Study of Structural Properties of Mesoporous Carbon From Fructose with Zinc Borosilicate Activator

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ABSTRACT

Zinc borosilicate (ZBS) activator has been used to synthesize a mesoporous carbon possessing uniformity of pore at low temperature. The synthesis involves caramelization and carbonization processes. The caramelization was conducted hydrothermally at 85 ^{o}C and thermally 130 ^{o}C sequentially. The carbonization was conducted at 450 ^{o}C under flow of nitrogen gas. The carbon products were washed with HF 48% solution, 1M HCl solution, and distillated water respectively. The solid products were characterized by nitrogen gas adsorption, infrared spectrophotometer, X-ray diffraction, and Transmission Electron Microscopy methods. Characterizations using nitrogen adsorption – desorption method shows the ZBS has pore uniformity at 30 nm (for pore cage) and 20 nm (for pore window). ZBS also built a larger mesopore volume than $ZnCl_2$, especially for area of pore size > 10 nm. The Infrared spectrophotometer confirmed that ZBS produced more functional groups of carbon surface than that $ZnCl_2$. The X ray diffractogram showed that ZBS created more amorphous pore wall of carbon than $ZnCl_2$.

Key words : *zinc borosilicate, $ZnCl_2$, mesoporous carbon, fructose, structural properties*

INTRODUCTION

Mesoporous carbon (pore size diameter 2-50 nm) is an interesting material, not only due to mesopore characteristics, especially connected to large pore size and pore volume, but also it has various applications, such as adsorben of large molecule [1], double layer capacitor [2], and template of other mesoporous oxides [3].

Some synthesis methods with hard template such as MCM-48, SBA-15, and KIT-5[4], or borosilicate [5], soft template such as triblock copolymer[6], and combination of hard and soft template, such as silica- triblock copolymer [7,8] have been studied. In general, those methods require high production cost, high temperature, and also long process, with high pore uniformity, even the borosilicate template [5] could create pore uniformity centered at 30 nm and 24 nm pore size.

Alternatively, mesoporous carbon which has large surface area and high mesoporosity can also be produced by chemical activators, such as metal salts [9-11]. Metal salt activator needs relatively lower cost and shorter steps of synthesis. Some researchers reported that $ZnCl_2$ is a chemical activator which tends to build porosity at low carbonization temperature, i.e. 450-600 ^{o}C [12-15]. Synthesis of carbon from fructose with $ZnCl_2$ activator successfully built pore uniformity (D_{max}) at 7 nm and pore wall of graphite structure at temperature of

450^oC [15]. It means that $ZnCl_2$ is beneficial to support an efficient process. However, this quality of pore is still poor for adsorption application, especially for adsorbate with pore diameter larger than 7 nm. $ZnCl_2$ can react with precursors of borosilicate to form zinc borosilicate. **Z**inc borosilicate ceramics contains 2 crystal structures, i.e. zinc silicate and zinc borate [16]. Both zinc borate [17] and zinc silicate [18] can be synthesized hydrothermally at around caramelization temperature of fructose [15]. Therefore, it is possible to use ZBS as carbon activator from fructose.

The purpose of this study is to investigate performance of ZBS as carbon activator to form pore structure of the carbon, with $ZnCl_2$ as a comparison. Beside that, effect of ZBS on surface functional groups and crystal structure of the mesoporous carbon is also studied.

EXPERIMENT
Chemical and Instruments

Chemicals D-fructose (Merck), $ZnCl_2$ (Merck), HCl 37% (Merck), H_3BO_3 (Merck), were used without purification process.

This research used some instruments, including FTIR spectrophotometer (Shimadzu), X-ray diffractometer (Philip), spectrophotometer FTIR (Shimadzu), Surface Area Analyzer (Quantachrome NovaWin2), and Transmission Electron Microscope (JEOL/EO). The functional groups of carbon were determined by FTIR spectrophotometer using KBr pellet method. Adsorption-desorption nitrogen isotherms were measured at the temperature of -196 ^oC by Surface Area Analyzer after degassing the carbons at 130 ^oC for 3 hr.

