TUNGSTEN CARBIDE PREPARATION USING CARBON FROM PALM KERNEL SHELLS AND ITS CATALYTIC HYDRODEHALOGENATION OF DICHLORODIFLUOROMETHANE

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For my beloved family & friends………

To my beloved family that never stopped giving of themselves in countless ways, both direct and indirect. I was going to start listing them all, but realized they are just too many to do that justice - so please accept the fact that 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.

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ABSTRACT

The importance of activated carbon as an adsorbent, catalyst and catalyst support has increased in industrial and environmental applications due to its special features; a very high surface area absorbency, inertness, and porosity. The surface structure and porosity of an activated carbon largely depended on the starting materials and the activation method used. In this study, activated carbons were prepared from palm kernel shell by chemical activation using zinc chloride, $ZnCl_2$ under both nitrogen flow and vacuum condition. The effects of impregnation ratio ($ZnCl_2$ to palm kernel shell) and activation condition on the surface properties of carbons were carefully studied in order to optimize these parameters. All the prepared activated carbons were characterized using FTIR, single point BET surface area, nitrogen adsorption analysis, FESEM-EDX and Thermogravimetry analysis. The selected activated carbons were used as a carbon source as well as catalyst support in the preparation of tungsten carbide, WC. The catalyst was prepared via sublimation technique where the metal precursor tungsten hexacarbonyl and activated carbon were milled together and heat-treated at 700ºC and 950ºC under helium flow. Two sets of WC catalysts with 6% and 15% tungsten content were prepared. The heat-treated catalysts were characterized by XRD, single point BET surface area and FESEM-EDX. The performance of the optimal prepared WC catalyst was tested on dichlorodifluoromethane, CFC-12 in hydrodehalogenation reaction. The results show that the impregnation ratio and the activation conditions had significant effect on the properties of activated carbon prepared. The activated carbon prepared with $ZnCl_2$ impregnation ratio of 1:1 under nitrogen gas flow (AC-1Z-N) showed the highest surface area, 878 m^2g^{-1} with micropore volume of 0.36 cm^3g^{-1}. The catalyst with 15% tungsten content supported on AC-1Z-N showed the highest formation of tungsten carbide and found to be very active in the hydro-dehalogenation reaction of CFC-12.

ABSTRAK

Kepentingan karbon teraktif sebagai bahan penyerap, mangkin dan penyokong mangkin semakin meningkat dalam industri kimia disebabkan ciri-ciri unik seperti luas permukaan yang luas, lengai and struktur keliangannya. Struktur permukaan dan sifat keliangan karbon teraktif sangat bergantung kepada bahan pemula dan kaedah pengaktifan. Dalam kajian ini, karbon teraktif telah disediakan daripada tempurung kelapa sawit melalui kaedah pengaktifan kimia menggunakan zink klorida, $ZnCl_2$ di bawah aliran gas nitrogen dan keadaan vakum. Kesan nisbah pengisitepuan bahan pengaktif $ZnCl_2$ kepada tempurung kelapa sawit telah dikaji untuk mendapatkan parameter yang optima. Pencirian teliti telah dilakukan menggunakan FTIR, penjerapan titik tunggal BET, analisis penjerapan nitrogen, FESEM-EDX dan TGA. Karbon teraktif yang terpilih telah digunakan sebagai sumber karbon dan juga sebagai bahan penyokong kepada mangkin tungsten karbida, WC. Mangkin WC telah disediakan melalui teknik pemejalwapan yang mana tungsten heksakarbonil dan karbon teraktif digiling dan dipanaskan pada suhu 700ºC dan 950ºC dalam aliran gas helium. Dua set sampel WC dengan kandungan tungsten 6% dan 15% telah disediakan. Pencirian mangkin WC yang terawat terma telah dilakukan menggunakan XRD, penjerapan titik tunggal BET dan FESEM-EDX. Prestasi mangkin telah diuji melalui tindak balas hidrodehalogenasi terhadap diklorodiflorometana, CFC-12. Keputusan pencirian menunjukkan bahawa nisbah $ZnCl_2$ kepada tempurung kelapa sawit dan keadaan pengaktifan memberi kesan yang penting terhadap sifat karbon teraktif. Karbon teraktif yang telah disediakan dengan nisbah $ZnCl_2$ kepada tempurung kelapa sawit, 1:1 (AC-1Z-N) mempunyai luas permukaan yang paling tinggi iaitu 878 m^2g^{-1} dengan isipadu mikroliang 0.36 cm^3g^{-1}. Mangkin dengan kandungan 15% tungsten yang disokong atas AC-1Z-N menunjukkan pembentukan tungsten karbida yang tertinggi dan didapati sangat aktif dalam tindak-balas hidrodehalogenasi CFC-12.

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LIST OF SYMBOLS / ABBREVIATIONS

°C	-	degree Celsius
µm	-	micrometer
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
ID	-	internal diameter
K	-	Kelvin
ksi	-	kips per linear foot
kV	-	kilo volt
mA	-	mili ampere
NA	-	nitrogen adsorption
mL	-	milliliter
nm	-	nanometer
rpm	-	rotation per minute

TG	-	Thermogravimetry
XRD	-	X-ray Diffraction
θ	-	Half angle of diffraction beam
λ	-	wavelength

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CHAPTER 1

INTRODUCTION

Activated carbons are carbonaceous materials that have highly developed porosity and internal surface area. They are widely used in a number of applications, such as separation and storage of gases; recovery of chemical products, removal of organic pollutants from drinking water and also as catalyst support. The increasing usage and competitiveness of activated carbon prices, has prompted the usage of agricultural by-products such as coconut shell (Azevedo *et al*., 2007), pistachio shell (Lua *et al*., 2004), saw dust (Mohanty *et al.,* 2005), and walnut shell (Alvim-Ferraz *et al*., 2003) as raw materials to prepare activated carbon. The physical properties of an activated carbon depend on the raw material and its treatment (Manocha, 2003).

