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MATERIALS AND NANOTECHNOLOGIES (E)

POLYMER ENGINEERING AND MATERIAL PROCESSING (F)

PROCESS SYSTEM ENGINEERING (G)

TRANSPORT PHENOMENA (I)

Characterizations of Carbon Nanospheres Prepared by Deposition Precipitation of Fe-Catalyst onto Activated Carbon Support

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Abstract

Carbon nanospheres (CNSs) are known as byproduct of carbon nanotubes synthesis. They are spherical in shape and range in size from roughly 50 nm to 1 µm and depending on the preparation method and raw carbon precursors, they may be hollow or solid core. Applications of CNSs under investigation include use as electrodes in supercapacitors or lithium batteries and catalyst support. In this study, CNSs were synthesized by pyrolysis process. Fe was used as catalyst, activated carbon as support, and palm oil was used as carbon precursors for CNSs growth. Prior to the synthesis of CNSs, Fe-catalyst on carbon supports was prepared by deposition precipitation by varying the amount of catalyst (10%, 20% and 30% wt with respect to the mass of carbon support). The effect of catalyst amount on the morphology and structural characteristics of carbon products was investigated by x-ray diffraction (XRD), BET surface area analysis and scanning electron microscope (SEM). Dense CNSs with turbostratic structures have been produced by pyrolyzing palm oil onto the activated carbon support under nitrogen atmosphere.

Keywords: Carbon nanospheres; Fe-Catalyst, Deposition Precipitation; Pyrolysis; Activated Carbon

1. Introduction

Recently carbon nanomaterials such as nanotubes, nanohorns, nanoribbons, so forth, have been intensively studied for many applications. Organic solvents such as hexane, toluene, benzene, natural oils [1], hydrocarbon gases [2, 3], and heavy hydrocarbons [4, 5] are used as carbon source for the growth of carbon nanomaterials. Various transition metals are commonly used for carbon nanomaterials synthesis, such as metallocene (Fe, Co, Ni) [6], and other metal salts are also used [7]. Various catalyst deposition methods, such as impregnation [8], deposition precipitation [9] are also used. Catalyst characteristic is an important aspect for the growth of carbon nanomaterials. The metal catalyst loading and particle size must be taken into consideration [10]. In this study, Fe-catalyst was deposited onto the surface of activated carbon by using deposition precipitation method. This method could give smaller catalyst particles and narrower size distribution in comparison with conventional impregnation method [11]. For Fe-catalyst, the ratio of Fe and urea is known to be 1 : 3 molar ratio [12]. CNSs alone have been used for

some applications, such as catalyst support [13], adsorbent in water treatment, electrochemical capacitors [14], and anode in sodium-ion batteries [15]. There are some researches concerning on growing carbon nanotubes (CNTs) [16, 17] and carbon nanofibers (CNFs) [8, 18] on surface of activated carbon. Composites of activated carbon and carbon nanomaterials are believed to be able to deliver more improved performance than ordinary activated carbon. For example, composite of activated carbon/CNTs gave higher capacitance when used as supercapacitor's electrode [19-21]. The presence of CNTs supported with activated carbon could increase adsorption capacity of Cr(VI) in comparison with ordinary activated carbon [17].

In this work, the synthesis of CNSs onto the surface of activated carbon, was carried out by simple carbonization method and utilizing palm oil as renewable and eco-friendly carbon source. Fe-catalyst loading was varied at 10%, 20%, and 30%. Characterization of carbon product was investigated by BET surface area analysis, SEM, TEM, and XRD. To the best of authors' knowledge, synthesis of CNSs on activated carbon surface has never been done before.

2. Experimental

Commercial activated carbon (Merck p.a.) was used as support for the growth of CNSs. Fe-catalyst was prepared by urea (technical grade) deposition precipitation of iron nitrate nonahydrate $(Fe(NO_3)_3.9H_2O$ – Merck p.a.). Activated carbon, $Fe(NO_3)_3.9H_2O$ (10%, 20%, and 30% mass ratio to activated carbon), and urea was homogenously mixed in 50 mL distilled water. These mixtures was shaken for 4 hours at 90ºC, and let cooled down for overnight. The activated carbon containing Fe-catalyst was separated from the liquid by centrifugation. The resulting solid then oven dried at 110ºC for 24 hours. The dried powder was mixed with palm oil at 1: 3 mass ratios. This mixture was carbonized using electrical furnace at 700ºC for 1 hour then let cooled down under N_2 atmosphere.

Morphology and structural characteristics of carbon product was investigated by BET, SEM, TEM, and XRD. BET surface area was analyzed using Micromeritics apparatus (NOVA 1000/ 3200e Quantachrome), and SEM images obtained by using FE-SEM, S4100, HITACHI. TEM images was obtained by using FEI Tecnai TEM, and XRD studies (Bruker D8 Advance, Cu-K α radiation) were also done to identify the products obtained.

