PREPARATION OF POROUS CARBONS FROM HALLOYSITE-SUCROSE MIXTURES

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Abstract—Porous carbons rich in mesopores and with large pore volumes have been prepared by polymerization and carbonization of a carbon precursor, sucrose, within a matrix of the natural clay, halloysite. The carbon precursor was impregnated into the pores of halloysite and mostly deposited on the external surface of the halloysite rods during impregnation. The inorganic matrix was removed by washing the carbon-mineral composite with HF and HCl. The resultant carbons were characterized by nitrogen adsorption analysis and were found to possess a large specific surface area, a large total pore volume and significant mesoporosity, without an activation process being involved. The pore volume and mesoporosity were up to 1.86 cm^3/g and 78%, respectively, even at low carbonization temperatures (500ºC). The size of the mesopores of the resultant carbons is mainly between 3 and 30 nm and the dominant pore size is ~3.7 nm. The carbonization temperature has significant effects on the pore-size distribution and structure of the resultant carbons and carbon-mineral composites, respectively. This process is relatively simple and expected to cost less than the high-temperature carbonization process in the preparation of mesoporous carbons with total pore volume and large specific surface areas.

Key Words—Adsorption, Electron Microscopy, Natural Clay, Pore Volume, Pore-size Distribution, Porous Carbon.

INTRODUCTION

Mesoporous carbons with a large total pore volume have attracted much attention because of their potential use in areas of growing interest, including catalyst support, electric double-layer capacitor (EDLC) electrodes, and adsorption of large molecules in liquid phase (Lee *et al.*, 1999; Kyotani, 2000; Alvarez and Fuertes, 2004). For such applications, a strict control of pore structure in the carbons is required if one wants to optimize their performance. Of late, the template approach has proved very feasible. Several authors employing this method (Jun *et al.*, 2000; Kruk and Jaronic, 2000; Joo *et al.*, 2001; Ryoo *et al.*, 2001; Shi *et al.*, 2004) synthesized carbons composed mainly of mesopores using inorganic silica materials such as SBA-15 (Jun *et al.*, 2000; Ryoo *et al.*, 2001; Shi *et al.*, 2004), SBA-1 (Kruk and Jaronic, 2000) and MCM-48 (Kruk and Jaronic, 2000; Joo *et al.*, 2001) as templates. However, almost all of the templates they used were artificial materials. To prepare mesoporous carbons in this way is not only expensive but also complex. However, choosing natural inorganic minerals, such as

clay and zeolite (Bandosz *et al.*, 1996; Meyers *et al.*, 2001; Barata-Rodringues, 2002; Liu *et al.*, 2005) as the inorganic matrix makes it more feasible. However, most carbons derived from carbon-mineral complexes have small specific surface areas and small pore volumes: the synthesis of materials within a matrix depends critically on the structure and properties of the matrix (Bandosz *et al.*, 1996). In this work, we report a facile method for synthesizing porous carbons, rich in mesopores, with a greater Brunauer-Emmett-Teller (BET) specific surface area and larger pore volume, from a halloysite-sucrose mixture. Halloysite is a typical kaolin clay mineral with greater purity and mesoporosity than other natural kaolin clay minerals. It also contains many types of water molecules within its structure and has a regular tubular morphology, which implies that using halloysite as a matrix should make it possible to synthesize porous carbons with a large specific surface area directly, without any additional activation processes. During the preparation of carbons, the inexpensive carbon source, sucrose, was dissolved in de-ionized water and introduced into the space of the template by the liquid-impregnated method (Ryoo *et al.*, 2001). In this work, we successfully prepared several kinds of porous carbons with large total pore volumes (the largest was ~2.16 cm^3/g), large degrees of mesoporosity, and large BET surface areas (>1000 cm^2/g) using halloysite as the matrix. These kinds of mesoporous carbons could be used in catalyst support, EDLC electrodes and adsorption for bulky molecules in the liquid phase.

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EXPERIMENTAL

Synthesis of porous carbons

The inorganic matrix used in this work was halloysite, a type of natural kaolin clay, in this case from Hunan Province, China. It is a tubular aluminosilicate with the chemical composition [$Al_2Si_2O_5(OH)_4.2H_2O$]. It was dried at 110ºC for 24 h before use. To polymerize and solidify the sucrose used in the process, sulfuric acid was used as the acid catalyst to prepare porous carbons (Joo *et al.*, 2001).

