Faculty of Engineering

POTENTIAL OF PALM KERNEL SHELL (PKS) AS CARBON SUPPORT TO BIMETALLIC CATALYST (Cu-Ce) IN A HYDROCARBON SELECTIVE CATALYTIC REDUCTION (HC-SCR) OF NOx

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POTENTIAL OF PALM KERNEL SHELL (PKS) AS CARBON SUPPORT TO BIMETALLIC CATALYST (Cu-Ce) IN A HYDROCARBON SELECTIVE CATALYTIC REDUCTION (HC-SCR) OF NO_X

MELVINA TAN

A dissertation submitted in partial fulfillment
of the requirement for the degree of
Bachelor of Engineering with Honours
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Dedicated to my beloved parents and my supervisor who always bestow me sustainable motivations and encouragements

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ABSTRACT

Generally, a lot of research has centered to developed carbon support catalyst in a Selective Catalytic Reduction technology to enhance catalytic activity at low temperature. However, the application of palm kernel shell as carbon supported catalyst for SCR has not being broadly studied. Furthermore, the common applications of ammonia in SCR are considered unsuitable and difficult to handle. Therefore, this study was to investigate the potential of palm kernel shell as carbon support to bimetallic catalyst (Cu-Ce) in Hydrocarbon Selective Catalytic Reduction (HC-SCR) to reduce NOx from diesel engine. Several analyses were conducted to study the characterization and activity of catalyst that were prepared by using deposition-precipitation method. Characterization analysis involved Fourier-Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), X-Ray Fluorescence (XRF) and Hydrogen Temperature-Programmed Reduction method (H_2-TPR). In addition, catalytic activity was performed to determine NOx reduction at various temperatures, mainly at 140°C, 180°C, 220°C, 260°C and 300°C. From the BET analysis, the best catalyst found was copper supported on palm kernel shell (Cu/PKS) while the lowest surface area and pore volume was shown by cerium loading (Ce/PKS). However, XRF result showed that metal loading of cerium supported on palm kernel shell (PKS) was the highest (91.2%) as compared to other types of metal catalyst studied. In terms of catalytic activity, raw PKS shows the highest NOx reduction by 61% at 220°C. Thus, PKS is a good support to metal catalyst Selective Catalytic Reduction (SCR) of NOx but excess addition of metal catalyst either cerium or copper inhibit the performance of bimetallic catalyst on activated carbon as overall.

ABSTRAK

Secara umumnya, banyak penyelidikan telah tertumpu terhadap pengunaan karbon sebagai peyokong kepada pemangkin dalam teknologi *Selective Catalytic Reduction* (SCR) bertujuan untuk meningkatkan aktiviti pemangkin pada suhu rendah. Walaubagaimanapun, penggunaan kulit isirung sawit sebagai karbon penyokong kepada pemangkin logam dalam teknologi SCR belum diselidik secara meluas. Tambahan pula, aplikasi *ammonia* dalam teknologi ini adalah sukar untuk dikendalikan. Oleh sebab itu, tujuan utama kajian ini dijalankan adalah untuk menyelidik kebolehupayaan karbon yang diperbuat daripada kulit isirung sawit untuk diaplikasikan ke dalam sistem Penurunan Bermangkin Terpilih (SCR) bagi mengurangkan kepekatan gas nitrogen oksida (NO_x) yang dibebaskan oleh enjin diesel. Modifikasi telah dilakukan terhadap pemangkin ini dengan mengunakan kaedah pemendapan mendakan untuk meningkatkan kebolehupayaannya dalam mengurangkan kepekatan nitrogen oksida. Pelbagai analisis telah dijalankan termasuk *Fourier-Transform Infrared Spectroscopy (FTIR),* kaedah *Brunauer–Emmett–Teller (BET), X-Ray Fluorescence (XRF)* dan *Hydrogen Temperature-Programmed Reduction (H_2-TPR)* untuk mencirikan pemangkin tersebut. Tambahan lagi, ujian pemangkin telah dilakukan bagi menyiasat pengurangan nitrogen oksida dalam pelbagai suhu seperti pada 140°C, 180°C, 220°C, 260°C and 300°C. Daripada analisis *BET*, pemangkin terbaik yang dikenal pasti ialah “Cu/PKS” manakala “Ce/PKS” menunjukkan luas permukaan dan isipadu liang yang terendah. Walaubagaimanapun, melalui analisis XRF, “Ce/PKS” menawarkan lebih banyak bahan logam, *serium(Ce)* berbanding pemangkin yang lain. Dari sudut aktiviti pemangkin pula, didapati kulit isirung sawit menawarkan peratusan tertinggi dalam pengurangan nitrogen oksida sebanyak 61% pada suhu 220°C. Kesimpulannya, kulit isirung sawit berpotensi diaplikasikan dalam sistem Penurunan Bermangkin Terpilih (SCR) tetapi pengunaan berlebihan bahan logam sama ada *serium (Ce)* mahupun *tembaga (Cu)* menghalang keberkesanannya untuk mengurangkan nitrogen oksida (NOx).

