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Comparative Studies of Pristine and Functionalized CNFs Surface Properties and their Performance in Iron Distribution

Nur Wasimah Abd Wahab[a,*], Suriati Sufian[b], Thien Duc Nguyen Van[c], Maizatul Shima Shaharun[d]

[a,b,c] *Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Tronoh, ,Perak, Malaysia*
[d] *Fundamental and Applied Science Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Tronoh, ,Perak, Malaysia*

Abstract

Carbon nanofibers (CNFs) is one of carbon material type and has received fascinating attention to be used a metal support. In this study, two portions of samples were prepared separately into pristine CNFs (CNF-P) and functionalized CNFs (CNF-2RX) sample. CNF-2RX sample was refluxed in HNO_3 solution for 2 h. Subsequently, surface properties for both samples were evaluated by BET, FESEM-EDX, TEM, XPS, and FTIR. Results have shown significant differences of surface properties between CNF-P and CNF-2RX. It revealed that CNF-2RX which has been introduced to HNO_3 treatment was increased 12.43 % of surface area, pore volume and formed oxygen surface group (carboxylic group) compared to pristine CNFs. Then performance of iron distribution and loaded onto two different types of supports which are Fe/CNF-P and Fe/CNF-2RX by DP method were characterized by TEM, BET and XRF. These results revealed high loaded of iron were obtained for both samples (Fe/CNF-P with 8.43 wt. % and 9.15 wt. % for Fe/CNF-2RX) but only Fe/CNF-2RX shown uniform and close distribution between iron particles. Deposition of iron particles at Fe/CNF-2RX were found to be at internal surface which cause decrease of support surface area and pore volume with confirmed that strong interaction by adsorption between iron and oxygen surface group at CNF-2RX surface have obtained.

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Keywords: Carbon nanofibers; functionalized carbon nanofibers;surface area;pore volume; oxygen containing group;iron particles

1. Introduction

Nowadays carbon nanofibers (CNFs) have received a fascinating attention to be used as a support instead of

* Corresponding author. Tel.: +06-013-6944689.
*E-mail address:*nur_wasimah@yahoo.com

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conventional catalyst support pertaining to chemical and physical properties offered [1-3]. CNFs is a type of carbon nanomaterial and consist of graphitic filaments with graphene layers are perpendicular to the filament axis and hence exposing the open graphic planes edge sites [4-6]. It consists of length reported of 0.1 to 1000 μm and diameter in range of 0.4 to 500 nm [7-9]. Because of high accessibility due to large surface area (100 to 200 m^2/g), high mechanical strength, thermal stability in range of 875 to1175 K, adjustable bulk density, chemical purity and chemical inert as described by number of studies which make them become an ideally suitable for future iron supported catalyst [1, 10-12].

Chemical inert of CNFs make them have hydrophobic character means it has less anchoring sites because of poor wettability and poor interaction between support surface and polar metal precursor [13]. However, this problem can be overcome by introducing oxygen surface group. For instance, Toebes *et al*. and Van Der Lee *et al.* also found it has correlation between numbers of oxygen group with highly dispersed of nickel and platinum in their studies. Recent study by Plomp *et al.* also found inducing CNFs into pre-treatment also can induced number of oxygen surface group at CNFs surfaces which could influence deposition of metal particles [3]. These groups can be created by introducing CNFs in heat treatment, oxidation by plasma treatment, and in nitric acid [3].

Heating treatment was popularly used to enhance the crystalline and defect structure of CNFs, but it forming weak interaction between CNFs and polar iron catalyst phase [14]. The common oxidation method was acid treatment that is important to produce oxygen surface group at CNFs surface as it can turning CNF hydrophobic into hydrophilic character [3, 12, 14, 15]. Presence of this group is significant in order to avoid any repulsion between metal precursors polar solvent and toward CNFs surface, hence interaction by adsorption between the precursor and CNFs surface material can be increased [3].

Studies on preparing functionalized CNFs as iron catalyst support is still a little compared to other metal catalyst. In this paper, we will be emphasizing on pristine and functionalized CNFs supported iron catalyst precursors by using deposition precipitation (DP) as a synthesis method. As the most challenging in preparing supported metal catalyst is to obtain a high loading with uniform distribution on the support surface because if poor interaction between metal active precursor and support surface is occurred, agglomeration and broad distribution among metal catalyst particles also can be obtained [1]. This method was used in this study as many reviewers have reported of uniform distribution, high dispersion and metal loading were obtained [16].

Deposition precipitation (DP) method involves interaction of polar metal precursor with support surface as a result of nuclei generation. Number of studies found that in DP method, decomposition of urea as precipitating agent will be releasing hydroxide ion (OH^-) which turn out to be essential to avoid precipitate onto the solution [17-20]. Hence, most nucleation rate were higher at the support surface rather than in solution which homogeneous solution can be formed [21]. From this reaction, interaction between metal catalyst precursor and hydroxide ion would form numbers of nuclei at support surface during deposition and resulting in uniform distribution and high metal loading onto support surface which makes DP method turn out to be a suitable process for the distribution and dispersion of iron catalyst.

Aim of this paper is to evaluate surface properties between pristine CNFs and functionalized CNFs. Secondly, is to observe performance of iron distribution and loading at different support types of pristine and functionalized CNFs by using DP as a synthesis method. Performances were characterized by FESEM-EDX, FTIR, TEM, BET, Raman analysis and XRF.

2. Experimental

2.1 Support preparation

CNFs of herringbone as supported iron catalyst was purchased from Carbon Nano-material Technology Co. Ltd. are used in this study. One portion of CNFs sample was functionalized in acid treatment (CNF-2RX) and second portion is a pristine CNFs without introduce to any pretreatment with recorded as CNF-P. The raw sample was refluxed for 2 h in 65 % concentrated nitric acid (HNO_3) at 90 °C. Subsequently, the treated CNFs was washed thoroughly in deionized water and repeatedly until pH reach neutral (~ 6) by filtered using cellulose nitrate membrane filter paper of 0.2 μm pore size. The resulting material was dried overnight at 90 °C in carbolite oven and recorded as CNF-2RX.