colloidal silica Luodx HS40 as the silica source based on the modification of reported methods.[10] Calcined silica MCM-48 was first modified by a simple silylation using trimethylsilyl (TMS) chloride according to methods described in literature.[11] After such a silylation, more than 90% of the silanol groups in the pores were replaced with TMS groups [eqn. (1)].

$$(silica){\equiv}SiOH + (CH_3)_3SiCl \rightarrow (silica){\equiv}SiOSi(CH_3)_3 + HCl \quad (1)$$
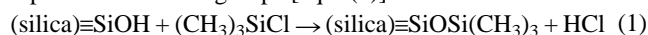
This was confirmed by the decrease of a signal at 960 cm^{-1} corresponding to Si–O stretching in the Si–OH groups before silylation and by the concomitant development of two new signals at 845 and 2960 cm^{-1} ascribed to attached OSi(CH$_3$)$_3$ groups in the infrared spectra as reported in previous work.[11–13] We denote TMS-modified MCM-48 as TMS-MCM-48 in order to distinguish it from pure silica MCM-48. Such TMS-MCM-48 showed higher hydrophobicity and nonpolarity[11,13] which were confirmed by a marked decrease of a broad signal centered at 3450 cm^{-1} due to physically attached water in the mesopore. The modified pores in the templates were filled by soaking the TMS-MCM-48 template into a carbon precursor solution of 80% divinylbenzene (DVB) with a free radical initiator, azobisisobutyronitrile (AIBN) (DVB–AIBN mole ratio $\cong$ 10).

Dissolved oxygen was removed by several freeze–pump–thaw cycles. Polymerization was performed by heating to 70 °C overnight. The resulting polymer was heavily cross-linked in the template pores. The template–polymer composites were then heated under N$_2$ gas flow at a heating rate of 1 °C min^{-1} to 750–850 °C and then held under these conditions for 7–10 h to carbonize the polymer. Porous carbon was obtained after subsequent dissolution of the silica framework in 48% aq. HF. The same procedures were also performed on calcined silica MCM-48 without any surface modification. The yield of obtained carbons was about 70–80% in both cases.

XRD patterns were measured at various stages during the course of synthesis (Fig. 1). Two intense peaks with about equal intensity at $2\theta = 1.6$ and 2.7 in synthesized carbon materials indicate long-range ordering of highly ordered uniform mesopores. It is interesting to note that the first intense peak not seen in parent MCM-48 template occurs in the synthesized carbons. The peak was suggested to occur due to the phase transition of MCM-48 with *Ia3d* space group to a new cubic phase with *I4*$_1$*32* space group due to shrinkage of the carbon walls upon removal of the silica framework.[8] Surprisingly, the overall XRD intensity for TMS-MCM-48 porous carbon was about two times higher than ones for the parent calcined silica MCM-48 template and for the MCM-48 carbon. Elemental analysis of the porous carbon replica shows a C:H mole ratio of about 23 (C 98.01 and H 0.35 wt%). Energy dispersive X-ray spectrophotometer analysis determined by field emission scanning electron microscopy also indicated a predominantly strong carbon signal at 0.270 keV with a weak residual undissolved silica signal at 1.752 keV.

TEM images from the thin edges of the porous carbon molecular sieves show a regular array of holes separated by walls (Fig. 2). The TMS-MCM-48 porous carbon showed much
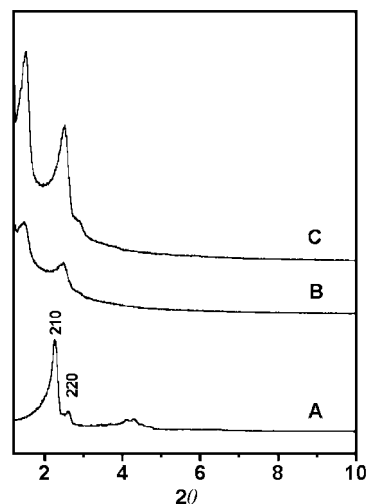

Fig. 1 X-Ray diffraction patterns of (a) calcined pure silica MCM-48 and mesoporous carbon obtained by using (b) silica MCM-48 and (c) TMS-MCM-48 as templates. These XRD patterns were obtained using a Rigaku D/MAX-III (3 kW). Each spectrum was measured under identical experimental conditions.
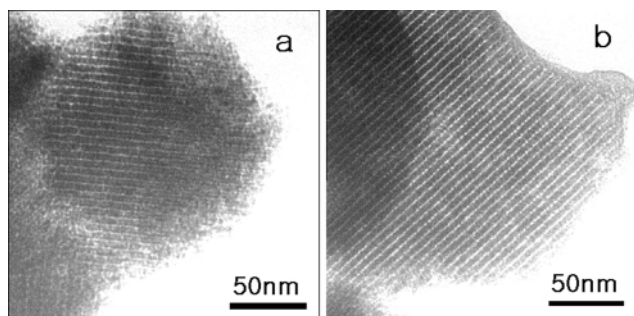
Fig. 2 Transmission electron micrograph (TEM) images of mesoporous carbon obtained by using (a) silica MCM-48 and (b) silica TMS-MCM-48 as templates.

