Faculty of Engineering

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

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Bachelor of Engineering with Honours
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POTENTIAL OF PALM KERNEL SHELL (PKS) AS CARBON SUPPORT TO BIMETALLIC CATALYST (Mn-Ce) IN HYDROCARBON SELECTIVE CATALYTIC REDUCTION OF NOx

TAN YONG CHIN

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 friends, who always bestow me sustainable motivations and encouragements

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ABSTRACT

Palm Kernel Shell (PKS) derived Activated Carbon (AC) has been chosen to be studied for its potential as the catalyst support to bimetallic catalyst in Hydrocarbon Selective Catalytic Reduction (HC-SCR) of NOx. The catalysts, Mn/PKS, Ce/PKS and Mn-Ce/PKS were prepared by using deposition precipitation method and calcination was performed at 250°C under ambient air. The catalysts and PKS were then characterized using Brunauer-Emmett-Teller method (BET), X-Ray Fluorescence (XRF), Hydrogen Temperature-Programmed Reduction (H_2-TPR) and Fourier Transform Infrared Spectroscopy (FTIR). The results indicate the successfulness of anchoring metal oxides on the catalyst. The catalysts and PKS were then tested with the exhaust from diesel engine at the flow rate of 1 L/min for preliminary study of de-NOx ability. Most of the catalysts show better NOx reduction efficiency at low temperature evidencing the potential of palm kernel shell as the catalyst support in low temperature HC-SCR system. PKS and Mn-Ce/PKS have the optimum operating temperature of 220°C while Mn/PKS and Ce/PKS optimum operating temperature were at 140°C and 300°C respectively. All catalysts exhibit NOx reduction less than 60% in this experiment possibly due to weak metal –support interaction and excessive metal loadings.

ABSTRAK

Karbon Aktif (AC) yang diperbuat daripada Kulit Isirung Sawit (PKS) telah dipilih untuk pengajian potensinya sebagai pemangkin sokongan untuk pemangkin dwilogam dalam Sistem Hidrokarbon Penurunan Bermangkin Terpilih (HC-SCR) untuk pengurangan nitrogen oksida (NOx). Pemangkin, Mn/PKS, Ce/PKS dan Mn-Ce/PKS telah disediakan dengan menggunakan kaedah pemendapan dan pengkalsinan telah dilakukan pada 250°di dalam persekitaran udara. Pemangkin dan PKS kemudiannya dicirikan menggunakan kaedah *Brunauer-Emmett-Teller* (BET), *X-Ray Fluorescence* (XRF), *Hydrogen Temperature-Programmed Reduction* (H2-TPR) dan *Fourier Transform Infrared Spectroscopy* (FTIR). Keputusan menunjukkan kejayaan pemendapan oksida logam pada pemangkin. Selepas itu, Pemangkin dan PKS kemudiannya diuji dengan ekzos dari enjin diesel pada kadar aliran 1 L/min untuk kajian awal keupayaan mengurangkan NOx. Kebanyakan pemangkin menunjukkan kecekapan pengurangan NOx pada suhu rendah yang membuktikan potensi karbon aktif daripada kulit isirong sawit sebagai sokongan pemangkin dalam sistem suhu rendah HC-SCR. PKS dan Mn-Ce/PKS mempunyai suhu operasi optimum pada 220°C manakala suhu operasi optimum untuk Mn/PKS dan Ce/PKS adalah pada 140°C dan 300°C. Semua pemangkin menmpamerkan pengurangan NOx kurang daripada 60% dalam eksperimen ini mungkin disebabkan oleh berlebihan beban logam.

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NOMENCLATURE

°C	-	Degree celcius
h	-	Hour
L/min	-	Liter per minute
min	-	Minute
t/yr	-	Tonne per year
wt%	-	Weight percentage
K	-	Kelvin
kg	-	Kilogram
g	-	Gram
%w/w	-	Weight per weight percentage
mL	-	Millimeter
mL/min	-	Millimeter per minute
°C/min	-	Degree celcius per minute
m^2/g	-	Meter square per gram
cc/g	-	Cubic centimeter per gram

ABBREVIATIONS

AC	-	Activated carbon
BET	-	Brunauer-Emmett-Teller
CO_2-TPD	-	Carbon Dioxide Temperature-Programmed Desorption
deNOx	-	NOx Reduction
DOC	-	Diesel Oxidation Catalyst
DPF	-	Diesel Particulate Filter
EGR	-	Exhaust Gas Recycling
FBN	-	Fuel-bound Nitrogen
FTIR	-	Fourier Transform Infrared Spectroscopy
GVW	-	Gross Vehicle Weight
H_2-TPR	-	Hydrogen Temperature-Programmed Reduction
HC	-	Hydrocarbon
HCCI	-	Homogeneous Charge Compression Ignition
HC-SCR	-	Hydrocarbon Selective Catalytic Reduction
HDD	-	Heavy Duty Diesel Engine
LDD	-	Light Duty Diesel Engine
LNT	-	Lean Nox Trap
NH_3-TPD	-	Ammonia Temperature-Programmed Desorption
PGM	-	Platinum Group Member
PKS	-	Palm Kernel Shell
PM	-	Particulate Matter
SCNR	-	Selective Non-Catalytic Reduction

SCR	-	Selective Catalytic Reduction
SD	-	Standard Deviation
SEM	-	Screening Electron Microscope
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Fluorescence

CHAPTER 1

BACKGROUND OF STUDY

1.1 Introduction

One of the greatest advantages of diesel engine is the greater fuel efficiency compared to petrol engine. However, excess emission of nitrogen oxide (NOx) and particulate matter (PM) become the intrinsic drawback of application of diesel engine (Herreros, George, Umar, Tsolakis, & O, 2014).