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NOMENCLATURE

a.u.	Arbitrary unit
°C	Degree Celsius
cc/g	Cubic centimeter to gram
cm^{-1}	Inverse centimeter
g	Gram
L/min	Liter per minute
m^2/g	Square centimeter per gram
min	Minute
nm	nanometer
ppm	Parts per million

ABBREVIATIONS

AC	Activated carbon
Al_2O_3	Aluminum oxide
Ba	Barium
BET	Brunauer-Emmett-Teller
C	Carbon
$Ce(NO_3)_2.6H_2O$	Cerium (III) nitrate, hexahydrate
CeO_2	Cerium dioxide
Ce/PKS	Cerium supported on palm kernel shell
CO	Carbon monoxide
$Cu(NO_3)_2.3H_2O$	Copper (II) nitrate, trihydrate
CuO	Copper oxide
Cu/PKS	Copper supported on palm kernel shell
Fe	Iron
FTIR	Fourier-transform infrared spectroscopy
GAC	Granular activated carbon
H_2-TPR	Hydrogen temperature-programmed reduction
HC	Hydrocarbon
KBr	Potassium bromide
Mn	Manganese
MoO_3	Molybdenum trioxide
N_2	Nitrogen
N_2O	Nitrous oxide
$(NH_2)_2CO$	Urea

NH_3	Ammonia
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxide
NSR	NO_x storage and reduction
O_2	Oxygen
PAC	Powdered activated carbon
PKS	Palm kernel shell
Pt	Platinum
Rh	Rhodium
SCR	Selective catalytic reduction
SiO_2	Silicon dioxide
SO_2	Sulfur dioxide
SO_x	Sulphur oxide
STP	Standard operating conditions for temperature and pressure
TGA	Thermo-gravimetric analysis
TiO_2	Titanium dioxide
TiO_3	Titanium trioxide
V_2O_5	Vanadium pentoxide
WO_3	Tungsten trioxide
XRD	X-ray diffraction
XRF	X-Ray fluorescence
ZrO_2	Zirconium oxide

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Air pollution is among the most vital environmental concerns worldwide. It is made up of sulfur oxides especially SO_2, carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NOx) and particulate matter. Among them, NOx are considered as the primary pollutants of the atmosphere. Generally, the major contributions to the air contaminants are from the combustion of fossil fuels used in incineration processes, vehicles and power plants. Therefore, demands for cleaner emissions and lower fuel consumption are really relevant in today's situations to control emissions of air pollutants especially NOx (Skalska et al., 2013).

There are a lot of technologies invented and used in the industry to eliminate NOx such as by using Selective Catalytic Reduction (SCR) with ammonia. This technology is considered as one of the promising technologies to treat flue gas due to its efficiency, selectivity and economics factor (Skalska et al., 2013). Currently, numerous types of catalyst have been examined to enhance the catalytic activity performance in NH_3-SCR processes. The most widely employed catalysts are made of metal oxides, which have an optimum temperature range of $300 - 400°C$. This temperature range exceeds the temperature range of effluent gases of medium-small stationary sources, which will be forced to conform to the upcoming legislation in the near future (Boyano et al., 2008). Asserted also by Lei *et al*. (2013), in order to avoid the deactivation by SO_2 and H_2O which take place at low temperature, many metal oxide catalyst such as CuO/Al_2O_3, V_2O_5-WO_3/TiO_3 and MoO_3/TiO_2 are operated at temperature higher than 623 K (Lei et al., 2013).

Therefore, recently various catalysts have been found and developed to perform high activities at low temperature as low as $200°C$. Among the reported catalyst, metal catalyst especially Ce, Fe, Mn, Cu supported on carbon material such as activated carbon have shown very high activity and resistance to the remaining SO_2 (Huang et al., 2007). The usage of activated carbon as catalyst support present additional advantages in many aspects due to its high specific surface area and thermal stability (Tang et. al, 2007). Furthermore, the abundance of raw material as carbon sources makes the applications of carbon-based catalyst more reliable. Coal, coconut shell and palm kernel shell are among the raw materials that are potentially to be utilized to produce activated carbon. In Malaysia, it was reported that 4.49 million hectares of the land is under oil palm cultivation in which 17.73 million tonnes of palm oil and 2.13 tonnes of palm kernel oil are produced per year (Malaysian Palm Oil Council (MPOB), 2012). In addition, at least 5 million tons of palm kernel shell are produced every year from Crude Palm Oil industry (Biofuel Resources (BR), 2012). From this, it is expected that the amount of palm kernel shell could be increased in coming years. Hence, there is a great advantages and potential in utilizing palm kernel shell to produce activated carbon due to its abundance.

