

Comparative characterization of porous carbon materials synthesized by the replication of different silicate templates

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Abstract

Two mesosilicates and mineral clay were used as inorganic templates for the synthesis of porous carbon materials. Carbons templated by two mesoporous silica sources (TEOS and silicate/SBA-15) have mesoporous structure with cylinders of hexagonal cross-section. The first carbon product used the TEOS/SBA-15 template gives a higher surface area and narrower pore sizes, thicker wall whereas the second one from silicate/SBA-15 exhibits a less ordered structure, lower surface area, and pore volume. The third carbon sample templated by mineral clay has a moderate surface area and micro- and mesoporous structure. The porous system was made by the slit-shaped spaces between carbon nanoparticles or nanosheets. A small amount of resided inorganic template components has a strong effect on the porosity of the synthesized carbon materials.

Keywords: porous carbon; SBA-15; CMK; ordered carbon materials; nanosheets, nanoparticles, clay.

1. Introduction

A wide variety of structured carbon materials such as carbon nanotubes, nanosheets, nanofibers, nanowires has shown many potential applications in heterogeneous catalysis, electrochemistry, host-guest chemistry, environmental technology and other fields [1-5]. Compared to the mesoporous silica families, nanostructured carbons are chemically inert under various harsh reaction conditions, i.e. they are stable in strongly acidic or basic environments, and withstand high temperature treatment in the absence of oxidants [2,3]. Moreover, these solids have high carbon content and the large surface reactivity, due to the existence of remarkable amounts of surface oxygen and hydrogen on channel walls [2,6-8]. The templated carbon materials have not only high surface area and porosity, tunable pore sizes, and large pore volume, but also are

rich in mesopore and/or macropores [6,7]. Thus, they can be used as efficient adsorbents, catalyst supports for the adsorption and/or conversion of macromolecules [2,3,5]. Therefore, a great effort of the structure-directed or templated synthesis of ordered carbon materials have been recently reported. During a templated synthesis method, precursor materials are inserted into the template framework in such a way that their final structure reflects somewhat the templating structure. For example, alumina [9,10], layered double hydroxides [11], zeolites [12,13], and mesoporous silicas [14-17], have been used as templates to produce nanostructured porous carbon materials (carbon nanotubes, nanofibers, nanosheets...). Recently, the template approach has been proved to be very feasible to prepare porous carbons with well controlled pore diameters [6,7,18-20]. In this report, we describe the use of some different inorganic templates for the tailored preparation of desired carbonaceous materials [21-23]. Carbon-containing precursors were introduced into the structured inorganic matrixes, polymerized, and then carbonized. The subsequent removal of the silica host by dissolving in a soluble solution leads to the intact carbon replica [5,14-17] or gives abnormal texture of carbonaceous materials [8,12]. The present article also debates on the carbon structures templated by different inorganic exemplars and introduces an efficient synthetic route for the preparation of nanoporous carbon materials.

2. Experimental section

2.1. Preparation of porous carbon materials

Mesoporous silica material, SBA-15, was synthesized using the triblock copolymer (Pluronic P₁₂₃, EO₂₀PO₂₀EO₂₀, (Sigma) as the directing-structure agent and commercial sodium silicate solution or tetraethylosilicate (TEOS) as the silica sources [20]. Typically, a quantity of 3.5g P₁₂₃ was dissolved in 9 mL of aqueous HCl solution (36 wt.%) and 30.8 g H₂O

at room temperature. The mixture was stirred at 35 °C for 3 h before adding 27.9 mL sodium silicate solution ($\text{Na}_2\text{Si}_3\text{O}_7$ with 25 wt.% SiO_2) or 6.8 g TEOS under vigorous stirring. The resultants were kept at 35 °C for 24 h with stirring and the white precipitates formed were then transferred to autoclaves kept at 95 °C for 72 h. Then, the precipitates were filtered and dried at 60 °C overnight prior to be calcined at 550 °C (3 °C/min) in air for 2 h to obtain the silicas denoted as silicate/SBA-15 and TEOS/SBA-15.