In the first case, 25.0 g of sucrose were dissolved in 50.0 g of de-ionized water to prepare the sucrose solution. The sucrose solution was introduced into 5.0 g of halloysite matrix by incipient wetness impregnation. Afterwards, 2.8 g of sulfuric acid were added into the mixture of halloysite and sucrose solution. This mixture was stirred for 5 days at room temperature. After that the mixture was filtered and washed three to five times with de-ionized water in order to remove the sucrose from the external surface of the halloysite particles followed by polymerization at 100ºC for 12 h, and subsequently heated at 150ºC for another 2 h. For the carbonization, the polymerized composites were heat treated under nitrogen atmosphere from room temperature to the preset temperature at a heating rate of 5ºC /min and then kept for 3 h in order to complete the carbonization. The carbonization temperatures were set at 500ºC, 600ºC, 700ºC, 850ºC, 900ºC and 950ºC. After carbonization, the halloysite-carbon composites were immersed in 40 wt.% HF solution and stirred for 3 h (10 mL of HF solution per gram of composite), then kept overnight, and re-stirred for 5 to 6 h at room temperature. This demineralization procedure was repeated once again to remove the inorganic matrix completely. Subsequently, the insoluble carbon was washed several times using de-ionized water, then treated with 36 wt.% HCl solution for 2 h to purify the carbons. Finally, the resultant carbons were collected by filtering and washing with de-ionized water and drying in an oven at 120ºC for 3 h.
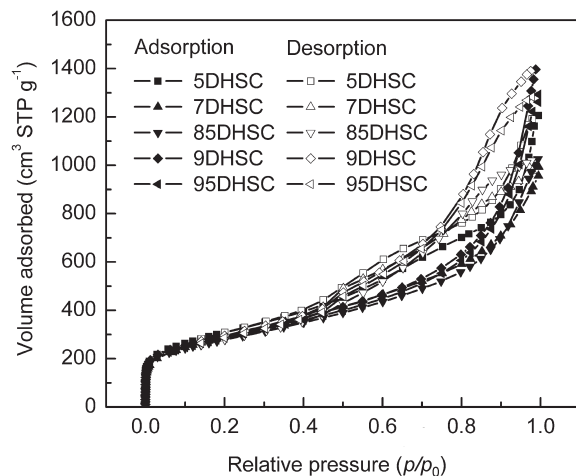
Samples in different synthesis stages were denoted here as H_0, HS, HSCC and DHSC, respectively, where H_0 is the original template halloysite, S represents sucrose, D represents de-mineral, HSCC represents the composite of halloysite and carbon after carbonization without de-mineral treatment, while DHSC represents the resultant carbon after removal of the template. In addition, in order to distinguish the samples obtained from different carbonization temperature, the composites after carbonization are denoted as 5HSCC, 7HSCC, 85HSCC, 9HSCC and 95HSCC, and the corresponding resultant carbons are denoted as 5DHSC, 7DHSC, 85DHSC, 9DHSC and 95DHSC, respectively. The number represents the corresponding carbonization temperature. For example, the number '5' represents 500ºC.

Characterization

Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP2010 system. The specific surface areas (S_{BET}) of all the carbons were calculated by the BET method using the adsorption data in the relative pressure range of $0.01-0.20$. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of ~0.99 ($V_{0.99}$). The micropore volume (V_{mic}) was calculated using the t-plot method. The mesopore volume (V_{meso}) was determined by subtracting the micropore volume from the total volume. The pore-size distribution curve was obtained using the Brunauer-Joyner-Halenda (BJH) method from the desorption branch. The crystalline phases in the samples were examined using X-ray diffraction (XRD, D/Max-rBX with CuKα radiation). Field emission scanning electron microscopy (FESEM) images were captured using a JSM-6700 FE-SEM device. Thermal analysis (TG-DTA) was carried out under nitrogen atmosphere on a high-temperature comprehensive thermal analyzer of type ZRY-2P.