Procedure

A 10 g fructose, 30 g of $ZnCl_2$, and 60 mL distilled water were placed in the becker glass and stirred. The mixture was evaporated at 85^oC for 4 h under stirring, followed by oven and heated at 130^oC for 1 h to form composite of caramel - activator. The composite was carbonized at 450^oC for 2 h under nitrogen gas flow to form composite of carbon - activator. The composite of carbon – activator was washed with 48% HF solution, 1M HCl solution, and distilled water respectively to separate activator from the carbon. The carbon product (carbon–Z-85) then was oven and dried at 130^oC for 6 h. The same procedure was applied with 3 components of activators, including 10 g silicagel, 10 g $ZnCl_2$, and 12.35 g H_3BO_3. The product is named as carbon–ZBS-85. The mesoporous carbons were sieved to get particle sizes of 100 – 120 mesh. The results were characterized, including pore size distribution, pore volume distribution, functional group, crystal structure, and pore morphology.

RESULT AND DISCUSSION

Mesoporous carbon was prepared from fructose using ZBS activator and $ZnCl_2$ as a comparison. The synthesis involves hydrothermal caramelization and low temperature carbonization processes (450^oC). ZBS was formed from silicagel, $ZnCl_2$, and boric acid. Those precursors are proton donors in the water [19, 20, 21], so that they are catalysts in caramelization reaction. Caramelization product is precursor of carbonization process which determines pore wall formation. In other side, ZBS also acts as pore template at carbonization process which determines pore size and pore volume. The Zn^{2+} cations in ZBS network may also act as chemical activator in carbonization process which support for low temperature process, i.e 450^oC. Pore characterization is performed from nitrogen adsorption – desorption

which was treated by Pierce Orr Dalla Valle methods [22]. Adsorption – desorption isotherm of the carbon is presented in Figure 1.
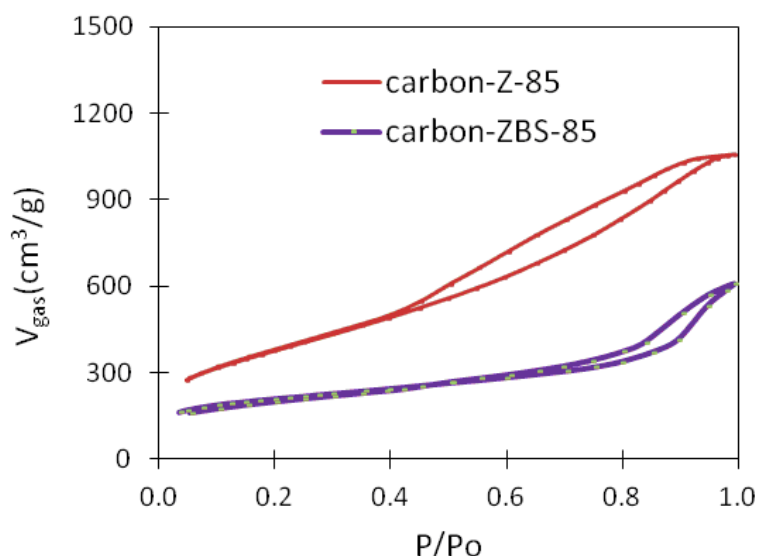

Figure 1. N_2 adsorption – desorption isotherm of carbon synthesized
with $ZnCl_2$ and ZBS activators

Figure 1 shows that the carbon synthesized from ZBS and $ZnCl_2$ exhibit isotherm pattern of isotherm type IV and hysteresis type I. The pattern of isotherm tipe IV showed that both carbons have mesoporous characteristics. Hysteresis tipe I indicate pore structure with shape of tube and balls [22]. Position of curve formed by ZBS is lower than curve formed by $ZnCl_2$. It indicates that ZBS creates less pore volume than $ZnCl_2$ [23-24]. Carbon-ZBS gives inflection point of curve at P/Po ≈ 0.9, whereas $ZnCl_2$ provides P/Po ≈ 0.5. Based on the Kelvin formula [22], ZBS builds larger pore size compared with pore size of $ZnCl_2$. ZBS gives the larger slope of inflection than $ZnCl_2$. It suggests that ZBS creates the higher pore uniformity than $ZnCl_2$, as supported by previous research [25, 26].