In the synthesis of porous carbons, 1.0 g of SBA-15 template was added into 5 mL of aqueous solution containing 1.25 g of glucose and 0.14 g of H_2SO_4 as reported else where [23]. The slurry was placed in an oven at 100 °C for 6 h and 160 °C for another 6 h. In order to fully polymerize and carbonize glucose inside the pores of SBA-15, 0.8 g of glucose, 0.09 g of H_2SO_4 , and 5 g of water were again added to the pretreated silica/glucose composite and the mixture was again subjected to the thermal treatment described above. The latter composite was then pyrolyzed in a 12 mm-diameter quartz tube at 890 °C for 6 h in flow of nitrogen. The mesoporous carbon solids were obtained by removal of silica framework using 4 M NaOH solution at room temperature followed by filtration, washing, and drying at 120 °C for 4 h, denoted as CS-1 and CS-2 corresponding to their silica templates of TEOS/SBA-15 and silicate/SBA-15, respectively.

Another template used in this study is treated clay (Di Linh, Lam Dong, Vietnam) with interlayer spacing of 14.8 Å [24]. Firstly, 15 g of the clay was added to HCl 0.5 M solution with continuous stirring for 24 h. The suspension was filtered, washed with deionized water, and dried in an oven. Metal cationic ions are removed by treatment with 0.5 M sodium chloride solution at room temperature for 24 h. The resultant was filtered, washed and then dried at 110 °C. Secondly, 5 g of pre-dried clay was mixed with 2 mL of a solution containing 1.5 g of glucose and 0.22 g of H_2SO_4 at room temperature. The slurry was then dried at 100 °C for 6 h before heating to 160 °C for 6 h (10 °C/min) in air. This process was repeated three times to enhance the amount of glucose inserting between interlayers of the clay template. Then, the obtained glucose/clay solid was carbonized in a flow of 50 mL/min of Ar at 750 °C for 6 h at a ramp of 5 °C/min. The clay template was subsequently removed using a 20 wt% NaOH/ H_2O -EtOH solution (v:v = 50:50) three times. The carbonized solid was washed by 1.0 HCl in order to remove the metal oxides three times prior to drying in an oven at 80 °C overnight. The final back carbon power was respectively designated as CC-3.

2.2. Physical characterization

X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument operating

at 40 kV and 40 mA using CuK_α radiation ($\lambda = 1.59$ nm). The scanning range of 2θ was from 0.5° to 10° with a step size of 0.008°. The surface morphology of mesoporous particles was acquired on the Field Emission Scanning Electron Microscopy (SEM) Hitachi S-4500, Japan, with the magnification of 600,000 times. The structural properties and morphology of mesoporous carbons were examined by a Japan Jeol. Jem.1010, Transmission Electron Microscopy (TEM) working at 300kV in bright field mode. The sample operation was accomplished by suspending the material in acetone and dispersing it on a holey carbon grid. The nitrogen adsorption and desorption isotherm at 77K was measured on an Autochem II 2920 Micrometrics (USA). The surface area values were determined using the BET (Brunauer-Emmet-Teller) equation and the pore size distributions and total pore volumes were obtained by applying the BJH (Barret-Joyner-Halenda) method to the desorption branch of the isotherms. The elemental analysis of samples was characterized by Energy-Dispersive X-ray Spectroscopy (EDS).

3. Results and Discussion

3.1. X-ray diffraction

Figure 1 displays the X-ray diffraction patterns of mesoporous silicas, mineral clay and their corresponding carbons prepared. For silica material TEOS/SBA-15, XRD pattern exhibits three well-resolved peaks at 2-theta of 0.92, 1.54, 1.72° (Fig. 1A). These peaks are firmly indexed to (1 1 0), (2 0 0), and (2 1 1) planes, characterizing for the $p6mm$ hexagonal symmetry [20,21]. Similar reflections are observed for silicate/SBA-15 material, but the intensities at 2-theta of 1.54 and 1.75° are very weak, indicating the less mesostructural ordering although the formation of the amorphous silica is not ruled out [6,10-13]. The hexagonal unit cell estimated from the d-spacing at (1 0 0) plane is about 10.7 ± 0.1 nm for both TEOS- and silicate-SBA-15 [5,14,17,19,22]. Such mesoporous silica materials were used as the hard templates in order to prepare mesoporous carbon materials via an impregnation of glucose, followed by the further pyrolysis under an inert atmosphere and removals of the silica framework. The recorded XRD patterns for the synthesized carbon materials display a sharp reflection peak, indexed as (1 0 0) reflection of 2-D hexagonal structure of the carbon material with the cell parameters of 8.1 nm (CS-1) and 7.7 nm (CS-2), as calculated by using the position of the (100) peak and Bragg's equation [22]. These results indicate that the structure of the synthesized porous carbon materials are close to that of CMK-3 family [5,14,17,23] and thus carbon materials are well replicated SBA-15 silica structure. They have a straight hollow core through