Based on a study done by Kawser and Farid (2000), Malaysia generates 7.7 million tonnes of empty fruit bunches 6.0 million tonnes of fibre and 2.4 million tonnes of palm kernel shell every year. These by-products often considered as waste and have cause significant disposal problem. Therefore, in this research palm kernel shell was used as a starting material to prepare activated carbon in addition it is also a feasible solution to this environmental issue. The prepared activated carbon is then used as the carbon source as well as catalyst support for tungsten carbide catalyst.

The most important parameters for the catalyst support are inertness, porosity and surface area (Cameron *et al.*, 1990) Activated carbon is a material that combines all these characteristics optimally and additionally it has unique properties like its stability in both acidic and basic media, high surface area, microporosity, and cost effectiveness (Jankowska *et al*., 1991, and Auer et al., 1998).

The catalytic properties of tungsten carbide have attracted interest since Levy and Boudard (1973) first discovered that the carbides of Groups 4 - 6 resemble the catalytic properties similar to those of Platinum group metals. Since then they have been investigated for application in heterogeneous catalysis. To date, the use of tungsten carbide as well as other transition metal carbides as heterogeneous catalysts has grown (Keller *et al*., 1991; Moreno-Castilla *et al*., 2001 and Oxley *et al*., 2004)

Several methods have been developed for the preparation of tungsten carbide and mostly involve solid precursor and reducing agent (Gao and Kear, 1997; Liang *et al*., 2003). In general the resulting carbide has a low surface area. Therefore in this research tungsten carbide catalyst supported on activated carbon was prepared to obtain a high surface area catalyst. The catalyst was then tested on hydrodehalogenation of dichlorodifluoromethane (CCl_2F_2; CFC-12).

The widespread application of CFCs in industry including refrigeration, foam blowing agent and cleaning agent cause severe damage to the ozone layer and contributed significantly to global warming. Thus, destruction of ozone depleting substances especially CFCs has been attract many researchers interest since their production and uses have been phase out under international agreement known as Montreal Protocol (UNEP 2000). Presently, several treatment technologies are available such as thermal incineration, catalytic conversion and activated carbon adsorption. Among them catalytic conversion of CFCs into valuable compounds like hydrofluorocarbon (HFC) seem to be an attractive technique (Yu *et al*., 2006).

In past few years, the catalytic performances of transition metal carbide catalyst for hydrodehalogenation of CFCs have been studied because of their low cost and Platinum-like behaviour in catalysis (Delannoy *et al*., 2000 and Oxley *et al.*, 2004);. Thus, the tungsten carbide catalyst prepared in this research can be a potential substitute for the traditional catalyst platinum and palladium.

In this study, high surface area tungsten carbide catalyst supported on activated carbon was prepared. Locally obtained palm kernel shell was used as starting material to produce activated carbon. The resulting catalyst was then tested in catalytic hydrodehalogenation reaction of dichlorodifluoromethane, CFC-12.

1.1 Problem Statement

Palm kernel shell, is an abundant tropical waste from palm oil processing mills in tropical countries like Malaysia and Thailand. They either treat the waste by disposing it or use it as fuel. To economically utilize these agricultural by-products, it is proposed to use them as prospective starting materials for the preparation of activated carbon.

For the past few years a number of studies have been conducted on the preparation of activated carbon from palm kernel shells. However, so far there is no research has been done on application of palm kernel shell base activated carbon as tungsten carbide catalyst support. Tungsten carbide catalyst has exhibited platinum-like catalytic properties but is difficult to prepare with high surface area. The present work was devoted to study kernel shell based activated carbon as the carbon source as well as catalyst support towards synthesis a high surface area tungsten carbide catalyst. The optimal prepared tungsten carbide catalyst was tested on catalytic hydrodehalogenation of CFC-12 to find an economic approach to the remediation of CFCs.

1.2 Objective of the Research

The objectives of this research are as follows:

1) To prepare high surface area activated carbon from palm kernel shells.

2) To study the surface physical properties of the prepared activated carbon support.

3) To prepare and optimize condition for high surface area tungsten carbide catalyst using activated carbon.

4) To carry out the catalytic testing of hydrodehalogenation of CFC-12 using the optimal laboratory prepared tungsten carbide catalyst.

1.3 Scope of Studies

The first part of this study is concentrated on preparing the high surface area activated carbon using locally obtained raw material, palm kernel shells. Activated carbons were prepared by chemical activation using zinc chloride under both nitrogen flow and vacuum conditions. The effects of impregnation ratio ($ZnCl_2$ to palm kernel shell) and activation condition on the surface properties of carbons were studied in order to optimize these parameters. The prepared activated carbons will be characterized using several techniques which are, Fourier transform infrared (FTIR), single point BET analysis, nitrogen adsorption, Field emission scanning electron microscopy (FESEM) and Thermogravimetry analysis (TGA).

The prepared activated carbons used as the carbon source as well as catalyst support for tungsten carbide catalyst. The catalyst was prepared via sublimation technique followed by heat-treatment.

Catalytic testing hydrodehalogenation of CFC-12 was carried out using the optimal laboratory prepared tungsten carbide. The performances of tungsten carbide catalyst at temperature range from 200ºC to 350ºC were studied as an alternative for the expensive commercially available catalyst.

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