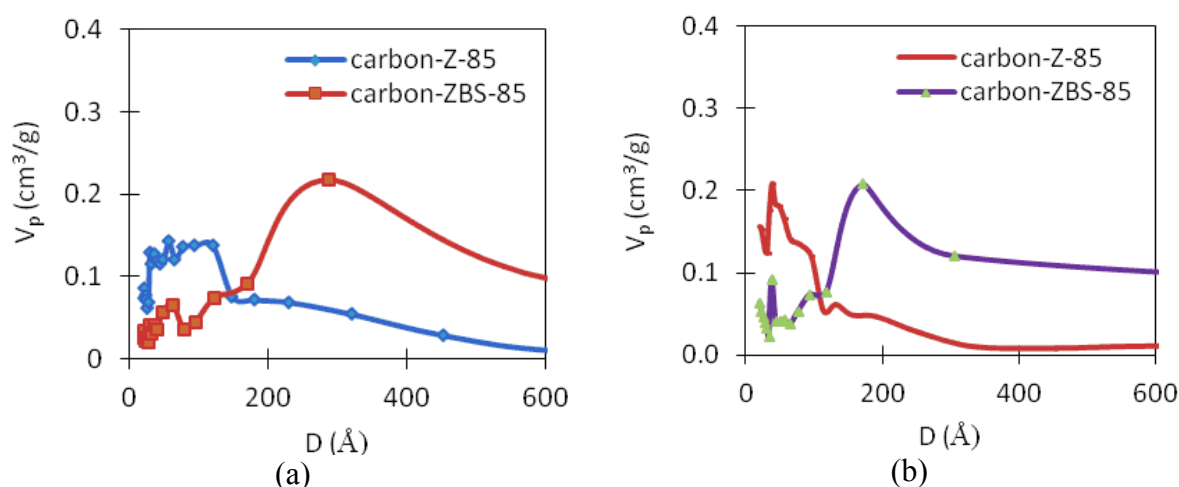(a)   (b)

Figure 2. Pore size distribution of mesopore carbon synthesized by using ZBS and $ZnCl_2$
based on : a) adsorption data and b) desorption data

Pore size distributions (PSD) of the carbons are reported in Figure 2. The PSDs are resulted in treatment of adsorption – desorption data using POD method. As previously reported that the PSD of adsorption data and deshas a correlation with pore cage and the PSD of desorption data has correlation with pore window [15].

In Figure 2, ZBS creates pore uniformity at $D_{maks} \approx 300$ Å (pore cage) and $D_{maks} \approx 200$ Å (pore window), whereas $ZnCl_2$ builds pore uniformity at $D_{maks} \approx 100$ Å (pore cage) and $D_{maks} \approx 50$ Å (pore window). It means that ZBS creates uniformity centered at larger pore size than $ZnCl_2$. It is probably because molar volume of ZBS is larger than ZnO. The previous research showed that ZnO phase is formed by reaction of oxide gasses and $ZnCl_2$ in carbonization process $\geq 400^oC$ [27]. The increasing of ZnO amount in ZBS could decrease both density and molar volume of ZBS [28]. Especially for pore cage, ZBS builds higher pore uniformity than $ZnCl_2$. It is probably due to the role of the undissolved silica which forms more uniform pore template than $ZnCl_2$. Theoritically, the undissolved silica particles are coated by network of ZBS to form pore cage. Those pore cages are connected each other by pore windows. The pore windows are probably built by zinc borosilicate network formed by dissolved silica, boric acid, and $ZnCl_2$. Chemically, ZBS probably can catalyze production of caramel resin more than $ZnCl_2$. Previous research [14] reported that fructose caramel is precursor of carbonization process. So, it can be predicted theoretically that improvement of caramel amount can improve the width of pore wall which prevents damage of pore in washing process. This is supported by absorbance data of 5- hydroxymethylfurfural (HMF), reported in Table 1. HMF is intermediate of caramel [15]. The HMF absorbance measurement with spectrophotometry UV-Vis has been used to detect caramel in sugar solution [29, 30].

Table 1. HMF absorbance of fructose solution after caramelization process for 1 h at 100 ^oC

Catalyst	λ_{max} (nm)	Absorbance of HMF
$ZnCl_2$	274.5	0.112
ZBS	281.5	0.280
No catalyst	278.5	0.051

The HMF absorbance in Table 2 indicates that ZBS is stronger catalyst than $ZnCl_2$ in caramelization reaction by giving the sequence of catalyst : ZBS > $ZnCl_2$ > no catalyst. That is probably because precursors of ZBS can result in more H^+ ions than $ZnCl_2$. Reaction of fructose to form HMF and from HMF to form caramel are catalyzed by proton [15]. The proton can be derived from silanol [16], boric acid [17], and hydrolysis of $[Zn(H_2O)_6]^{2+}$ complexe [18] in the water.

