UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF CARBON NANOMATERIALS USING CHEMICAL VAPOR DEPOSITION TECHNIQUE FOR LIQUID ADSORPTION

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By

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SYNTHESIS OF CARBON NANOMATERIALS USING CHEMICAL VAPOR DEPOSITION TECNIQUE FOR LIQUID ADSORPTION

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September 2011

Chair: Professor Fakhrul Razi Ahmadun, PhD

Faculty: Engineering

The synthesis of Carbon Nanotubes (CNTs) and Helical Carbon Nanofibers (HCNFs) using Floating Catalyst-Chemical Vapor Deposition method (FC-CVD) is reported. Acetone and ethanol are used as carbon sources, hydrogen as carrier gas, argon as purging gas and ferrocene as catalyst. The effect of carbon sources (acetone and ethanol), reactor temperatures (600-1000°C), and hydrogen flow rate (50 – 400 mL/min) are investigated. The CNMs produced are characterized by Thermo Gravimetrical Analysis (TGA), elemental analysis, Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and textural analysis.

The optimum condition achieved for synthesizing high yield and high purity of CNTs and HCNFs are at reactor temperature of 700°C and hydrogen flow rate of 100 mL/min and 150 mL/min, respectively. For CNTs, the highest yield obtained is 9 g carbon produced/g catalyst with the percentage purity of 92.49%. On the other hand, the highest yield achieved for HCNFs is 7 g carbon produced/g catalyst with the percentage purity of 90.63%. Increasing of temperatures and hydrogen flow rates indicates the decreasing in the surface area and the pore volume of CNTs and HCNFs. The maximum BET specific surface area and the pore volume obtained for CNTs are 90 m^2/g and 0.509 cm^3/g, respectively. Meanwhile, for HCNFs, the highest BET specific surface area and the pore volume achieved for CNTs are 89 m^2/g and 0.1927 cm^3/g, respectively. Acid and heat modification affects the BET specific surface area negatively. Nonetheless, HNO_3 modification improves the oxygen functional groups but in contrary, heat modification reduces the functional groups on the surface of CNTs and HCNFs.

Performance of CNTs and HCNFs are evaluated using the Methylene Blue (MB) and phenol adsorption. The equilibrium adsorption data of MB and phenol on the as-synthesized CNTs and as-synthesized HCNFs are investigated. The as-synthesized HCNFs show the highest adsorption capacity for MB and phenol at room temperature with the value of 33.17 mg/g and 11.33 mg/g, respectively. The Redlich-Peterson isotherm model fitted the experimental data as it has the highest R^2 and lowest SSE value. The kinetics of MB adsorption onto CNTs and HCNFs at different initial concentrations fitted the pseudo-second order model which provides the best correlation of the data.

The MB and phenol adsorption isotherms at room temperature show that the acid-modified CNMs has the lowest adsorption capacity, resulting from the reduction in their BET specific surface area and the existence of surface oxygen functional groups in abundance. However, heat-modified CNMs have the highest adsorption capacity for MB and phenol, contributed by the basicity surface, in spite of their low surface area. The adsorption capacity of MB and phenol onto acid-modified CNMs decreased 3-9% as compared to as-synthesized CNTs. The adsorption capacities of CNMs are as follows: **Heat-modified CNMs > As-synthesized CNMs > Acid-modified CNMs**

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai keperluan untuk ijazah Doktor Falsafah

SINTESIS BAHAN NANO KARBON MENGGUNAKAN TEKNIK PEMENDAPAN WAP KIMIA UNTUK PENJERAPAN CECAIR

Oleh

NORZILAH BINTI ABDUL HALIF

September 2011

Pengerusi: Profesor Fakhru'l razi Ahmadun, PhD

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Sintesis tiub nanokarbon (CNTs) dan karbon heliks nanofiber (HCNFs) menggunakan teknik pemangkin terapung pemendapan wap kimia (FC-CVD) dilaporkan. Aseton dan etanol digunakan sebagai sumber karbon, hidrogen sebagai gas pembawa dan ferosena sebagai pemangkin. Kesan sumber karbon (aseton dan etanol), suhu reaktor (600-1000 °C), dan kadar aliran hidrogen (50 – 400 mL/min) telah dikaji. CNTs yang dihasilkan dicirikan dengan analisis haba gravitian (TGA), analisis unsur (EDX), mikroskop elektron imbasan (SEM), pengubah Fourier inframerah (FTIR) dan analisis tekstur.