RESULTS AND DISCUSSION

Nitrogen adsorption analysis

The nitrogen adsorption-desorption isotherms and BJH pore-size distributions are shown in Figures 1 and 2. All the carbons possessed remarkable adsorption uptake and exhibited typical type IV with H3 type hysteresis loops (Gregg and Sing, 1982). This indicates that all the carbons possess a high proportion of mesopores and the pore is slit-shaped. In addition, almost all the isotherms possess a very narrow platform, which indicates that all the resultant carbons possess very few micropores. From the BJH pore-size distributions obtained (see Figure 2), it can be seen that all the resultant carbons possess narrow mesopore size distributions between ~3 and 30 nm and all the carbon samples show a very sharp peak at ~3.7 nm. The carbonization temperature has many effects on the pore-size distribution of resultant samples. At lower

Figure 1. N_2 adsorption isotherms of the resultant carbons.

Table 1. Specific surface area and pore characteristics of halloysite and the resultant carbons.

Sample	S_{BET} (m²/g)	S_{mic} (m²/g)	V_{total} (cm³/g)	V_{meso} (cm³/g)	V_{micro} (cm³/g)	Mesoporosity (%)
H_0	78	15	0.21	0.18	0.01	86
5DHSC	1070	108	1.86	1.46	0.04	78
7DHSC	1050	88	1.48	1.10	0.03	74
85DHSC	990	196	1.59	1.21	0.09	76
9DHSC	1050	159	2.16	1.77	0.07	82
95DHSC	1020	152	1.95	1.57	0.06	80

S_{BET}: BET specific surface area. S_{mic}: specific surface area of micropores. V_{total}, V_{meso} and V_{micro}: volumes of total pores, mesopores and micropores, respectively. Mesoporosity = V_{meso}/V_{total}

carbonization temperature, the pore-size distributions in mesopore and macropore ranges become broader. The pore-size distribution changed from nearly unimodal distribution (5DHSC) to bimodal (9DHSC) or tri-modal distribution (95DHSC) with increasing carbonization temperature. These results may be attributed to the burning of micropores and the smaller mesopores into the corresponding mesopores or larger mesopores with increasing carbonization temperature.

Table 1 summarizes the BET specific surface area (S_{BET}), micropore surface (S_{mic}) and pore volumes of halloysite and the resultant carbons. The mesoporosity of halloysite and resultant carbons obtained under different conditions were calculated using the ratio of the V_{meso} and the value of the volume at a relative pressure of ~0.99. It can be seen from Table 1 that most carbons possess mesopore volumes which are as large as the total pore volumes (the largest mesopore volume is 1.77 cm³/g and the corresponding total volume is 2.16 cm³/g). The resultant carbons obtained using halloysite as the template also exhibit significant mesoporosity and have small micropore surface areas, indicating that the BET specific surface areas of the resultant carbons are contributed by the mesopores. It is noteworthy that the pore volume and BET specific surface area of resultant

carbons are also high even at low carbonization temperature (500ºC). As most carbons with large specific surface areas are usually obtained at higher carbonization temperatures ($\geqslant$700ºC), this method maybe an energy-efficient means of preparing porous carbons with larger specific surface areas. All the BET specific surface areas and total pore volumes in Table 1 are much larger than were obtained by Barata-Rodrigues (2002) (total pore volume is 0.538 cm³/g and S_{BET} is 446 cm²/g) who used another type of natural clay, Wyoming bentonite, as a template, and furfuryl alcohol as the carbon precursor. The main reason for this difference may be ascribed to the different inorganic matrix and carbon precursor used.

X-ray diffraction (XRD)

The XRD patterns of the original halloysite and of the halloysite dried at 110ºC are both shown in Figure 3. The halloysite used consists mostly of halloysite-10 Å, and that interlamellar spacing of original halloysite is easily transformed into 7 Å when drying at 110ºC. Halloysite-10 Å can also be transformed into halloysite-7 Å at room temperature while the inversion is irreversible (Zheng *et al.*, 1987). Figures 4 and 5 show
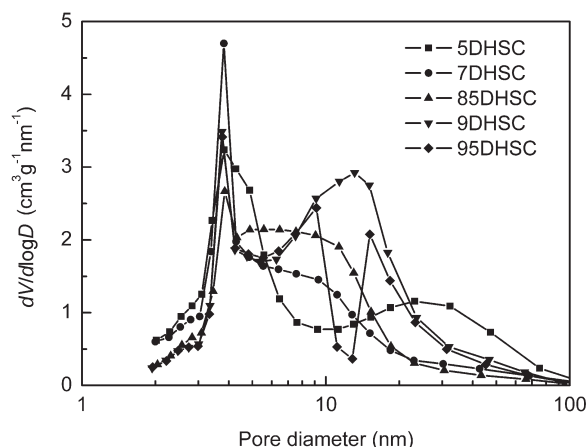

