The effect of activated carbon support surface modification on characteristics of carbon nanospheres prepared by deposition precipitation of Fe-catalyst

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Abstract. In this study the effect of activated carbon support modification to synthesis of CNSs was observed. Modification of activated carbon was done by using nitric acid. The effect of modification was analyzed from its FTIR spectra. The Fe catalysts were deposited on to the support by using urea deposition precipitation method at various initial catalysts concentration. CNSs was synthesized by utilizing cooking palm oil as renewable carbon source, and pyrolized at 700˚C for 1 hour under nitrogen atmosphere. The products obtained then analyzed using SEM-EDS, TEM, XRD, and Raman spectroscopy. The modification of activated carbon support had increased the oxygen functional group. This increase resulted on increase of metal catalysts deposited on activated carbon surface. Peak of C (100) was observed, while ID/IG of samples were obtained around 0.9, which is commonly obtained for CNSs. High catalysts loading on modified activated carbon support caused decomposition of CNSs and formation carbon onion.

1. Introduction

Metal catalysts play important role on carbon nanomaterial synthesis. Transition metal catalysts are usually used in carbon nanomaterial synthesis, both in metallocene forms (Fe, Co, Ni, etc.) [1], and in salt forms [2]. The loading of metal catalysts, and its size should be considered carefully in synthesis of carbon nanomaterials [3]. Generally, the increase of oxygen functional groups on activated carbon could increase the adsorption of metal ions [4, 5]. This characteristics could be used to increase the metal catalyst loadings on activated carbon support. Xiong, et al. (2014) obtained increase of Niobia catalyst loading on activated carbon support by modifying activated carbon’s functional groups using nitric acid [6]. Similar results were also obtained for different metal catalyst on activated carbon support [7, 8]. It is known that the surface modification of activated carbon increase its hidrophilicity.

There are several methods used in catalyst deposition on the surface of supports, namely impregnation and deposition precipitation. In this study, we used urea deposition precipitation method for catalyst preparation. This method has some advantages, such as smaller metal particle size, more homogenous catalyst distribution, higher catalyst loading, reproducible, and strong interaction of catalyst and support, compared with impregnation method [6, 9]. Tripathi, et al. (2012) synthesized CNSs and CNTs from castor oil by utilizing this method to obtained nano-sized Ni and Co catalyst[10].

In this study, the effect of activated carbon support’s modification to the synthesis of CNSs was studied. The modification was done using simple wet oxidation method of nitric acid. Fe-catalyst loading was varied at 10%, 20%, and 30% of initial catalyst concentration. The CNSs synthesis was done using simple batch pyrolysis method, utilizing cooking palm oil as carbon source. The effect of modification to activated carbon’s functional group was studied using Fourier Transform Infrared Spectroscopy (FTIR), while the product of CNSs synthesis was observed using Scanning Electron
Microscope- Energy Dispersive X-ray Spectroscopy (SEM-EDS), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Raman spectroscopy.

2. Experimental
Commercial activated carbon (AC), obtained from Merck (p.a.), was used as support for the growth of CNSs. The modified activated carbon used in this experiment was obtained by using nitric acid modification (HNO$_3$ 65%– Merck p.a.). Activated carbon was mixed with nitric acid at mass ratio 1:1. This mixture was shaken for 4 hours at 60°C, and then repeatedly washed by aquadest until pH 6.5-7.0. The modified activated carbon then oven dried at 110°C for 24 hours (AC-NA). Fe-catalyst was prepared by urea (technical grade) deposition precipitation of iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O – Merck p.a.). Activated carbon, Fe(NO$_3$)$_3$.9H$_2$O (10%, 20%, and 30% mass ratio to activated carbon), and urea (1.5 moles per mole of iron [11]) was homogenously mixed in 50 mL distilled water. These mixtures was shaken for 4 hours at 90°C, and let cooled down for overnight. The activated carbon containing Fe-catalyst was separated from the liquid. The resulting solid then oven dried at 110°C for 24 hours. The dried powder was mixed with palm oil at 1:3 mass ratios. This mixture was carbonized using electrical furnace at 700°C for 1 hour then let cooled down under N$_2$ atmosphere. The sample was labelled AC-xx or AC-NA-xx, where xx is the initial Fe-catalyst concentration.

The effect of surface modification to the surface functional group of activated carbon was studied using FTIR (Shimadzu FTIR 8400, KBr pellet method). Morphology and structural characteristics of carbon product was investigated by SEM-EDS (FE-SEM, S4100, HITACHI), TEM (FEI Tecnai TEM), Raman spectroscopy (Renishaw inVia Spectrometer System) and XRD (Bruker D8 Advance, Cu-Kα radiation).

3. Results and Discussions
The effect of activated carbon to the surface functional groups was studied by FTIR spectra, presented in Figure 1. It could be observed some increase of stretching vibration of AC-NA at wavelength ranges of 1060-1200, 1530-1570, 1710, 3300-3400cm$^{-1}$. Based on the FTIR assigments of functional groups on carbon surfaces, these bands were assigned to stretching of C-OH (phenolic, ethers), quinones, carboxylic acid, and alcohols respectively [12, 13]. The increase of these bands indicates that surface modification of activated carbon have developed surface oxygen functional groups on the activated carbon. This result is confirmed by EDS atomic composition analysis presented in Table 1.