It is undeniable that the usage of ammonia in SCR system promises a good efficiency in reducing NOx. However, applications of ammonia are considered unsuitable and difficult to handle especially in automotive vehicles application. This is due to the hazardous and toxicity characteristic in reaction (Sawatmongkhon, 2011). Thus, SCR of NOx to N_2 using hydrocarbons (HC-SCR) is another alternative to replace ammonia as it provides a convenient and inexpensive process for the lean NOx reduction using fuel or unburned hydrocarbons as reducing agent (Garc et al., 2001). Furthermore, hydrocarbon is easy to handle and can be applied in any applications of SCR system due to its low hazardous effects.

In addition, in HC-SCR technology, the most active catalyst should have acidic sites, an active phase like copper and cobalt or for a wider activity, element such as Ag or a mixture of metals. Hence, the presence of metals such as copper or cerium as catalyst in HC-SCR can increase the efficiency of the SCR system in promoting good conversion of NOx. Hence, all factors such as the selection of reducing agents and catalyst are very important in ensuring good efficiency of SCR system.

1.2 Problem Statement

Recently, most research conducted on Selective Catalytic Reduction (SCR) catalyst has centered on carbon support catalyst in a SCR reaction with NH_3 as reductant to enhance catalytic activity at low temperature. However, the application of palm kernel shell as carbon supported catalyst for SCR has not being broadly studied. In Malaysia there are potential of agricultural waste for the production of the activated carbon such as palm kernel shells due to the availability and inexpensive material with high carbon and low inorganic content (Jabit, 2007). Therefore, the potential of activated carbon mainly derived from palm kernel shell as the support for bimetal catalyst (Cu-Ce) is to be explored in this study. In addition, the usage of hydrocarbon as reductant to serve as alternative to ammonia is also examined.

1.3 Research Questions

i. It is possible to apply porous carbon derived from palm kernel shell as HC-SCR catalyst support?
ii. Which catalyst (Cu or Ce) gives more impacts to NOx conversion?
iii. What is the optimal temperature of the catalyst that favor maximum NOx reduction in HC-SCR system?

1.4 Scope of Study

The main focus in this research is the application of agricultural waste as catalyst support on the SCR system. Palm kernel shell (PKS) is the agricultural waste that has the potential to be converted to activated carbon. Activated carbon plays an important role as a support to bimetallic catalyst (copper and cerium) embedded on it. With this, deposition-precipitation was chosen as catalyst preparation method to combine the activated carbon and metal catalyst in order to produce the SCR catalyst. In this study, the characterization of catalyst were carried out in terms of its surface functional group, surface area and pore volume, metal oxide loading and reduction temperature. In addition, catalyst activity was studied by monitoring the NOx reduction for raw PKS and different metal on activated carbon namely as Cu/PKS, Ce/PKS and Cu-Ce/PKS catalyst.

1.5 Research Aim and Objectives

The research aim and objectives are set and elaborated further is this section in order to solve the problems that are arise in problem statement.

1.5.1 Aim

To study the potential of palm kernel shell as carbon support to bimetallic catalyst (Cu-Ce) in Hydrocarbon Selective Catalytic Reduction (HC-SCR) of NOx.

1.5.2 Objectives

The objectives of the experiment to achieve the aim are as elaborated in each point stated below:

i. **To synthesize SCR catalyst from palm kernel shell activated carbon.**

Deposition-precipitation technique was carried out to synthesize SCR catalyst made from metal catalyst supported on activated carbon derived from palm kernel shell.

ii. **To characterize SCR catalyst developed from agricultural waste based activated carbon.**

The characterization of SCR catalyst developed from palm kernel shell was studied by using equipments such as Fourier-Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) method, X-Ray Fluorescence (XRF) and Hydrogen Temperature-Programmed Reduction (H_2-TPR). The characteristics examined by using those equipments were the surface functional group, surface area and pore volume, metal oxide loading and reduction temperature of catalyst.

iii. **To study the catalyst activity**

Catalyst activity was studied by monitoring the NOx reduction at operating temperature of 140°C, 180°C, 220°C, 260°C and 300°C for raw PKS, Cu/PKS, Ce/PKS and Cu-Ce/PKS. It was believed that metal catalyst supported by activated carbon able to perform high activities at low temperature as low as $200°C$ (Huang et al., 2007).