entire length of carbon bulk as in good agreement with microscopic observations below [14,17,24].

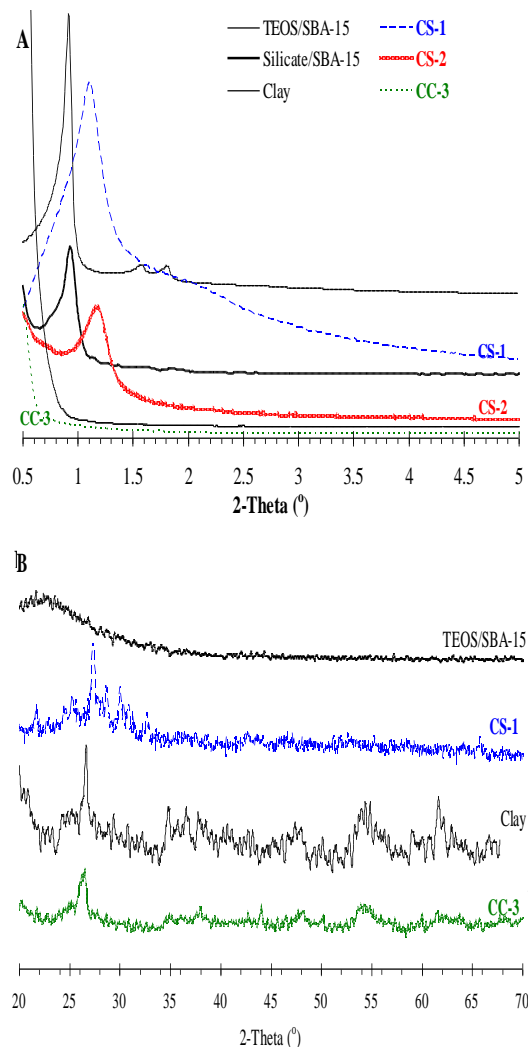


Figure 1. XRD patterns at small (A) and large angles (B) for inorganic templates and final carbon products

A replacement of mesosilicate templates by mineral clay is expected to have a different carbon product structure (sample CC-3). It is not surprising to see the absence of reflection peaks at small angles for both clay template and montmorillonite-templated carbon (Figure 1A) [24]. At large reflection angles, the treated clay appears a set of peaks at 2-theta of 17.4; 21.6; 24.4; 26.8; 31.8° characterizing for the presence of montmorillonite phase [24,25]. After carbonizing carbohydrates followed by removals of inorganic components, XRD pattern of sample CC-3 shows no 2-theta reflection angles matched with those of clay template. Instead, it presents a small peak around 26° and a low intensity signal at 44°, representing the reflections of graphite phase [26-28]. There is some broadening in this peak implying inhomogeneity in the porous structure of the examined pattern [8,11,13,27].

3.2. Microscopic examination

The structure and morphology of the synthesized porous carbon materials were investigated by TEM and SEM techniques. Some representative micrographs of three carbon samples are depicted in Figures 2 and 3.