3. Results and Discussion

The SEM images of the carbon products are shown in Fig 1. The effect of the catalyst concentration can be qualitatively observed from the SEM images. At higher catalyst concentration, more CNSs are observed. At 30% Fe-catalyst, the CNSs become denser, and covering the surface of activated carbon. In Fig 1.d., it can be observed that CNSs are not present as a single sphere, but as conglomeration of spheres [22].

CNSs is known to be hollow or solid, depending on the synthesis method [22]. From TEM images of CNSs, shown in Fig 2, it can be observed that the CNSs obtained is a solid sphere, decorated with Fe-catalyst. The result from TEM analysis is in accordance with SEM analysis, which the higher Fe-catalyst, the denser CNSs obtained on the surface of activated carbon. At 10% Fe-catalyst, the presence of Fe-catalyst is hardly observed. This condition is not favorable for the growth of CNSs so that it is hardly observed. While at 20% Fe-catalyst, more Fe-catalyst was deposited on the activated carbon support, thus more CNSs was obtained. However from TEM analysis, it can be visually observed that the CNSs

obtained was at various size. At 30% Fe-catalyst, more catalyst was deposited on the activated carbon support. This condition lead to denser and more homogenous CNSs size.
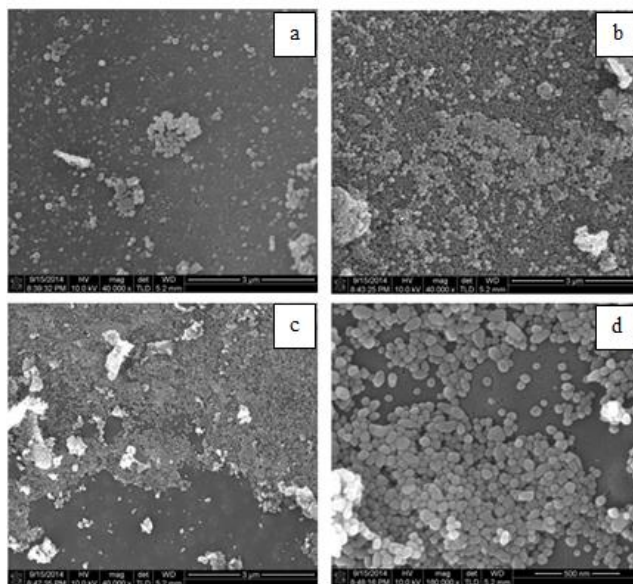

Fig 1. SEM images of CNSs at 10% (a), 20% (b), 30% (c) Fe-catalyst (40,000×) and (d) 160,000× magnification of 30% Fe catalyst
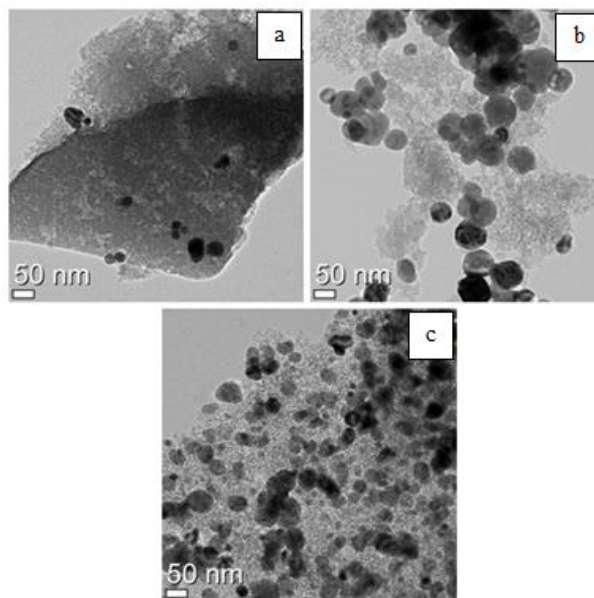

Fig 2. TEM images of CNSs at 10% (a), 20% (b), 30% (c) Fe-catalyst

The pore characteristics of product obtained are shown in Fig 3 and Table 1. Isotherm adsorption curves of all catalyst concentration are presented in Fig 3. It can be seen that all samples showing type IV isotherm. According to IUPAC classification of isotherm adsorption, type IV isotherm indicates mixture of micropore and mesopore characteristic [23]. In Table 1, it can be seen that variation of Fe catalyst gives effect on the surface area, pore volume and diameter. There is decrease on the activated carbon surface area, indicating some of activated carbon pores are covered by CNSs and Fe-catalyst. However, there is no significant difference of 10% and 20% Fe-catalyst's pore characteristics. Greater decrease of surface area is obtained at 30% Fe-catalyst. However, the decrease of surface area and pore volume is not as big as one obtained by Chen et.al (2008) who synthesized CNFs on surface of activated carbon. Chen, et al (2008) observed 90% surface area decrease when growing CNFs using ethylene as carbon source, Fe-catalyst, and activated carbon support. This result was obtained due to perfect covering of CNFs on activated carbon surface [8]. Thus, in this research, it can be said that at 30% Fe-catalyst, CNSs and catalyst gave the best covering on the activated carbon, in comparison with 10% and 20% Fe catalyst. However, CNSs obtained are not completely covering the activated carbon surface and pores.