Keadaan optimum yang telah dicapai untuk mensintesiskan CNTs dan HCNFs yang mempunyai hasil dan berketulenan tinggi adalah pada suhu reaktor bersuhu 700°C dan kadar aliran hidrogen masing-masing sebanyak 100 mL/min dan 150 mL/min. Untuk CNTs, hasil tertinggi yang diperolehi adalah 9 g karbon termendap/g pemangkin dengan ketulenan sebanyak 92.49%. Sebaliknya, hasil maksima yang dicapai oleh HCNFs adalah 7 g karbon termendap/g pemangkin dengan ketulenan 90.63%.

Peningkatan suhu reaktor dan kadar aliran hidrogen menunjukkan pengurangan dalam luas permukaan dan isipadu liang CNTs dan HCNFs. Luas permukaan dan isipadu liang maksimum bagi CNTs adalah masing-masing sebanyak 90 m^2/g and 0.509 cm^3/g. Sementara itu, untuk HCNFs, luas permukaan isipadu dan liang maksimum adalah masing-masing sebanyak 89 m^2/g and 0.1927 cm^3/g. Pengubahsuaian asid dan haba ke atas CNTs memberi kesan negatif kepada luas permukaan. Sebaliknya, pengubahsuaian asid menggunakan HNO_3 meningkatkan kumpulan berfungsi oksigen pada permukaan CNTs dan HCNFs.

Prestasi CNTs dan HCNFs dinilai dengan penjerapan MB dan phenol. Data penjerapan keseimbangan pada suhu bilik menunjukkan bahawa HCNFs mempunyai keupayaan penjerapan pada MB sebanyak 33.17 mg/g dan phenol sebanyak 11.33 mg/g. Model isoterma Redlich-Peterson didapati sesuai dengan data eksperimen kerana ia mempunyai nilai pekali penentuan, R^2 yang tertinggi dan nilai ralat piawai kuasa dua (SSE) yang terendah. Kinetik penjerapan MB ke atas CNTs dan HCNFs

pada kepekatan awal yang berbeza didapati mematuhi model tertib *pseud*o kedua yang menyediakan data kolerasi terbaik.

Penjerapan isoterma MB dan phenol pada suhu bilik menunjukkan bahawa CNMs yang diubahsuai dengan asid mempunyai kapasiti penjerapan terendah yang disebabkan oleh pengurangan luas permukaan spesifik dan kewujudan kumpulan berfungsi oksigen di permukaannya. Walau bagaimanapun, CNMs yang diubahsuai dengan haba mempunyai kapasiti penjerapan yang tinggi untuk MB dan phenol yang disebabkan oleh permukaannya yang beralkali sekalipun mempunyai luas permukaan yang rendah. Kapasiti penjerapan MB dan phenol ke atas CNMs yang diubahsuai dengan asid berkurangan sebanyak 3-9 % dibandingkan dengan CNMs yang tidak diubahsuai. Secara keseluruhan, kapasiti penjerapan CNMs adalah seperti berikut: **CNMs diubahsuai dengan haba > CNMs tidak diubahsuai > CNMs diubahsuai dengan asid**

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I certify that a Thesis Examination Committee has met on 13 September 2011 to conduct the final examination of Norzilah binti Abdul Halif on her thesis entitled "Synthesis of carbon nanomaterials using chemical vapor deposition technique for liquid adsorption" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

NORZILAH BINTI ABDUL HALIF

Date: 13 September 2011

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