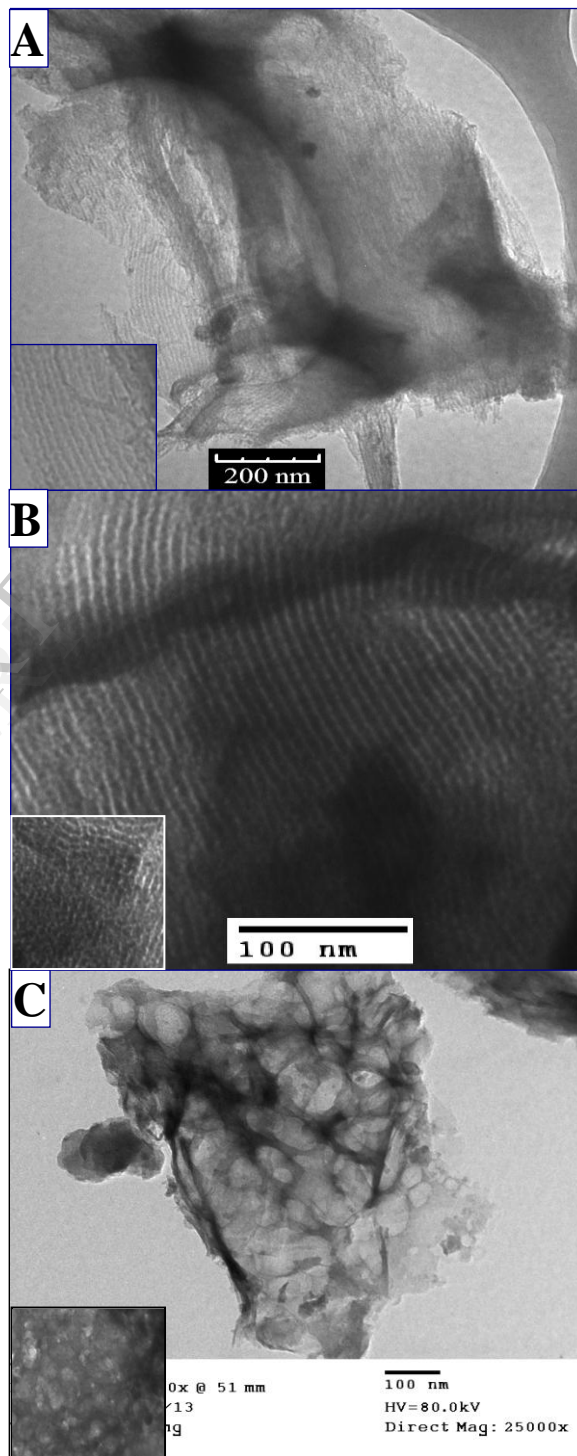


Figure 2. TEM images of CS-1 (A), CS-2 (B) and CC-3 (C)