NOx have contributed to most of the air quality related environmental issue such as photochemical smog, nitric acid, acid rain, global warming and health effect on human (Kang, Duck, Man, & Eui, 2006). Regulations and legislation are becoming more stringent against NOx emission from both mobile and stationary sources due to its harmfulness towards environmental and health (Li, Chang, Ma, Hao, & Yang, 2011).

The operation of diesel engine in lean-burn conditions made application of conventional three ways catalytic converter restricted because the net oxidizing condition of exhaust severely inhibits NOx reduction (Ezike, 2011). Nevertheless, several technologies have been introduced to counter this shortcoming such as Lean NOx Trap (LNT), Ammonia Selective Catalytic Reduction (NH_3-SCR), combination of both LNT and NH_3-SCR, Hydrocarbon Selective Catalytic Reduction (HC-SCR), diesel oxidation catalysts (DOCs), and Diesel Particulate Filter (DPF) (Herreros et al., 2014; Theinnoi, Tsolakis, Sitshebo, Cracknell, & Clark, 2010). Among them, SCR system is the most preferable for its high efficiency as LNT exhibit CO2 penalty in trapping the NOx while the main focus of DPF and DOCs are to cope with the emissions of CO, HCs and PM (Chaieb et al., 2014; Fogel, Doronkin, Gabrielsson, & Dahl, 2012; Sitshebo, Tsolakis, Theinnoi, Rodríguez-fernández, & Leung, 2010).

Comparing both HC-SCR and NH_3-SCR, HC-SCR seems to be more preferable alternative since HC-SCR eliminates the need of additional reductant tank and the ability of HC-SCR to utilize the unburned hydrocarbon as reducing agent

(Sawatmongkhon, 2011). Besides, HC-SCR is prominent compared to NH_3-SCR because NH_3-SCR comes along with the problem of high cost of control, handling and safety system especially in mobile diesel-fueled engines (Garc & Lecea, 2001). Apart from that, in light duty diesel engine especially the exhaust is not in steady state making the injection of ammonia as reductant becomes difficult as excess ammonia will cause ammonia slip while HC-SCR eradicate this problem (Sawatmongkhon, 2011).

Many types of catalyst have been studied to be used in SCR system. They can be classified as i) noble meals, ii) metal oxides, and iii) transition metal-modified zeolites (Skalska, Miller, & Ledakowicz, 2013). In Miyadera (1993) pioneering research work, it was reported that Ag/Al_2O_3 is the most capable catalyst in HC-SCR. However, constrained operating temperature window (300–500°C) made it not suitable in application in diesel-vehicle as diesel engine exhaust typically range around 150°C to 250°C for light duty diesel engine (Chaieb et al., 2014; Jin et al., 2012). Thus it is necessary to develop a catalyst that can operate in that low temperature range. Research found that carbon supported catalyst have good activity at low temperature (150°C to 250°C) and resistance to deactivation by SO_2 (Garciabordeje, 2004).

The high surface resulted from high micropore and mesopore volumes made activated carbon useful in catalytic reaction (Yang, Chiang, & Burke, 2011). Appropriate modification of carbon characteristics and adopt with catalytically active phase is necessary for improvement of NOx reduction activity as activated carbon by itself show low activity. There are several other advantages of utilizing carbon as catalyst support such as the ease of preparation process, cheaper cost, availability of the resources, mechanical resistance toward abrasion and good performance at low temperature (Boyano, Gálvez, Lázaro, & Moliner, 2006). Furthermore, huge amount of agriculture waste is produced in Malaysia which can be utilized as to produce activated carbon such as empty fruit bunches, palm mesocarp fiber and palm kernel shell. Since Malaysia is one of the largest producer and exporter of palm-oil based product, the utilization of agricultural waste, particularly palm kernel shell in this study would be an added advantage due to their availability and low price (Jamaluddin et al., 2013; Yacob, Wahab, Suhaimi, & Amat Mustajab, 2013).

Many transition metal oxides are widely studied as the active phase of carbon supported catalyst because of their high activity for low temperature SCR of NO. However, both manganese oxides and cerium oxides catalysts have draws major attention of researcher in recent year. This is due to Mn-based catalyst exhibit high SCR activity at low temperature due to existence of numerous type of labile oxygen which is essential to complete the catalytic cycle while Ce-based catalyst contains outstanding oxygen storage and oxidation-reduction properties (Cao et al., 2015; Wu, Jiang, Liu, Wang, & Jin, 2007).