Mesopore volume distribution of the carbons is exhibited in Figure 3. As reported by previous research, the mesopore volume distribution in area of D > 10 nm determines performance of carbon as adsorbent of large molecule such as cyanocobalamine [1]. The mesopore volume was calculated with POD table. As reported by Lowell et al [22], the calculation using POD table gives good agreement with BJH method.
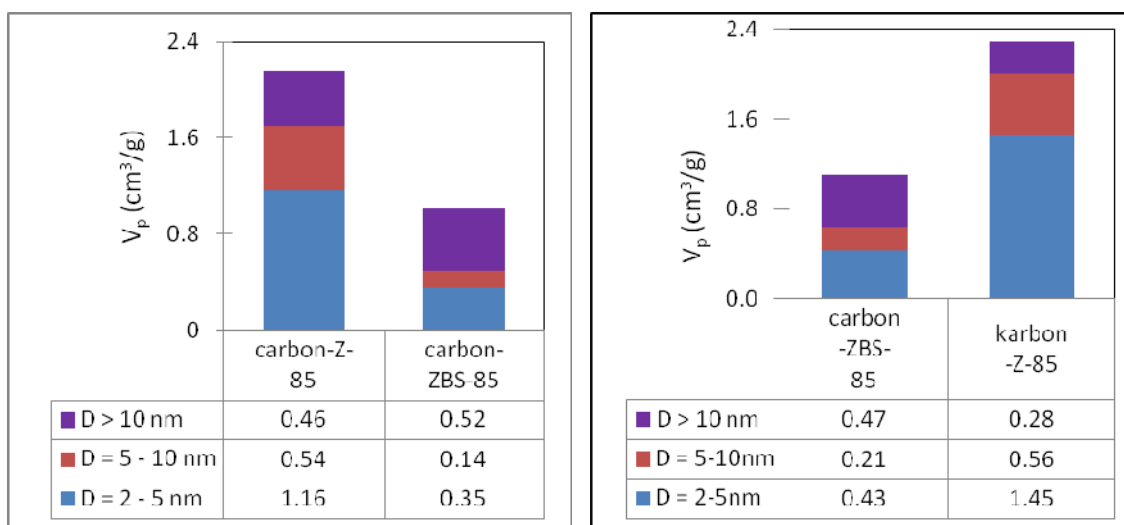
Figure 3. Mesoporous and macroporous volume distribution of carbon prepared from fructose with $ZnCl_2$ and ZBS activators: a) based on adsorption data, b) desorption data

Figure 3 show that ZBS gives larger mesopore volume of carbon than $ZnCl_2$ in area of $D_{meso} \geq 10$ nm. Connected with PSD in Figure 2, it is because ZBS creates higher peak in area of $D_{meso} \geq 10$ nm than $ZnCl_2$. It occurs possibly due to physical factor, i.e larger molar volume of ZBS than $ZnCl_2$ as explained before. Oppositely, $ZnCl_2$ results in much larger mesoporous volume of carbon than ZBS in area of $D_{meso} < 10$ nm. Based on PSD in Figure 2, it is because $ZnCl_2$ creates higher and wider distribution peak involving much more points of data in area of $D_{meso} < 100$ Å than the peak built by ZBS in area of $D > 100$ Å. Physically, it occurs probably due to various size of $ZnCl_2$ particles created along crystallization of $ZnCl_2$ in caramelization process. Chemically, it may be because carbon-Z-85 was prepared with more $ZnCl_2$ than carbon-ZBS-85. $ZnCl_2$ is a chemical activator of carbonization process, whereas silicate and borate tends to have a role as pore template. Although chemically $ZnCl_2$ just builds less caramel than ZBS (Table 1), but it can carbonize the caramel more effectively than ZBS.

TEM characterization shows the morphology of pore structure of $ZnCl_2$ and ZBS activator which is exhibited in Figure 4.
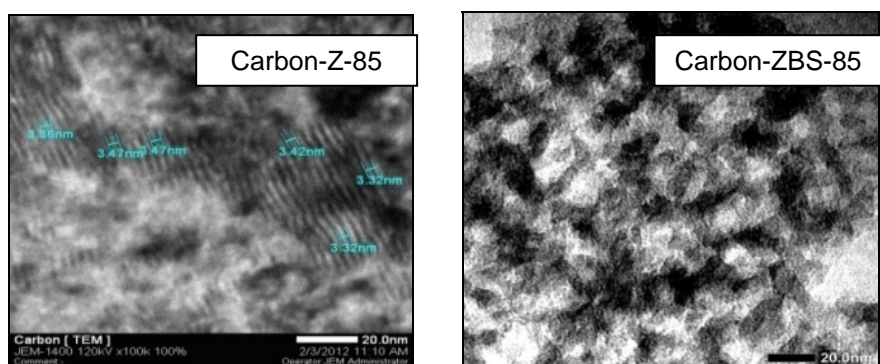

