CHARACTERIZATION AND ADSORPTION STUDIES OF CARBON NANOTUBES / NANOFIBERS FOR METHANE STORAGE

By

ABD ULHAMID BELAL MOHAMED DANNA

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in fulfillment of the Requirement for the Degree of Master of Science

October 2004

DEDICATED

To

My Parents, wife, brothers and sisters

Abstract of the thesis presented to the Senate of University Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

CHARACTERIZATION AND ADSORPTION STUDIES OF CARBON NANOTUBES / NANOFIBERS FOR METHANE STORAGE

By

ABDULHAMID BELAL MOHAMED DANNA

October 2004

Chairman: Associate Professor . Sunny E. Iyuke, Ph.D.

Faculty: Faculty of Engineering

Natural gas (NG), which contains about 95% methane is currently gaining global acceptance as fuel for combustion engines because it is environmentally friendly and clean, naturally abundant, and cheaper than gasoline or diesel. Upon combustion when compared to gasoline or diesel it emits much less carbon dioxide (a major greenhouse gas) as well as several other air pollutants. However, the biggest challenge facing NG use as fuel for the transport industries is its storage. Therefore, carbon nano-structures have been synthesised using a typical floating catalyst chemical vapour deposition (FC-CVD) in a horizontal tubular reactor, which was fabricated in the Department of Chemical & Environmental Engineering, University Putra Malaysia. Ferrocene was used as the catalyst (Fe) precursor, benzene as the carbon source, while a mixture of hydrogen and argon was used as the carrier gas for both ferrocene and benzene vapours. The temperatures for the synthesis were varied between 1000 to 1200^{0}C to produce four distinct nanostructures, which are carbon

nanotubes (CNTs), nanofibers (CNFs), nanoparticles (CNPs) and nanoporous carbon bulky balls (CNPBs). Upon scanning with scanning electron microscope (SEM) and transmission electron microscope (TEM), the diameters of the carbon nanostructures obtained ranged from 2 to 100 nm. Further characterisation with Accelerated Surface Area and Porosimetry system (ASAP 2000), using liquid N_2 (77 K) for the Brunaur-Emmett-Teller (BET) surface characterisation, the surface areas, pore sizes and micropore volumes were found to be in range of 5.06 to 69.2 m^2/g, 6.4 to 225.4Å, and 8.03 x 10^{-4} to 13.7 x 10^{-3} cm^3/g, respectively for 0.602g samples. All samples had hysteresis indicating mesopore condensation of N_2 with highest amount adsorbed on CNTs. CNFs and CNPs indicated the different type of isotherm with methane according to the BDDT (Brunauer, Dening, Dening and Teller) classification. A very great size difference was seen between N_2 and CH_4 hysteresis, which was due to the molecular structure, solid-like and liquid-like phases proposed for CH_4 adsorption in and on the carbon nanostructure, respectively. A remarkable storage capacity of methane was achieved with these particles with storage capacity of 5.35 cm^3/g for CNTs, 1.48 cm^3/g for CNFs, and 0.3651 cm^3/g for CNPBs at room temperature and atmospheric pressure.

.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENCIRIAN DAN KAJIAN PENJERAPAN KARBON NANOTIUB / NANOFIBER UNTUK SIMPANAN METHANE

Oleh

ABDULHAMID BELAL MOHAMED DANNA

October 2004

Pengerusi: Profesor Madya. Sunny E. Iyuke, Ph.D.

Fakulti: Kejuruteraan

Gas asli, mengandungi 95% methane, kini telah digunakan sebagai bahan bakar engin pembakaran disebabkan ia merupakan satu bahan bakar yang kurang membahayakan alam sekitar serta bersih. Ia juga mempunyai bekalan semulajadi yang mencukupi dan murah dari segi kos berbanding dengan gasolin dan disel. Sebagai bandingan dengan pembakaran yang menggunakan gasolin dan disel, gas asli juga melepaskan karbon dioksida (satu gas kesan rumah hijau yang utama) yang rendah, begitu juga dengan bahan-bahan pencemaran udara yang lain. Walau bagaimanapun, pencabaran yang utama atas penggunaan gas asli sebagai bahan bakar untuk industri pengangkutan adalah cara penyimpanannya. Oleh sebab itu, kita telah sintesiskan karbon nano-struktur, dengan menggunakan satu mangkin terapung enapan wap kimia yang biasa, dalam satu reaktor tuib tegah. Reaktor tersebut telah difabrikasikan di Jabatan Kejuruteraan Kimia dan Alam Sekitar, Universiti Putra Malaysia. *Ferrocene* adalah digunakan sebagai pelopor (Fe) mangkin, benzene sebagai sumber karbon, dan satu campuran hidrogen dan argon adalah digunakan