![Figure 1. FTIR spectra of activated carbon before and after modification](image_url)

The effect of activated carbon support modification could be observed from the EDS atomic composition analysis, presented in Table 1. The AC-NA samples had more Fe composition than the
unmodified AC samples. The similar effect of activated carbon modification to deposition of various metal catalysts, such as Nb [6], Fe [7] and Pt [8] has been reported before. This increase was possible due to the increase of functional groups, thus making the carbon surface more hydrophilic [6], thus resulting on an increase of interaction between metal catalysts with the support.

The SEM images of AC and AC-NA samples at various samples are presented in Figure 2. It could be observed that CNSs are present as conglomeration of spheres, as stated by Nieto-Marquez (2010) [14]. The effect of catalyst concentration could be observed from the SEM images. There are increasing amount of spheres with higher catalysts concentration, as the catalysts promote the growth of carbon nanomaterial. It could be visually observed that smaller CNSs was obtained with higher catalysts concentration. This result is confirmed by observation of TEM analysis. Similar result of catalyst concentration to the formation of CNSs has been reported before [15]. However, there are no spheres observed in AC-NA 30 samples.

The result observed from TEM analysis is in accordance with SEM analysis, which the higher catalyst concentration, the more CNSs are obtained, and its size became smaller. It also could be observed that the CNSs presented as dense spheres decorated with iron catalysts. For AC-NA 30 samples, it could be observed onion-like spheres (carbon nano onion) were formed. We speculate carbon onion were formed from decomposition of CNSs at high catalysts concentration. It is known that carbon onion is formed by several graphitic layers with few nanometers in thickness, with or without catalysts trapped within its structure [16]. This results is supported by XRD and Raman analysis of the samples.

| Sample | %mass | Sample | %mass |
|--------|-------|--------|-------|
| C      | O     | Fe     | C     | O     | Fe     |
| AC     | 98,31 | 1,69   | AC    | 90,46 | 9,5    | 0,04  |
| AC 10  | 84,27 | 11,76  | AC-NA 10 | 83,15 | 3,75   | 13,1  |
| AC 20  | 86,14 | 9,62   | AC-NA 20 | 78,38 | 11,92  | 9,7   |
| AC 30  | 67,87 | 16,51  | AC-NA 30 | 51,5  | 18,78  | 29,72 |

XRD spectra of standard activated carbon, AC, and NA 10, 20, and 30 are presented in Figure 4. It could be observed that standard activated carbon had wide broad peak at 20 of 20-30˚, and 40˚, indicating amorphous structure of activated carbon [17]. The spectra of AC 10, 20, 30, and NA 10, 20 show no significant difference, where C (100) and Fe peaks are observed. The C (100) peak is observed at 43˚, indicating weak graphitization of carbon structure that is normally observed in CNSs [14]. Iron peaks are also observed at 30˚ (220), 35.4˚ (311), 57.09˚ (422), and 62.4˚ (440), indicating magnetite (Fe₃O₄) structure [18]. Strong peak of C (002) at 26.5˚ is observed at NA 30 sample, indicating sp² carbon structure of graphite, while sharp peaks at 45˚ and 65˚ are body centered cubic α-Fe catalyst [19]. The α-Fe is known as graphitization catalysts, thus influencing formation of graphitic C (002) structure.
Figure 2. SEM images of AC 10 (a), AC 20 (b), AC 30 (c), and AC-NA 10 (d), AC-NA 20 (e), and AC-NA 30 (f) at 160,000x magnification

Figure 3. TEM images of AC 10 (a), AC 20 (b), AC 30 (c), and AC-NA 10 (d), AC-NA 20 (e), AC-NA 30 (f)
Figure 4. XRD spectra of AC Standard, AC 10, 20, and 30 (a), and AC-NA 10, 20, and 30 (b)

Raman spectra of AC and AC-NA are presented in Figure 5. There are two peaks observed on all AC and AC-NA samples. The D peak of disordered graphite structure is observed at 1344 cm⁻¹, and the G peak of sp² bonded carbon atoms bonded in hexagonal lattice at 1593 cm⁻¹. Although more CNSs are observed in SEM and TEM images, the ID/IG ratio show similar number around 0.9, indicating similar graphitic structure are obtained, with formation of graphitized carbon (CNSs), and smaller number of structural defects [20]. ID/IG ratio of CNSs have been reported to be around 0.86 to 1.20 [21-23]. For AC-NA samples, increase of Fe-catalyst leads to higher G peak and lower ID/IG ratio of 0.67. This result indicates formation of more graphitized carbon at higher catalyst concentration. The 2D peak is also observed in AC-NA 30 at 2700 cm⁻¹. It is known that the 2D peak of Raman spectra of carbon materials is highly sensitive to stacking of graphene sheets [24].

Figure 5. Raman spectra of AC 10, 20, 30 (a) and AC-NA 10, 20, 30 (b)

4. Conclusions

In summary, in this paper we have presented the effect of activated carbon support modification by utilizing simple wet oxidation method. The modification had successfully increased the oxygen functional groups and oxygen contents on the activated carbon support. The increase of oxygen functional groups, increase the activated carbon’s hydrophilicity and its interaction with metal catalysts, thus more catalysts were deposited on its surface, influencing the formation of CNSs. At high metal catalysts concentration, carbon onion was obtained as product. We speculate the carbon onion was formed from decomposition of CNSs due to high metal catalysts content in the support.
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