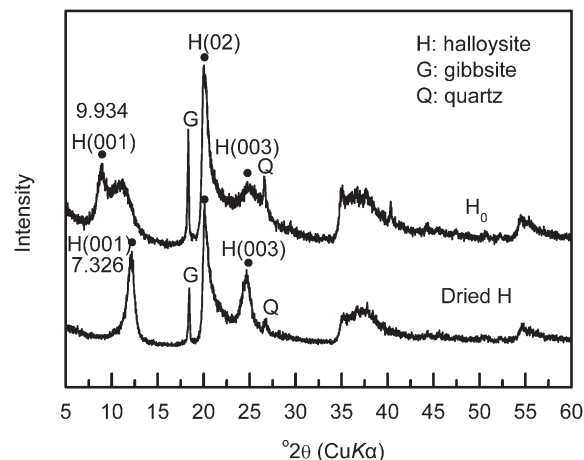Figure 2. BJH pore-size distribution curves of the resultant carbons.

Figure 3. XRD patterns of halloysite H_0 as received, and of the dried sample.
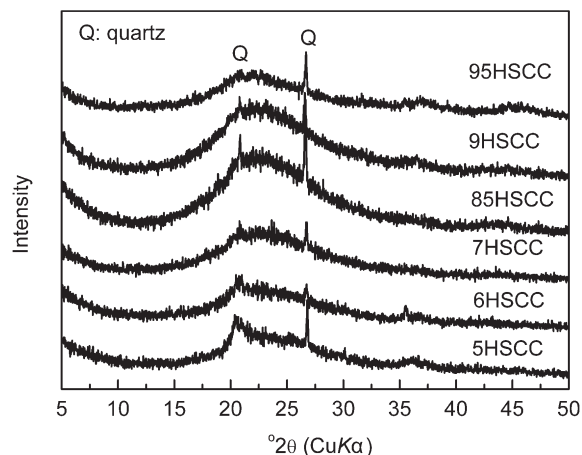
Figure 4. XRD patterns of carbonized composites and HSCC composites.

XRD patterns of halloysite-carbon composites and several resultant carbons obtained at different carbonization temperatures, respectively. As can be seen in Figure 4, there are no diffraction peaks for halloysite after high-temperature carbonization, as halloysite is structurally unstable, but the quartz peaks are preserved and the broad diffraction effect due to X-ray amorphous carbon shows a significant increase with increasing carbonization temperature.

The XRD patterns of carbons using halloysite as a matrix (Figure 5) show two broad diffraction effects at angles of ~23 and 44°2θ, corresponding to X-ray amorphous carbon. The diffraction peak at ~35°2θ (95DHSC) was caused by a small impurity in the inorganic matrix which was retained in the resultant carbons. The EDS element analysis of 95DHSC suggests that there is a small amount of Al, C, O and F in the resultant carbons. From Figure 4, the weak peak at ~35°2θ can also be found in the composite of 95HSCC, which might be an α-Al_2O_3 phase which was formed at
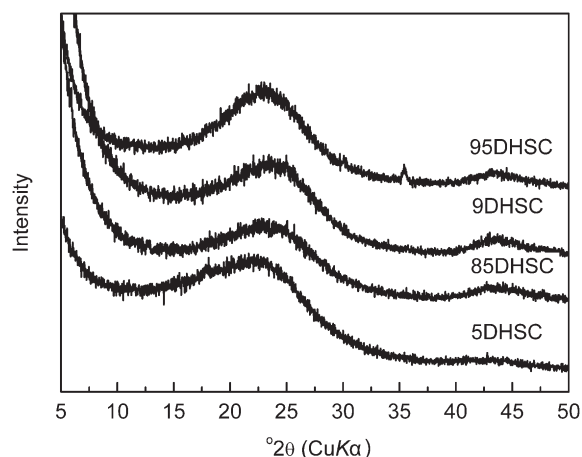
950°C. The Al_2O_3 was entrapped in the resultant carbons and it is difficult to remove completely by acid treatment.