sebagai gas angkut untuk kedua-dua wap *ferrocene* dan benzene. Suhu sintesis adalah berbeza antara 1000 hingga 1200^{o}C untuk menghasilkan empat nanostruktur yang berlainan jenis, di mana mereka adalah nanotiub (CNTs), nanofibers (CNFs), nanozarah (CNPs) dan karbon bola bernanoporos besar (CNPBs), Atas penskanan dengan mikroskop skan elektron dan mikroskop pancaran elektron, diameter karbon nanostruktur yang didapati berada dalam lingkungan antara 2 hingga 100nm. Pencirian lanjutan dengan menggunakan Sistem Luas Permukaan Terpecut dan Porosimetri (ASAP, 2000), yang menggunakan N_2 cecair (77K) untuk pencirian permukaan Brunaur-Emmett-Teller (BET), luas permukaan, saiz ruangan, dan isipadu mikro adalah didapati berada dalam lingkungan antara 5.06 hingga 69.2 m^2/g, 6.4 hingga 225.4Å dan 8.03x 10^{-4} hingga 13.7 x$10^{-3}$$cm^3/g$ masing-masing, untuk sampel berjisim 0.602g. Semua sampel telah dihisterisis menunjukkan pengewapan mesopore N_2 dengan kuantiti tertinggi yang terjerap dalam CNTs. CNFs dan CNPs telah menunjukkan jenis isotherma yang berbeza dengan methane dirujukkan kepada pengelasan BDDT. Satu pembezaan saiz yang besar boleh diperhatikan antara penghisterisisan N_2 dan CH_4, di mana ia disebabkan struktur molekul, fasa perupaan-pepejal dan perupaan-cecair dicadangkan akan berlaku pada penyelapan CH_4 ke dalam dan ke luar nanostruktur karbon masing-masing. Kapasiti simpanan methane yang ajaib telah dicapaikan dengan zarah-zarah tersebut, 5.35 cm^3/g untuk CNTs, 1.48 cm^3/g untuk CNFs, dan 0.3651 cm^3/g untuk CNPBs pada suhu bilik dan tekanan atmosfera.

ACKNOWLEDGEMENTS

Every praise is due to Allah alone, the Merciful and peace be upon His prophet who is forever a torch of guidance and knowledge for humanity as a whole.

I am very much thankful to Associate Professor Dr. Sunny.E. Iyuke for his encouragement, expert guidance, and valuable supervision throughout this research project that only expert could offer. I would also like to thank my supervisory committee. Associate Professor Dr. Fakhru'l Razi Ahmadun and Dr. Chuah T. G, Ph.D. for their continuous contributions.

I would like to acknowledge the support and inspiration given by the Libyan community members in Malaysia. Special thanks are also due to all staff of University Putra Malaysia for their help and support.

Abdulhamid Belal M. Danna

I certify that an Examination Committee met on 4th October 2004 to conduct the final examination of Abdulhamid Belal Mohamed Danna on his Master of Science thesis entitled "Characterization and Adsorption Studies of Carbon Nanotubes/Nanofibers for Methane Storage" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Mohamad Amran Mohd Salleh, Ph.D.
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Azni Idris, Ph.D.
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Robiah Yunus, Ph.D.
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Abu Bakar Mohamad, Ph.D.
Professor
Faculty of Engineering
Universiti Kebangsaan Malaysia
(independent Examiner)

GULAM RUSUL RAHMAT ALI
Professor/Deputy Dean
School of Graduate Studies
Unviresiti Putra Malaysia

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committees are as follows:

Sunny E. Iyuke, Ph.D.
Associate. Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Fakhru'l-razi Ahmadon, Ph.D.
Associate. Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

CHUAH TEONG GUAN, Ph.D.
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D.
Professore / Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations, which have been duly, acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

_____

Abd ulhamid Belal M.Danna

Date:

TABLE OF CONTENTS