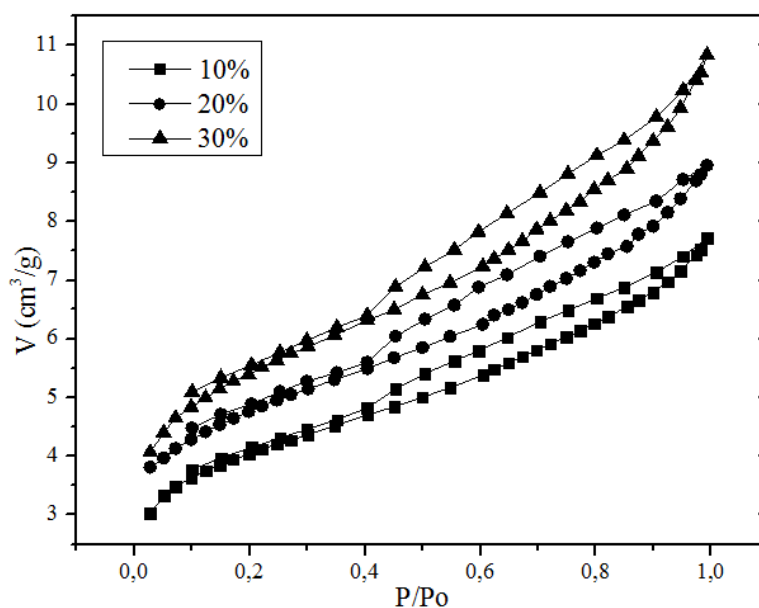Fig 3. Isotherm adsorption of samples prepared at 10%, 20%, and 30% Fe-catalyst concentrations

Table 1. Pore characteristic of activated carbon at various Fe-catalyst ratio

Parameters	AC Standard	10%	20%	30%
S BET (m^2/g)	775.62	426.63	423.15	361.56
Pore Volume (cm^3/g)	0.63	0.39	0.38	0.34
Pore Diameter (Å)	32.71	36.58	35.97	38.01

XRD result for activated carbon at various Fe-catalyst concentration is shown in Figure 3. From XRD result, it can be seen that every sample shows peak at 43° indicating (100) sp^2 structures of carbon [24], however no C (002) peak (26,5°) is observed. Fe peak is observed at 30° (220), 35,4° (311), 57,09° (422), and 62,4° (440) [25] which belong to magnetite (Fe_3O_4) content on the activated carbon. Weak peak of C (100) could mean that CNSs formed has weak graphitization, which is normally observed in CNSs characteristics [22]. At 10% Fe-catalyst the C (100) peak observed is weaker than 20% and 30% Fe-catalyst. Thus it can be assumed that 10% Fe-catalyst is not enough to promote growth of CNSs.
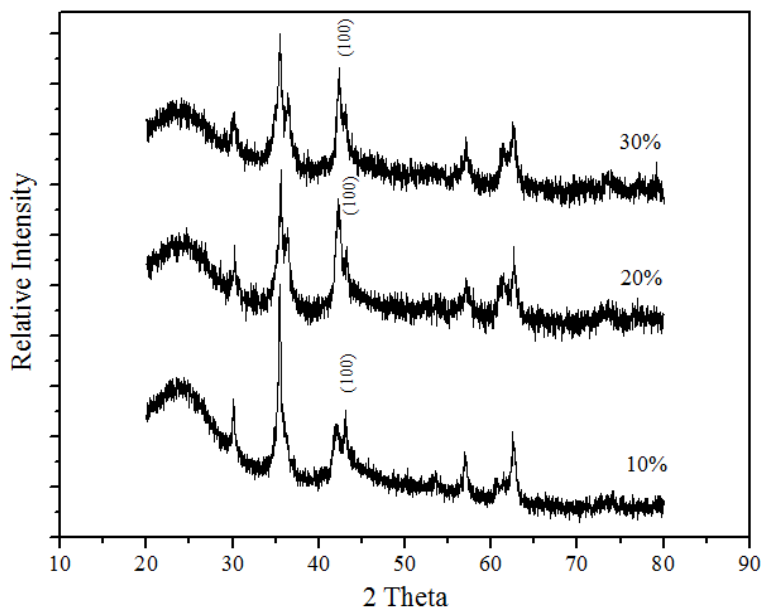
Fig 4. XRD pattern of samples prepared at various Fe-catalyst concentrations

4. Conclusion

CNSs from palm oil as carbon source was successfully synthesized on the surface of activated carbon support using Fe-catalyst with simple pyrolysis technique. Dense CNSs was observed at 30% Fe-catalyst, while low Fe-catalyst could not provide adequate catalyst for the growth of CNSs. Further characterization, such as Raman analysis, EDS, should be considered. Specific application of activated carbon/ CNSs composites will be carried out in our future works.

Acknowledgements

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