Thermogravimetric and differential thermal analysis

The TG-DTA curves for original halloysite (H_0) and the polymerized mixture of halloysite and sucrose (HS) are shown in Figure 6. The endothermic peaks of halloysite at 90°C and 515°C are due to dehydration of interlayer water and dehydroxylation of octahedra (Zheng *et al.*, 1987; Chi *et al.*, 1995; Zeng *et al.*, 1996; Xiao *et al.*, 1997; Yi *et al.*, 1997; Islam *et al.*, 2002; Singer *et al.*, 2004). The second endothermic peak at a temperature of 281°C confirms the presence of gibbsite in the halloysite. The fourth endothermic peak at a temperature of 930°C is due to the derivation of structural water (Islam *et al.*, 2002). The DTA curve of the polymerized composites (HS) below 550°C is similar to that of original halloysite (H_0) but apparently is different at >550°C. It shows a very sharp endothermic trend and we reason that both the diffusion of water vapor from the inner to the outer part of the sample and the activation of carbon need considerable energy during the carbonization and activation stages. We think that the water present between the mineral layers is an important factor that can influence the microstructure of resultant carbons and mineral-carbon composites. The water released from the parent matrix during simultaneous dehydroxylation-carbonization can create small pores the sizes of which depend on the extent of water available and the thickness of the carbon deposit. Both factors are responsible for the subtle differences in the microstructures of the final materials.

Scanning electron microscopy

Figure 7 shows SEM images of (a) halloysite, (b) polymerized composites (HS), (c) carbonized composites (HSCC), and (d) the resultant carbons (DHSC) prepared at 850°C. The morphology of the resultant
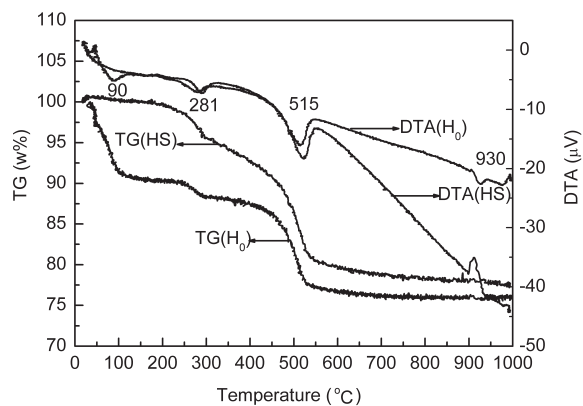

Figure 5. XRD patterns of several resultant carbons.

