MICROWAVE ASSISTED TUNGSTEN CARBIDE FROM WASTE KERNEL SHELL FOR REMEDIATION OF CHLORODIFLUOROMETHANE

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

JULY 2010

For my beloved family & friends………

I dedicated this work to my beloved family and friends that never stopped giving of themselves in countless ways, both direct and indirect. All of you are all mentioned in my daily prayer of thanks to a loving God who will convey that thanks in His own way back to you all.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my respectful supervisor, Prof. Dr. Abdul Rahim Yacob for all his guidance, motivation and continuous support encouraging me in my thesis writing. His kindness and generosity in sharing knowledge and experience is very much appreciated.

I also would like to thank all the Chemistry Department's staff, Ibnu Sina Institute and Mechanical Engineering Faculty especially for Encik Fuaad Omar, Puan Nurul Hajar, Encik Hamzah, Encik Kadir and Encik Adnan in helping me to solve my problems through out the period of my research. Not forget to my all my friends in Physical Chemistry Laboratory for their continuous support.

I'm very grateful to the research group, Dr. Abdul Rahim Yacob, Asyraf, Aqmar, Sheila, Raizul, Ekin and Nooridayu for being so cooperative and contribute brilliantly idea in completing this research successfully. To all my colleagues, thank you so much for all those times, advices and efforts. I must express my profound thanks to the Ministry of Science and Innovation (MOSTI) for the scholarship and Chemistry Department of Malaysia (Johor Branch).

Last but certainly not least, to my adored husband Mr Janizan Abu Kassim, my dad Mr Hanapi Sarmidi and my mom, Mrs Kamariah Marwi, not forget to my twin sister, Siti Zulaiha. I would like to thank all of you from bottom of my heart for being so supportive. Not forgotten to my dearest friend Farizsya, Faridah, Azian Murni and Pn Shalaz for the kind motivation whenever I'm down. Thank you so much.

PREFACE

This thesis is the result of my work carried out in the Department of Chemistry, Universiti Teknologi Malaysia between July 2008 and June 2010 under the supervision of Prof. Dr. Abdul Rahim Yacob. Part of my work described in this thesis has been sent for exhibition participations and reported in the following publications:

1) Abdul Rahim Yacob, Siti Zubaidah Hanapi, Nurul Aqmar Siam. (2009). ‘Nano-tungsten carbide prepared from waste palm kernel shell for remediation of chlorofluorocarbon (CFC) for safer environment. Gold Prize. Seoul International Invention Fair 2009 (Siff 2009) on 3 to 7 December 2009, Seoul International Invention fair 2009.

2) Abdul Rahim Yacob, Siti Zubaidah Hanapi, Viccinisvarri a/p Inderan
“Nano tungsten carbide supported on carbon from palm kernel shell in remediation of chlorofluorocarbon”
Journal IEEE Explore 2.6, 556-563, 2009.

3) Abdul Rahim Yacob, Siti Zubaidah Hanapi, Viccinisvarri a/p Inderan, Ratnasari Dewi Dasril
“Nano-tungsten carbide prepared from palm kernel shell for catalytic decomposition of hydrazine”
Proceedings of the 2009 International Conference on Chemical, Biological and Enviromental Engineering (CBEE 2009), 334-338, 2009

4) Siti Zubaidah Hanapi, Nooridayu Masrom, Abdul Rahim Yacob (2010) "Synthesize tungsten carbide from waste palm kernel shell by Intermittent Microwave Heating (IMH)" Chemistry: Fundamentals and Applications, SSR Technology, Perpustakaan Negara Malaysia : 217-224

5) Siti Zubaidah Hanapi, Nooridayu Masrom, Abdul Rahim Yacob. Poster presentation "Synthesize tungsten carbide from waste palm kernel shell by Intermittent Microwave Heating (IMH)"in 2nd Junior Chemist Colloqium on 30 June-2 July 2009. Faculty of Resource Science and Technology, Universiti Malaysia Sarawak (UNIMAS)

6) Abdul Rahim Yacob, Siti Zubaidah Hanapi and Nurul Aqmar Siam. Silver Medal 'High Surface Area Tungsten Carbide in Remediation of Freon Gas (CFC12)". Malaysian Technology Exhibition (MTE 2009) on 18-21 February 2009 in PWTC, Kuala Lumpur.

7) Abdul Rahim Yacob, Siti Zubaidah Hanapi and Nurul Aqmar Siam. Silver Medal 'High Surface Area Tungsten Carbide in Remediation of Freon Gas (CFC12)". Industrial Art and Technology (INATEX) on 16-20 August 2008, Universiti Teknologi Malaysia.