Figure 4. TEM photo of mesoporous crbon from fructose by using $ZnCl_2$ activator and ZBS activator

Figure 4 show that carbon –ZBS-85 has more cages than carbon-Z-85. The carbon – ZBS-85 also tends shows random pattern of the pore wall (dark part), whereas the carbon - $ZnCl_2$ shows line pattern which has the width similar to distance of graphene layers in graphite structure, i.e 0.3354 nm [30].

TEM characterization just gives the physical image of pore wall, but can not give quantitative graphitization level. Beside that, pattern of layers given by TEM is not specific. For example, fluorinated carbon F-FDU16-67 [31] and hexagonal structure of CMK 3 [32] also showed layer pattern like graphite. So that, characterization with X - ray diffractometry has been conducted to investigate the carbon crystal structure and reported in Figure 5 and Table 2
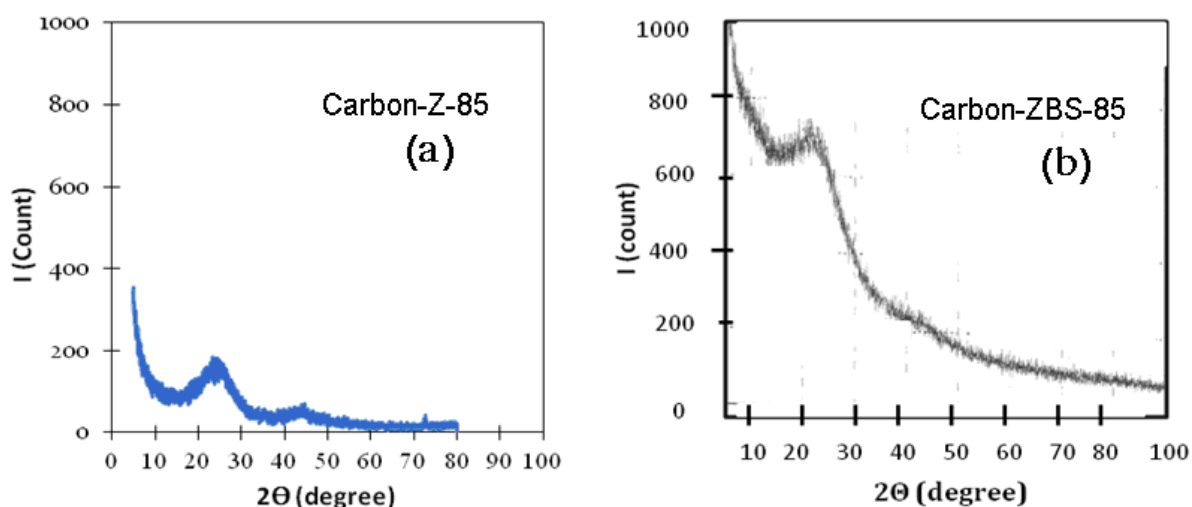

Figure 5. Diffractogram pattern of mesoporous carbon from fructose by using $ZnCl_2$ and ZBS activator

The Figure 5 shows difractogram patterns of the carbons which are similar with the diffractograms of the carbon presented by previous research [14, 33]. Based on checking with data of JCPDS – ICDD card no. 02 - 0456, the carbon - $ZnCl_2$ has 2 peaks which have a good agreement with 2 peaks of standart graphite (Table 3). The main peak of the carbon gives degree of non graphitization only 27.78%. This value supports TEM image (Figure 4) as the graphite structure. The carbon – ZBS-85 shows only 1 peak with value of d = 4.10 Å (Table 3) and gives level of non graphitization 73.33% (Table 3). It indicates the amorph structure, supporting TEM image (Figure 4).