Figure 6. TG/DTA curves of halloysite H_0 and of polymerized composites HS.
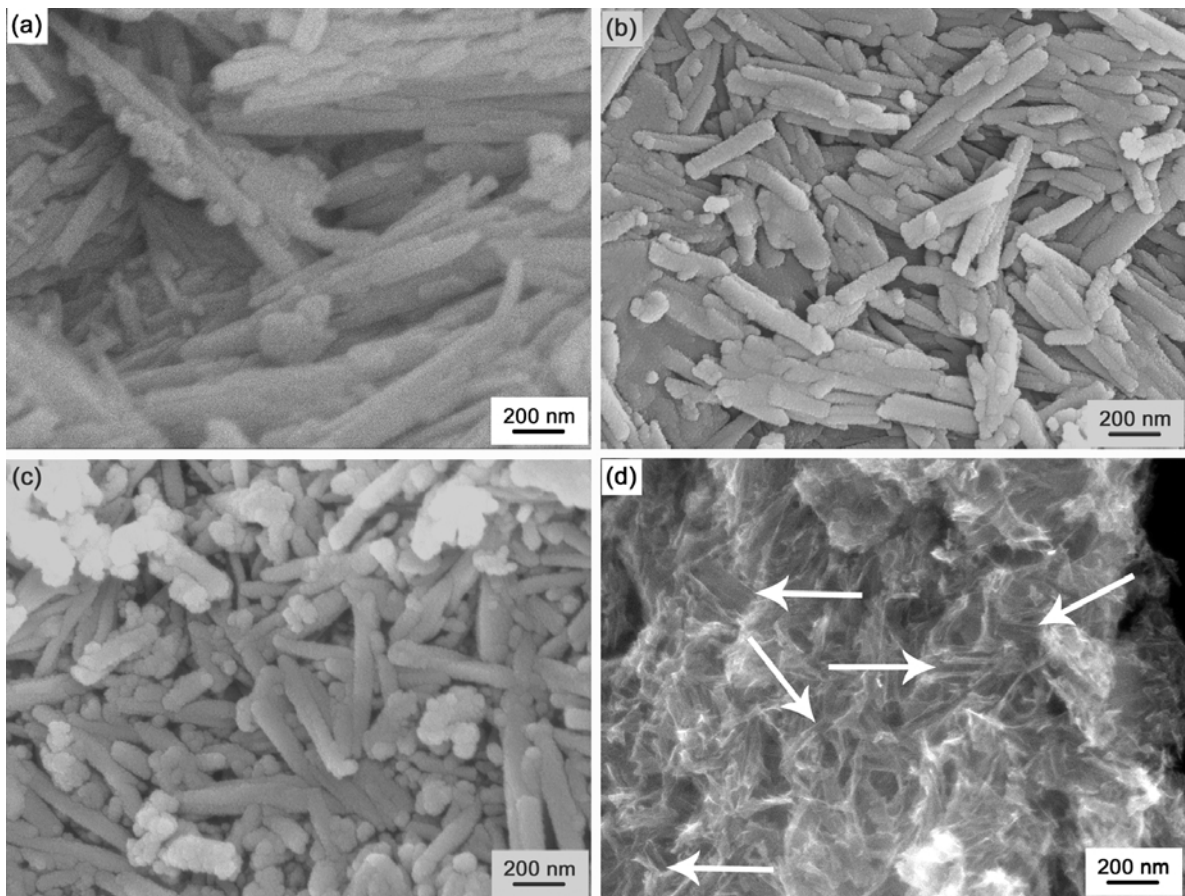
Figure 7. SEM images of samples halloysite H_0 (a), polymerized composites HS (b), carbonized composites HSCC (c), and the resultant carbon DHSC (d).

carbon (d) is apparently different from those of the former three images. The parent mineral was composed of aggregation of bundles of needle-like halloysite rods. Besides the similarities, the surfaces of polymerized composites and carbonized composites look rough, and the arrangement of the rods is more random in comparison with the original halloysite. The former is due to the deposition of the carbon source on the outer surface of halloysite, and the latter can be ascribed to the subtle change of polarity from mineral to carbon. With the resultant carbons (see Figure 7d), we could not find needle-like tubes in the SEM image, suggesting that very little carbon precursor was impregnated into the pores of halloysite. The very thin carbon membrane, which forms on the inner surface of halloysite during carbonization, breaks during the demineralization step. The apparent network structure of the resultant carbons was formed in the bulk material. If the diameters of the grooves are compared with those of the original halloysite tubes, it can be seen that the dimensions of the grooves are similar to those of the original tubes or those of aggregations of the host tubes. These resemblances indicate that the carbon precursors are mainly retained on the external surface of the halloysite tubes that formed grooves (indicated by arrows) when halloysite was removed at the demineralization step. On the other hand, this observation gives further support to the conclusions drawn from the XRD analysis.

CONCLUSIONS

Carbons with large total pore volumes and significant mesoporosity (74–82%) can be prepared from halloysite-sucrose mixtures. The size of the mesopores of the resultant carbons is between 3 and 30 nm, and the dominant pore size is ~3.7 nm. The mesoporous carbons with larger specific surface areas and larger total pore volumes (1.86 cm^3/g) can be derived even under low carbonization temperature (500°C), and the carbonization temperature can affect the BJH pore-size distributions of the resultant carbons, though it has no apparent effects on the pore volume or specific surface area. The mechanism of mesoporosity development might be that the carbon source was impregnated into the pores of the halloysite clay and deposited mostly on the external surface of the halloysite tubes. The water released from the mineral matrices maybe act as an activation agent that can activate the carbon during carbonization. The

method proposed here is a relatively simple way to prepare porous carbons rich in mesopores, and it is a useful means of mass producing porous carbons. This kind of carbon may be used in EDLC and adsorption of large molecules in the liquid phase.

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