`ABSTRACT

The production of activated carbon production has been utilized from local waste palm kernel shell by chemical activation using phosphoric acid (H_3PO_4), a strong dehydrating agent. In this study, the effect of different acid concentration ranging from 10% to 50% was studied to establish the optimal condition to produce high surface area activated carbon. The activated carbon preparation includes soaking and dehydration of palm kernel shell in H_3PO_4 at 120 ºC and activation at 500 ºC. The activated carbon prepared was characterized by Nitrogen Adsorption analysis, FTIR, FESEM and TGA. The highest surface area of activated carbon prepared was used as the carbon source and selected as support in tungsten carbide (WC) synthesis. In this study, the WC catalyst was prepared via solid-state reaction using modified microwave oven and this method is named as Microwave-Assisted Method using two different precursors, tungsten metal and tungstic acid for comparison. Two sets of samples for each precursor were prepared with 6% and 15% tungsten respectively. Catalyst with high crystalinity structure was used to study the catalytic activity by hydrodehalogenation (HDH) reaction of Chlorodifluromethane (HCFC-22). Characterization results showed that acid concentration is an important factor for pore development and porosity of the activated carbon produced. The highest BET surface area was achieved when the palm kernel shell soaked in 50% phosphoric acid (AC50) with surface area of 1227 m^2g^{-1}. Meanwhile, catalyst with 6% tungsten (WC-M2) prepared from tungstic acid precursor produced better crystalinity of tungsten carbide (WC) than when tungsten powder was used as precursor. This catalyst is also found to be reactive to hydrodehalogenation of HCFC-22 with 84% conversion.

ABSTRAK

Penghasilan karbon teraktif telah dimanfaatkan dari sisa tempurung kelapa sawit melalui kaedah pengaktifan kimia menggunakan agen nyahpenghidratan yang kuat iaitu asid fosforik, H_3PO_4. Dalam kajian ini, kesan kepekatan asid antara 10% hingga 50% telah dikaji untuk memperolehi keadaan optimum dalam menghasilkan karbon teraktif dengan luas permukaan tertinggi. Penyediaan karbon teraktif melibatkan proses rendaman dan nyahhidratan tempurung kelapa sawit dalam larutan asid fosforik pada suhu 120 ºC dan kemudian diaktifkan pada suhu 500 ºC. Karbon teraktif yang dihasilkan ini kemudian dicirikan menggunakan kaedah Penjerapan Nitrogen, FTIR, FESEM dan TGA. Karbon teraktif yang mempunyai keluasan permukaan yang paling tinggi akan digunakan sebagai sumber karbon dan menjadi penyokong dalam sintesis pemangkin tungsten karbida, WC. Dalam kajian ini, pemangkin WC telah disediakan melalui tindakbalas keadaan-pepejal menggunakan ketuhar gelombang yang telah diubah suai dan dinamakan Kaedah Perbantuan Gelombang menggunakan dari dua pemula berlainan, logam tungsten dan asid tungstik. Dua set sampel bagi setiap pemula disediakan dengan kandungan tungsten 6% dan 15% masing-masing. Pemangkin dengan ciri-ciri kristal terbaik akan digunakan untuk mengkaji aktiviti pemangkinan melalui tindakbalas hidrodehalogenan (HDH) terhadap Chlorodiflouromethane (HCFC-22). Hasil pencirian menunjukkan kepekatan asid menentukan pembentukan liang dan keporosan karbon teraktif yang dihasilkan. Luas permukaan tertinggi diperolehi apabila tempurung kelapa sawit (AC50) direndam didalam larutan asid fosforik berkepekatan 50% iaitu 1227 m^2g^{-1}. Dalam pada itu, pemangkin dengan 6% tungsten (WC-M2) yang disediakan dari asid tungstik memberikan struktur kristal lebih baik dengan tungsten karbida (WC) berbanding menggunakan logam tungsten. Pemangkin ini juga didapati reaktif dengan peratus pertukaran sebanyak 84% terhadap HCFC-22

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LIST OF SYMBOLS / ABBREVIATIONS

˚C	-	degree Celsius
μm	-	micrometer
θ	-	Half angle of diffraction beam
λ	-	wavelength
AC	-	Activated Carbon
BET	-	Brunauer-Emmett-Teller
cm	-	centimeter
DTA	-	Differential thermal analysis
EDX	-	Energy Dispersive X-ray analysis
Eq.	-	Equation
FTIR	-	Fourier Transformation Infra red
g	-	gram
GC	-	Gas Chromatography
HDH	-	Hydrodehalogenation
IMH	-	Intermittent Microwave Heating
K	-	Kelvin
kV	-	kilo volt
mA	-	mili ampere
MA	-	Mechanical Alloying
MAM	-	Microwave Assisted Method
mL	-	milliliter
NA	-	nitrogen adsorption
nm	-	nanometer