Table 3. X-ray diffractogram data of carbon-ZBS-85 and carbon -Z-85

Activator	Sample			Standart graphite (*)			Deviation of d_{002} value toward d_{002} of ideal graphite (%)**
	2θ (⁰)	I (count)	d(Å)	2θ (⁰)	d(Å)	hkl	
$ZnCl_2$	24.58	180	3.61	26.506	3.36	2	27.78
	44.72	69	2.02	44.599	2.03	101	
ZBS	21.64	3219	4.1			-	73.3

*Result of checking with standard graphite in JCPDS - ICDD card no. 02 – 0456. **Deviation percentage of d toward d value of ideal graphite [34]

$ZnCl_2$ tends to form graphite structure than ZBS probably because $ZnCl_2$ is a stronger activator of pyrolisis in carbonization reaction than ZBS so that the former creates more regular arrangement of graphene layers than latter. It may be because the Zn^{2+} metal ion is stronger Lewis acid than B and S because of its condition as ion. Interaction of Zn^{2+} and base Lewis in network of ZBS probably can impede performance of Zn^{2+} as activator too.

The surface chemistry of the carbon is described by functional groups. The surface functional group is responsible for physicochemical and catalytic properties [35]. O-containing functional groups play a key role in metal ion or organic adsorption [36]. The functional group of the carbon products were measured by using FTIR spectrophotometry and presented in Figure 6.

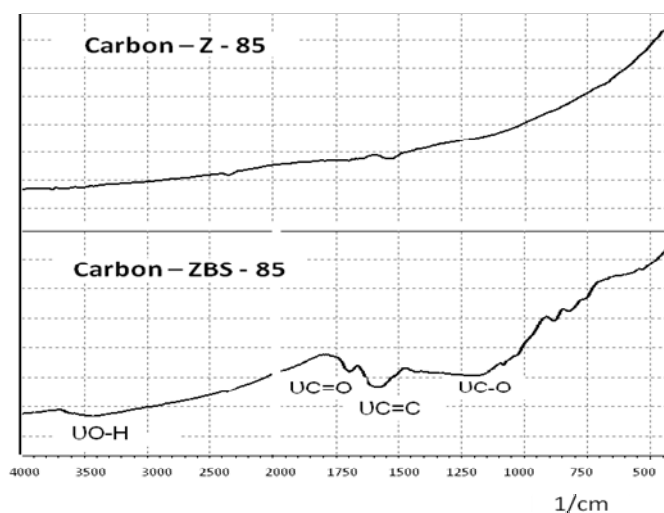Figure 6. FTIR spectra of caramel and mesoporous carbon from fructose with activators of $ZnCl_2$ and ZBS

Figure 6 shows that carbon-ZBS-85 shows bands in 1207.36 cm^{-1}, 1586.34 cm^{-1}, 1698.21 cm^{-1}, and 3422.45 cm^{-1}. By reffering to some previous researchs [37, 38, 39], those bands of FTIR spectra characterize C-O, C=C at aromatics rings, C=O, and O-H bonds respectively. The OH bond can be attributed to the surface hydroxyl groups and the adsorbed H_2O [38]. The surface hydroxyl may be connected to carboxyl, phenol, and lactol [40]. The C=O bond can be cetone, lactone, and carboxyl [41]. Appearance of C=C aromatics indicates disappearing of bond symmetry due to connection of oxygenated functional groups[40, 42]. Carbon-ZBS-85 shows more FTIR bands than carbon-Z-85. It indicates that $ZnCl_2$ provides more complete reaction of carbonization than ZBS. It is probably because Zn^{2+} cation is Lewis acid which is a stronger dehydration agent than S and B in carbonization reaction. Dehydration reaction supports pyrolitic decomposition which impedes tar formation and improves carbon product [43]. If connected to Table 2, carbonization gives more influence toward functional group of carbon surface than caramelization process. It is probably because the carbonization is directly connected to formation of graphene layers.

CONCLUSION

In synthesis of carbon, development of the porosity, wall structure, and functional groups of carbon surface were affected by kind of activators. Characterization by adsorption – desorption nitrogen method shows that in the range of $D_{meso} \geq 10$ nm, ZBS forms carbon which has larger mesopore volume and also higher pore uniformity than $ZnCl_2$. The pore uniformity created by ZBS is centered on 30 nm (pore cage) and 20 nm (pre window). Based

on TEM characterization, ZBS builds more porosity but more amorphous pore wall than $ZnCl_2$. X – ray characterization confirms that ZBS creates amorphous structure, while $ZnCl_2$ gives graphite structure. Study of FTIR spectrophotometry shows that ZBS gives more functional groups of the carbon surface than $ZnCl_2$.

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