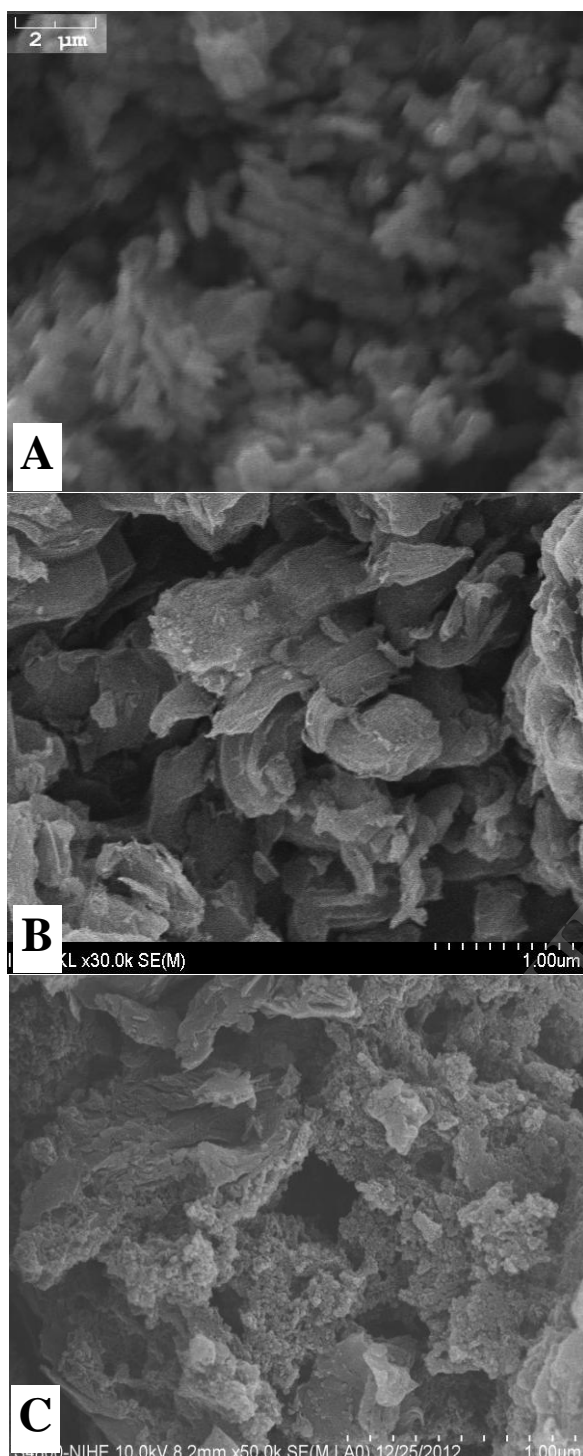


Figure 3. SEM micrographs of sample CS-1 (A), CS-2 (B) and CC-3 (C)

Figure 2 presents some representative TEM images of the carbon samples viewed parallel to the direction of the uniform carbon channels [17,18]. These parallel lines are probably subjected to the projection of the

mesopores formed in the space previously occupied by the walls of the SBA-15 [19,20]. Thus, the diameter of these channels is associated with the thickness of the silica walls. Indeed, Figure 2A also indicates that the CS-1 sample is consisted of numerous nanofibers, which bundle up carbon nanorods [18]. This is strongly supported by SEM micrograph. Figure 3A shows rod-like shape of CS-1 particles with lengths as long as several hundreds of nanometers whereas the CS-2 has morphology of irregularity larger particles (Fig. 3B). A more detailed examination of TEM image in Figure 2B indicates the formation of hexagonally packed cylindrical channels, confirming the templated-synthesis of mesoporous carbons from silicate/SBA-15 exemplars [5,22,28].

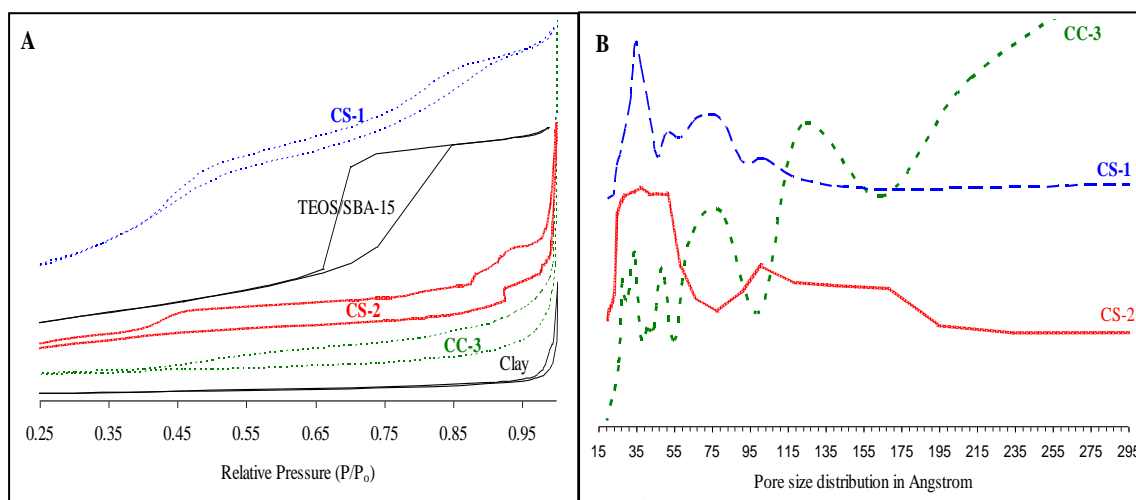
Under micrometer level, clay templated carbon sample CC-3 shown in Figure 2C is consisted of spherical carbon nanoparticles with the diameter in the range of 20-40 nm while SEM micrograph of the original clay (not shown here) presents the layered structure [24]. In some areas, SEM picture of CS-2 (Fig. 3C) appears filmy bulk which is formed by the agglomeration of carbon nanoparticles. As seen in Figure 2C, TEM image of CC-3 sample shows the presence of semi-structured layers and/or nanosheets in addition to various hundreds of nanofibrous carbons [13,26].