Thus, based on this reference temperature ($200°C$), that temperature range was selected in order to study the effects of low and high temperature on each catalyst.

1.6 Rationale and Significance of Research

The rationale and significance of this research can be classified and further explained as below:

i. Usage of biomass/waste to wealth project

The abundance of biomass from oil palm industry has contributed the chance to implement ‘waste to wealth’ project. By using the biomass of oil palm the by product from oil palm plantations, mills and refineries can be reduced.

ii. Nature & Environment

The production of activated carbon can reduce the polluted gases such as NOx as activated carbon can be used as catalyst support in SCR system.

iii. Economy

The availability of palm kernel shell in abundance make it easy to get and cheap in market. By reusing this by product, the profit can be doubled and ‘waste to wealth’ project can be implemented.

1.7 Summary of Chapter 1

As conclusion, carbon supported catalyst is another good alternative to be applied as SCR catalyst. Based on the studies that had been done before, palm kernel shell has shown a great potential to be synthesized as activated carbon. Therefore, the characterization and catalyst activity need to be performed as the next step in this study is to prove the effectiveness and its potential.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, harmful emission gas, NOx was discussed further in terms of its formation, sources of emissions and the effects towards environmental and human health. Besides that, related technologies such as NOx Storage Catalyst, Dry Sorption, NOx Decomposition and Selective Catalytic Reduction (SCR) used to control NOx emissions were also examined and compared. Among those technologies, Selective Catalytic Reduction (SRC) was chosen to be applied in catalytic activity studies due to several advantages it offered in reducing NOx. Lastly, included also in this chapter was about the activated carbon applications.

2.2 Nitrogen Oxide (NOx)

NOx are among the harmful air pollutants formed during the combustion of fossil fuel and biomasses. The abbreviation of NOx refers to the cumulative emissions, mainly of nitric oxide (NO) and nitrogen dioxide (NO_2). In incineration processes, NOx emitted is typically consists of a mixture of 95% NO and 5% NO_2 (Jablonska & Chmelarz, 2013). Generally, NO is considered the most difficult to be removed from ambient air as it is nearly insoluble in water whereas NO_2 is relatively easy to be removed due to its ability in dissolving well in water (Wang et al., 2014).

2.2.1 Formation of NOx

Basically, the formation of NOx occurs in three primary mechanisms (Jablonska & Chmelarz, 2013). The first mechanism is the thermal NOx or known as Zeldovich mechanism. This kind of mechanism involves direct reaction between air N_2 and O_2 at high temperature (Sawatmongkhon, 2011). Thus, the amount of NO produced is affected by the amounts of N_2 and O_2 that are available in the combustion environment. For this mechanism, it assumes that initially O*-radicals attack N_2 molecules as presented in Equation (2.1) below. The N* radicals produced from the reaction then react with O_2 and subsequently form NO with O shows as in Equation (2.2). Equation 2.3 below shows that the N* radicals also react with OH to produce NO (Mahmoudi et al., 2010).

$$O + N_2 \leftrightarrow NO + N \quad (2.1)$$

$$N + O_2 \leftrightarrow NO + O \quad (2.2)$$

$$N + OH \leftrightarrow NO + H \quad (2.3)$$

In addition, the corresponding NO then can be converted forward to NO_2 or back to NO as it attack O and HO_2 respectively as shows by Equations (2.4) and (2.5) below:

$$NO + HO_2 \rightarrow NO_2 + OH \quad (2.4)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (2.5)$$

Fuel NOx is another NOx formation mechanism. Typically, around 20-40% of fuel burning nitrogen is converted to NOx in combustion processes (Mahmoudi et al., 2010). Fuel NOx is known as oxidation of N-containing compounds present in fuel or biomass (Jablonska & Chmelarz, 2013). Generally, fuel nitrogen is made up of nitrogen atoms bonded to carbon or to other atoms. It formation rates are much higher than thermal NOx formation rates due to the presence of bonds that break more easily than the diatomic N_2 bonds. The formation of fuel NOx can be described as Equation (2.6) and (2.7) below where C (N) represents nitrogen in the char, and I (N) represent nitrogen-containing intermediate species such as CN, HCN, NH and NH_2 (Mahmoudi et al., 2010):

$$C(N) \rightarrow I(N) \quad (2.6)$$

$$I(N) + O \text{ (or } O_2\text{, OH)} \rightarrow NO + \cdots \quad (2.7)$$

Besides that, prompt NOx are also known to be as one of the mechanism for NOx formation. However, it contributes minimally to the total NOx emissions during