1.2 Problem Statement

Many researches have been conducted to study the potential of carbon based transition metal oxide catalyst as SCR catalyst in reducing NOx. Among them, manganese oxide (MnO) and cerium oxide (CeO) have attracted the most attention because Mn-based catalysts always exhibit outstanding activity at low temperature due to the existence of various labile oxygen and CeO_2 is adopted due to its excellent oxygen storage and oxidation–reduction properties (Cao et al., 2014). However, the researchers were more concerned with the potential of catalyst in NH_3-SCR system instead of HC-SCR. Besides, the utilization of agricultural waste as catalyst support has not yet been fully explored. Since Malaysia has abundant supply of palm oil based product which in turn generate huge amount of agricultural waste, the potential of agricultural waste based carbon as the support to bimetallic catalyst (CeO and MnO) catalyst in HC-SCR system is to be investigated.

1.3 Aim and Objectives of Study

Due to worldwide stringent regulation regarding NOx emission and abundant of agricultural waste especially palm kernel shell in Malaysia, this research aim to study the potential of palm kernel shell derived activated carbon based catalyst in selective catalytic reduction of NOx in HC-SCR system. The objectives of research can be specified as follows:

I. To synthesize SCR catalysts from palm kernel shell activated carbon using deposition-precipitation technique.
II. To characterize the synthesized catalyst.
III. To study the catalyst activity under different operating condition.

1.4 Scope of study

The main aim of the research is to study the potential of palm kernel shell derived activated carbon to act as the support for NOx selective catalytic reduction catalyst in HC-SCR system.

The catalysts were prepared using deposition-precipitation method with palm kernel shell activated carbon. The catalyst loading was fixed at 10 wt% and the metal ratio of Ce:Mn was varied at 0:1, 1:1 and 1:0. The pore volume and pore structure, surface area, catalyst loadings, degree of dispersion for catalyst, redox properties, and surface functional group are used to characterize the catalysts.

Last but not least, the catalyst activity was studied in HC-SCR system by varying the reaction temperature.

1.5 Methodology

In order to achieve the objectives as mentioned in Section 1.3, the study has been divided into few stages as the followings:

I. *Stage 1: Literature Review*

Information on NOx formation and its impact on environment were first collected. Besides, the recent status of NOx combat technologies was determined. Next, previous studies on SCR system catalyst were also reviewed in this stage. The catalyst preparation method, characterization techniques and also the activity of catalyst were the main focus in the review.

II. *Stage 2: Catalyst Synthesis*

The catalysts were synthesized using deposition-precipitation method by mixing metal salts and urea under certain temperature. The catalyst loading was fixed at 10% while the metal ratios were varied at 0:1, 1:1 and 1:0.

III. *Stage 3: Catalyst Characterization*

At this stage, the catalysts synthesized were characterized. The purpose of characterization was to quantify the physical and chemical properties for catalyst which accountable for performance of catalyst in the reaction (Ronald, Robert, & Suresh, 2002). In quantifying the physical properties of catalyst, the pore volume and surface area were determined through Brunauer-Emmett-Teller (BET) equation in a N_2 adsorption of catalyst at 77K. Besides, catalyst loading and degree of dispersion of catalyst were determined by using X-Ray Fluorescence (XRF). On the other hand, Hydrogen Temperature-Programme Reduction (H_2-TPR) and Fourier Transform Infrared Spectrometer (FTIR) were employed for chemical properties quantitative measurement. H_2-TPR aimed to determine the redox properties of the catalyst by measuring the amount of H_2 reduced at range of temperature. FTIR was employed to determine the surface functional group of catalyst.

IV. *Stage 4: Catalyst Activity Test*

In catalyst activity test, the reactions were carried out at different temperature. The optimum temperature was determined by correlating to reduction of NOx.

1.6 Rational and Significance of Study

The rational behind this study is the contribution in conserving the environment. Malaysia and Indonesia are known as the world’s largest producers for palm oil which accounts for the total of 85% of the world palm oil production. However, 4 kg of dry waste are produced from 1 kg of palm oil (Sulaiman, Abdullah, Gerhauser, & Shariff, 2011). Thus, utilization of agricultural waste is necessary to minimize the impact of disposal as well as optimizing the revenue from the agriculture.

On the other hand, the successful study of the potential of agricultural waste based catalyst in HC-SCR system will help in combating the air pollution gas (NOx) which cause the severe environmental and health issue. This implies the improvement of the effectiveness of the system and also minimization of capital cost for such technology.

1.7 Summary

In a nutshell, this chapter generally discussed the technology in handling the NOx, which is one of the severe pollutant gases. Several abatement technologies have been introduced and HC-SCR system was found to be more advantageous technology over the others due to the ease of handling and the ability to utilize the unburned hydrocarbon from the exhaust. However, the potential of agricultural waste based catalyst to act as HC-SCR catalyst have not yet been explore. Besides, the agricultural waste issue in Malaysia especially palm oil waste is also discussed and utilization of the waste will help in reducing environmental issue as well as optimizing the profit. Thus, this study investigates the potential of palm kernel shell activated carbon-based catalyst in selective catalytic reduction of NOx in a HC-SCR system.