3.3. Nitrogen adsorption-desorption isotherm

Analysis of nitrogen sorption would bring much useful information about the texture and porosity of all final carbon products (CS-1; CS-2; CC-3). The BET surface areas of the inorganic templates and templated carbon products are reported in Table 1. In overall, the specific surface area of produced carbons is much higher than that of their corresponding inorganic templates [17,28]. Figure 4 displays the nitrogen adsorption/desorption curves for all carbon samples. The isotherms for CS-1 and 2 are classified to type IV with steps at relative pressure of about 0.42-0.45 due to the capillary condensation in the ordered mesoporous structure [15,29]. CS-2 sample moreover presents a plateau isotherm curve (Fig. 4A) corresponding to a lowered pore volume and surface area by the probability of partial pore blocking. The surface area and pore volume of CS-1 and CS-2 are about 1390 m²/g and 1.75 cm³/g; 413 m²/g and 0.51 cm³/g, respectively. In addition, the CS-2 shows a higher tailed-relative pressure, reflecting a wider pore size distribution. Indeed, the pore size distributions calculated by the BJH (Barrett-Joyner-Halenda) algorithm center at 3.4 nm for CS-1, but two overlapping peaks ranged from 2.5 to 5.1 nm in addition to a broad band at 9.7 nm are observed on sample CS-2 (Fig. 4B). These pore size values are close to the thickness of SBA-15 walls (~ 3 nm).

Table 1. BET surface areas of templates and their corresponding templated carbons

Sample	S_{BET} (m^2/g)	S_{external} (m^2/g)	S_{micro} (m^2/g)
TEOS/SBA-15	734.9	600.9	134.0
Clay	24.0	17.6	6.4
CS-1	1390.6	987.4	413.2
CS-2	413.7	239.6	174.4
CC-3	288.5	152.9	135.6

**Figure 4.** Nitrogen isotherm curves (A) and pore size distributions (B) of mesoporous carbon materials

Moreover, an enlarged pore diameter in the case of CS-2 may be associated with amorphous silica amount deposited on the pore wall of starting mesoporous silicate/SBA-15 template as indicated by XRD patterns (Fig. 1) and nitrogen sorption analysis [16]. The presence of a small amount amorphous silica in pore walls leads to the formation of thicker silica walls. Consequently, the pore size distribution of the second carbon samples shows a broadened peak and slightly shifts to higher pore size values. The less ordered and inhomogeneous nature of the CS-2 sample is demonstrated by the appearance of some regions of enhanced contrast, which are probably attributed to the presence of Si retained [13,28]. In other words, silica framework was incompletely removed by NaOH solution under these typically experimental conditions (Section 2). The presence of unetched Si leads probably to a significant decrease in the specific area and the pore volume of the nanoporous carbon sample, evidenced by nitrogen sorption measurements (Table 1). To prove this hypothesis, we have collected energy-dispersive X-ray (EDS) spectra and the signals are presented in Table 2 below.

Isotherm curve of CC-3 clearly appears a broad hysteresis loop which strongly indicates the presence of mesopores in such a material. This latter carbon sample has a H2 hysteresis loop which characterizes for open capillaries of complex shapes, pores with narrow and wide section [8,20,29,31]. Samples CC-3 was obtained by carbonization of glucose within the montmorillonite