ODP	-	Ozone Depletion Potential
rpm	-	rotation per minute
TG	-	Thermogravimetry
TMC	-	Transition Metal Carbide
XRD	-	X-ray Diffraction
W	-	Watt
WC	-	Tungsten Carbide
v/v	-	Volume/Volume
w/w	-	Weight/Weight

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CHAPTER 1

1.1 General Introduction

Activated carbons have a wide application with mostly used as adsorbent for emoval of pollutants from wastewater, in food industries, chemicals, pharmaceutical and medicine. Carbon precursor may come from organic material that are rich in carbon content such as lignite and wood while charcoal was known as the most commonly used precursor (Prahas *et al*., 2008). Due to the expensive cost for the production of activated carbon, a new carbon source from cheap and abundant waste has been studied to replace charcoal. Many agricultural by-products such as grain sorghum (Diao *et al*., 2002), waste tea (Yagmur *et al*., 2008), Bamboo (Ip *et al*., 2008), Kraft lignin (Fiero *et al*., 2006), Rice hull (Guo and Rockstraw *et al*., 2007), Jackfruit peel (Prahas *et al*., 2008), chestnut (Gomez *et al*., 2004) and date stones (Haimour and Emeish *et al*., 2006) have been discovered to be potential carbon precursor for activated carbon production. Activated carbon produced from this agricultural waste, can also facilitate the disposal problem and reduce pressure on forest clearing while these agricultural waste products also have no economical value and nonrenewable.

The physicochemical properties of activated carbon are greatly depending on the starting material and the method used for the production. There are two common methods for the preparation of activated carbon discussed by many literatures namely by physical activation and chemical activation. Chemical activation had been found as the most excellent way to generate high surface area and high pores volume of activated carbon (Yacob[c] *et al.*, 2009). Other advantage includes low cost production, because of reaction takes place at lower temperature and higher yield attained compared to physical activation (Hu *et al*., 2001).

Chemical activation involves usage of activating agent for the activation process and the most frequently used activating agents are zinc chloride, potassium hydroxide, sodium carbonate and phosphoric acid. Phosphoric acid is preferred because of the problem of corrosion, inefficient chemical recovery and environmental disadvantages associated with $ZnCl_2$ consistent discussed by Diao *et al.* (2002). Phosphoric acids is a strong dehydrating agent and present some advantages as to generate non-polluting waste and ease of elimination by leaching with water, thus can be easily recovered for further use. When compared to potassium hydroxide however phosphoric acid only develops small porosity but it increases the yield of activated carbon (Prahas *et al*., 2008).

Tungsten is a very hard and dense metal, mined from wolframite ore and symbolized as W. Tungsten combined with carbon alloy to form Tungsten Carbide which is second hardest material in the world after diamond, four times harder than titanium, twice as hard as steel and virtually unscratchable. Appeared as grey-black solid and has crystal hexagonal structure, generally used as metalworking tools, mining tools, wear-resistant components and in catalytic uses.

Transition metal carbides have attracted much interest in catalytic activities due to a number of valuable properties such as high melting temperatures, great hardness, high chemical resistance, electrical and thermal conductivities of metallic character and also a number of special properties, examples its capacity to be transformed to the superconducting state at relatively high temperatures and high emission properties. It is also commercially produced and as one of the oldest and well investigated powder metallurgy products (Nersisyan *et al*., 2005). There are a number of processes exist for tungsten carbide synthesis and each process has diverse characteristic of the powder produced such as Self Propagating High Temperature Synthesis and Combustion Synthesis, Mechanical Alloying, Intermittent Microwave Heating, Direct Carburization and Field Activated Combustion (Koc and Kodambaka., 2000).

Tungsten Carbide has been proved as an excellent catalyst for many gas conversion and reduction reactions such as in electrocatalytic hydrogen oxidation (Hara *et al*., 2007), methane to carbon monoxide and hydrogen (Claridge *et al*., 1998), methanol electrooxidation (Yi *et al*., 2006), ethylene hydrogenation (Moreno *et al*., 2001), hydrodehalogenation (Oxley *et al*., 2004) and hydrodechlorination (Delannoy *et al.*, 2000). In this study catalytic properties of the tungsten carbide prepared will be tested on Hydrodehalogenation (HDH) of Chlorodifluoromethane (HCFC22). Previous HDH studies have focused on nobel metals Pd, Pt and Rh, unfortunately these metals are also a hydrogenation catalyst though the selectivity of these metals for HDH are poor. Studied by Oxley *et al.* (2004) found that tungsten carbide is active, stable and selective catalyst for the HDH of halogenated organic compound such as CFCs, PCB and their analogs.