better overall structural order than the MCM-48 porous carbon, which is also in good accordance with XRD results. The specific surface areas of the carbons were found to be 1200 ± 50 m^2 g^{-1} for nitrogen BET adsorption measurements. The pore size distribution data calculated from the adsorption branch of nitrogen adsorption–desorption curves by the BJH (Barrett–Joyner–Halenda) method showed that pores are uniform with quite narrow pore size distribution centered at 2.4 ± 0.2 nm.

Thermogravimetric (TG) weight change was recorded to study the thermal stability of carbons formed by carbonization of DVB in MCM-48 template under an O$_2$ atmosphere (Fig. 3). There was significant weight loss in a narrow temperature range at *ca.* 830 K for DVB carbon. The high temperature for DVB carbon, in good agreement with those for nanotubes and other graphitized carbons[14,15] indicates that the DVB carbon may have a graphitic nature. The corresponding TG temperature was near to 680 K for sucrose carbon in previous work.[8] This clearly indicates the DVB carbon with much improved thermal stability. Mechanical strength measured by monitoring XRD intensity changes after each pressurizing cycle of the pelletized carbon (100 mg and 1/2 inch diameter) for 1 min with gradually increasing pressure indicates that the DVB carbon was stable with no significant intensity change at pressures less than 4.0 ton cm^{-2} and above that, started decreasing its intensity slowly with 75% XRD intensity maintained at pressures of 4.8 ton cm^{-2} compared to the original intensity at atmospheric pressure. Calcined silica MCM-48 with high crystalline order and its silylated MCM-48 prepared here were stable at pressures of less than 2.4–2.7 ton cm^{-2} and *ca.* 3.0 ton cm^{-2}, respectively, but above these pressures, they started losing their crystallinity. This indicates that the mesoscopic porous carbon prepared here has much higher mechanical strength than the silica template.

In this work, we have obtained high quality mesoporous carbon with much better structural order for TMS-MCM-48 compared to those for MCM-48. This is unclear, but is perhaps
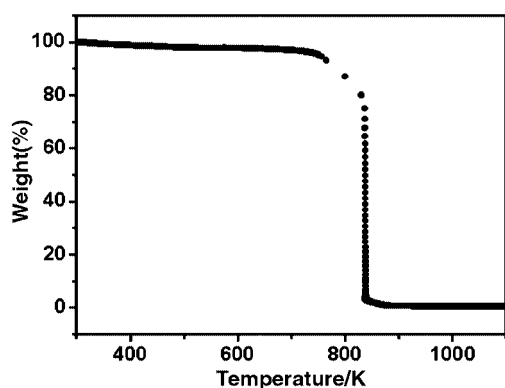
due to the removal of oxygen sources in TMS-MCM-48 which are an effective quenching agent for DVB radical polymerization by replacing Si(OH)$_{1 \text{ or } 2}$ with SiOSi(CH$_3$)$_3$ *via* silylation. TMS-modified pores are also extremely hydrophobic compared to unmodified ones,[11,13] repelling more water molecules which can also be potential radical reaction quenchers and thus allowing more room for carbon precursors to fully fill the mesopore channels. Carbon prepared with phenol and formaldehyde was shown to have low thermal stability and lower structural ordering.[8] Also when we measure the XRD intensity ratios of the mesoporous carbon *versus* the parent calcined pure silica MCM-48 template as determined from a flat base line, our high quality carbon showed a much higher ratio of 2.2–2.5 than carbons prepared by carbonization of sucrose of about 1.3–1.6.[8] In addition, MCM-48 templated DVB carbon shows higher thermal stability than the corresponding sucrose carbon.

In summary, two major factors were considered in this work to improve the quality of mesoporous carbons: hydrophobicity of the template channels and the carbon precursor. The surface modification of the MCM-48 template and the use of DVB as a carbon precursor are considered to be a most efficient way of synthesizing highly ordered mesoporous carbons with greater structural integrity and thermal stability. We are currently carrying out further studies to evaluate this method which can be extended to the preparation of other high quality mesoporous carbons. We have synthesized carbons in the MCM-41 template using the same method. TEM pictures of the extracted carbon fibers showed continuous linear patterns due to carbon nanofibers, but in general not as orderly as the MCM-48 templated carbon because the fibers are not bound to each other in MCM-41. The highly ordered mesoporous carbon materials with superior structural integrity and thermal stability will find many new advanced applications in the future.

Fig. 3 Thermogravimetric weight change curve under an O$_2$ atmosphere for MCM-48 templated carbons prepared by the carbonization of DVB.

Notes and references

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