interlayer spaces and the small voids between fine nanoparticles. The surface areas of such carbon products are rather high with the micropores occupying approximately 52% of the total surface area (Table 1). In this context, the mesopore area is ascribed as the nitrogen adsorption in many slit-shaped capillaries formed between small carbon particles and/or carbon nanosheets (Fig. 2 and 3) those are shown in Fig. 4B [27]. On other hand, micropores are formed by the negative replication of imperfection of clay structures and the defects in the carbon product particles after treated in HCl solution [13,23,25]. The presence of inorganic impurities in the original clay also leads to the formation of micropores after treating the final solid products in an acidic condition (see Section 2) [23]. Another hypothesis is that the specific spatial arrangement of interlayers during thermal treatment processes such as polymerization, carbonization. Teresa J. Bandoz et al. [30] indicated that the kinetic of the dehydroxylation process is much more facile than the carbonization of carbon precursors between smectite interlayers under thermal treatment condition. Thus, the carbon layers obtained from the matrix have a developed microporosity during the thermal treatment step [4,26]. Furthermore, this process makes carbon layers be crushed into smaller particles as observed in Fig. 3C. Thus, clay-templated carbon material is expected to possess a multiple-porous system. Indeed, Figure 4B indicates a set of pore size distribution (PSD) maxima at 2.7, 3.4 nm and a wide peak centered

at 4.8 nm for sample CC-3. This sample also has one broad PSD peak centered around on 7.5 nm indicating the presence of secondary mesopores [4,26]. Thereby, the clay has acted as an excellent template to generate micro- and mesoporous carbon sample CC-3 although the final carbon product still contains a small quantity of inorganic template component (Table 2).

3.4. EDS analysis

Energy-dispersive X-ray spectroscopy (EDS) technique was used to investigate the elemental composition of sample surface. EDS spectra of all samples have been collected after three washing times. The peak intensity of Si is rather higher and unchanged after washing several times for CS-2 and CC-3 samples while that for CS-1 is very low [27,28]. This observation indicates that silica host in silicate/SBA-15 and clay is very hard to remove completely under reported experimental condition, in contrast to TEOS/SBA-15 template [24,28]. The elemental composition on sample surface is given in Table 2.

Table 2. EDS results of final carbon products

Element	Atom, %		
	CS-1	CS-2	CC-3
C	91.19	81.12	71.83
O	8.69	13.47	22.37
Na	-	1.08	0.41
Si	0.01	2.69	2.34
Mg	-	-	0.29
Al	-	0.91	1.10
Others	0.11	0.73	1.66

As seen in Table 2, all samples are consisted mainly of carbon and oxygen atom. It is not surprising as observed a significant amount of atomic oxygen in the templated carbon sample [27]. Since the carbon precursor is glucose, the carbon channel walls and the external surface are believed to possess a remarkable amount of OH groups, in harmony with the results on carbonaceous materials prepared through the replica of mesoporous silica templates [2,8,17,21]. Thus, a significant amount of oxygen is always present in the final carbon product. EDS analysis also reveals that a small quantity of Na, Mg, Al, Si... retains after washing the carbon solids under severe acidic and basic conditions. The retained inorganic content dramatically lowers internal surface and porosity of the final carbon products as indicated in Table 1 and 2.

4. Conclusions

Three porous carbon samples derived from different inorganic templates were synthesized. Two of them were replicated by similar mesoporous silicas

obtained from different silicate sources and the morphological resemblance between templates and the corresponding carbon products were observed. The first mesosilicate sample prepared from tetraethyl orthosilicate (TEOS/SBA-15) shows a highly ordered structure while the second silica sample (silicate/SBA-15) is much less structural ordering. Both samples are used as the mesoporous silica templates for the synthesis of structured carbon materials and their structure ordering has a strong effect on the pore size distribution and the texture of the synthesized carbon materials. These two synthesized carbon materials have mesoporous structures with cylinder channels and ordered hexagonal structure. The porous system was formed by the inverse replica of the silicate walls. The replication of TEOS/SBA-15 template yielded a mesoporous carbon (CS-1) with a high surface area, pore volume and narrower pore size, thicker carbon wall whereas the second one templated from silicate/SBA-15 shows a less ordered structure, lower surface area, and pore volume. The third carbon sample synthesized by mineral clay mold, CC-3, exhibits a moderate surface area. It possesses a multiple-pore system and nanoparticles. All carbonaceous materials are composed of unetched Si, Na, Al ions. A high amount of retained inorganic template components gave rise to a lower surface area and inhomogeneous composition of the synthesized carbon materials.

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