1.2 Problem Statement

The production of palm oil as the major commodity export in Malaysia has generated 3.96 million tonnes of solid waste and is increasing each year (Yusof *et al.*, 2006). This solid waste has no economical value, thus it is either left for abundant or burnt as a fuel. To make it extremely useful for industrial application, it’s been proposed to use this agricultural waste product as a carbon precursor in activated carbon production. The best and optimized carbon was then selected for tungsten carbide synthesis reactions.

Nearly all the technique for synthesis tungsten carbide involves dense procedure, time consuming, and expensive process and requires high temperature up to more than 1000 ºC. The production of tungsten carbide by this method usually used expensive source likes methane and carbon dioxide as a carbon source. Unfortunately, these method gives low surface areas of catalyst hence reduce the catalytic activity. This study however will produce high surface area WC catalyst from prepared high surface area activated carbon. Application of radiation frequency using microwave energy is seem as a new develop technique in WC synthesis. In this study, a simple homemade microwave was modified for activation purpose. The catalyst prepared then will be used to study the catalytic properties towards dehydrohalogenations of HCFC-22.

Chlorofluorocarbon (CFC) or known as 'ozone killer' can cause significantly stratospheric ozone depletion and global warming. This man-made chemical has been designed since 1930's and most widely used in its liquid form in mobile air conditioning and aerosol. Today, the consumption of CFC has increase rapidly with the spread new uses such as cleaning solvents, blowing agents, fire extinguisher or fire suppression agent and also medical propellant (Tien Tsai, 2005).

Chlorodifluoromethane ($CHClF_2$) referred as HCFC-22 or early known as CFC-22 was a promising substitute of Trichlorofluorocarbon (CFC-11) and Diflurodichlorocarbon (CFC-12) that already had been phase out from Montreal Protocol from usage or manufacturing. However, it should be noted that HCFC-22 contains single chlorine atom that also can cause ozone depletion and global warming. Even the ozone depletion potential of HCFC-22 is only 0.055, it is no longer can be accepted. Under Montreal Protocol, the substitute of the halogen compounds of CFC-11 and CFC-12 must have zero depletion potential. McCulloch (1999) reported that in some cases, the potential replacement compound has not yet been commercialized, therefore the demand of chemical with similar chemical properties such as HCFC may continue till 2050.

Difluromethane, HFCs containing neither chlorine nor bromine, do not contribute to ozone depletion. HFCs is one of the fluorocarbon family and have much common properties with CFCs that meet desirable properties for consumer applications. Unlike CFCs, they break down easily in the lower atmosphere resulting in much shorter lifetimes and reduce potential to contribute to ozone depletion and to global warming compared to CFCs (Midgley, 1997).

1.3 Objective of the research

The main objectives for this research are;

1. To prepare high surface area of activated carbon from waste palm kernel shell (PKS) via chemical activation with various concentration of phosphoric acid.
2. To synthesize tungsten carbide using microwave energy from two different precursor, tungsten powder and tungstic acid.
3. Catalyst with best crystalinity structure prepared from method above will be used to study Hydrodehalogenations (HDH) catalytic activity towards Chlorodifluoromethane (HCFC-22) at different temperature ranging from 100 ºC to 300 ºC.

1.4 Scope of Studies

This research has 3 main parts; preparation of activated carbon, tungsten carbide synthesis by Microwave Assisted Method and catalytic hydrodehalogenation of HCFC-22. The first part was to obtain high surface area activated carbon from chemical activation with various concentration phosphoric acid. Different concentration of acid ranging from 10% to 50% was applied during impregnation and activation of raw palm kernel shell. For the activation part, the regular box furnace will be used and the reaction will be performed under ambient condition. It is expected that the physical characteristic of the activated carbon will be varied depending on concentration acid used and finally high surface area will be achieved. Various spectroscopic methods include Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FTIR), Nitrogen adsorption and Field Emission Scanning Electron (FESEM) will be used to study the physical characterization.

The second part of this study is to prepare tungsten carbide using modified home-made microwave using tungsten powder and tungstic acid supported on the chosen prepared activated carbon. Activated carbon with highest surface area prepared from activation with phosphoric acid above will be used as a precursor for both tungsten carbide syntheses. Finally, the results of two mode of preparation will be compared. The end product will be characterized by X-Ray Diffraction (XRD) as well as Nitrogen adsorption.

Finally, the catalyst properties of tungsten carbide prepared will be tested on catalytic hydrodehalogenation of HCFC-22. A mini gas reactor was specially designed for the catalytic reaction of prepared catalyst towards CFCs. The experimentation is carried out at temperature range from 100 ºC to 300 ºC and identification will be done by Gas Chromatography Flame Ionization Detector (GC FID) with Gas-Pro Column.

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