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CALCIUM-BASED MIXED OXIDE CATALYSTS FOR TRANSESTERIFICATION OF PALM OIL TO BIODIESEL

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By

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CALCIUM-BASED MIXED OXIDE CATALYSTS FOR TRANSESTERIFICATION OF PALM OIL TO BIODIESEL

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Chair : Tan Yen Ping, PhD

Faculty : Science

Rapid population growth and industrial revolution have resulted in non-renewable energy natural resources scarcity on a global scale and global warming. The energy crisis issue and environmental awareness have urged the development of cleaner alternative fuels. Biodiesel, a renewable energy with biodegradable characteristic showed a great potential to be explored to satisfy the world energy demand while simultaneously maintain the sustainability of the environment. In this study, various calcium-based mixed oxide catalysts were studied and evaluated to develop an effective catalyst with high activity and durability for biodiesel production process. Investigations were carried out on different compositions of calcium and niobium ($CaO-Nb_2O_5$), calcium and cerium ($CaO-CeO_2$), and, calcium and nickel (CaO-NiO) mixed oxides. These catalysts were characterized by x-ray diffraction (XRD) analysis, thermal gravimetric analysis (TGA), Fourier-transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), x-ray fluorescence (XRF) spectroscopy, temperature-programmed desorption of CO_2 (TPD-CO_2) and nitrogen sorption with Brunauer-Emmett-Teller (BET) surface area analysis.

The catalytic activities of the mixed oxides were tested by transesterification of palm oil. Effects of reaction time, methanol to oil ratio, reaction temperature and the amount of catalysts were investigated to optimize the yield of fatty acid methyl esters (FAME). The optimum FAME yield, 96 %, was observed in $CaO-Nb_2O_5$ system when the reaction mixture were refluxed in the condition of 65 ^oC with methanol to oil ratio equal to 12, a reaction time of 2 h, and 3 wt.% of catalyst. Meanwhile, under optimum conditions of 5 wt. % catalyst loading, 12:1 methanol to oil molar ratio, and 65 ^oC reaction temperature, $CaO-CeO_2$ and CaO-NiO mixed oxides produced biodiesel yields of 95 % and 91 %, respectively, but with a reaction time of 4 h and 3 h, respectively. In term of durability, $CaO-Nb_2O_5$, $CaO-CeO_2$ and CaO-NiO mixed oxides can be reused 6, 6 and 5 times, respectively without significant losses of catalytic activities (FAME yield > 70 %). Pores filling and lixiviation of calcium into the reaction medium and products are the major factors for the deactivation of catalysts.

Biodiesel production was optimized by using response surface methodology (RSM) in conjunction with central composite design (CCD). It was found that CaO-Nb_2O_5 achieved an optimum level of biodiesel yield, 97.05 % at 2.49 h reaction time, 3.54 wt. % of catalyst loading and methanol to oil molar ratio of 13.20. Meanwhile, CaO-CeO_2 achieved optimum biodiesel yield of 96.39 % under the following reaction conditions: reaction time: 3.67 h, catalyst amount: 4.03 wt. %, methanol to oil molar ratio: 14.17. Besides, under the reaction conditions: reaction time: 3.73 h, catalyst amount: 3.34 wt. %, methanol to oil molar ratio: 12.23, the optimum biodiesel yield achieved by CaO-NiO catalyst was 92.93 %.

In a nutshell, although pure calcium oxide shows the promising results in biodiesel production, it tends to leach out into the reaction medium and products. However, the mixed oxides prepared in this study greatly improve the performance and stability of the calcium by reducing its lixiviation into reaction medium and products. Among the three mixed oxides, CaO-Nb_2O_5 and CaO-CeO_2 mixed oxides are the best catalysts for transesterification process, either in terms of biodiesel yield (≥ 95 %) or the stability of the catalysts (both can be reused 6 times). Therefore, these catalysts are the potential substitute for the current applied homogeneous catalysts (NaOH, KOH) in the biodiesel industry, where no post-treatments of biodiesel are needed and thus it is more environmentally benign.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMANGKIN CAMPURAN OKSIDA BERASASKAN KALSIUM UNTUK TRANSESTERIKASI MINYAK SAWIT KEPADA BIODIESEL

Oleh

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Kadar pertumbuhan penduduk sedunia yang tinggi and revolusi industri yang pesat telah menyebabkan kekurangan sumber-sumber tenaga semula jadi yang tidak boleh diperbaharui dan pemanasan bumi. Isu krisis tenaga dan kesedaran alam sekitar telah menggesa pembangunan tenaga baru yang lebih mesra alam. Biodiesel merupakan tenaga yang boleh diperbaharui dan mempunyai ciri-ciri boleh terbiodegradasi. Ini menunjukkan biodiesel mempunyai potensi yang besar untuk dikaji selidik bagi memenuhi keperluan tenaga sedunia dan tanpa mengganggu keseimbangan alam sekitar. Dalam kajian ini, pelbagai jenis pemangkin campuran oksida berasaskan kalsium telah dikaji dan dinilai bagi menghasilkan pemangkin yang efektif dengan aktiviti dan kestabilan yang tinggi untuk proses penghasilan biodiesel. Kajian ini telah dijalankan ke atas pelbagai komposisi campuran oksida kalsium dan niobium ($CaO-Nb_2O_5$), campuran oksida kalsium dan serium ($CaO-CeO_2$) serta campuran oksida kalsium dan nikel (CaO-NiO). Pemangkin tersebut telah dicirikan dengan mengguna analisis pembelauan sinar-x (XRD), analisis gravimetri terma (TGA), spektroskopi inframerah tranformasi Fourier (FT-IR), mikroskopi elektron pengimbasan (SEM), pendarfluor sinar-x (XRF), nyahjerapan CO_2 terprogram suhu (TPD-CO_2) dan penjerapan nitrogen melalui analisis luas permukaan Brunauer-Emmett-Teller (BET).

Aktiviti pemangkinan campuran oksida tersebut diuji dengan transesterifikasi minyak kelapa sawit. Kesan parameter seperti jangka masa tindak balas, nisbah metanol kepada minyak, suhu tindak balas dan amaun pemangkin telah disiasat untuk mengoptimumkan hasil metil ester asid lemak (FAME). Hasil optimum FAME setinggi 96 %, telah diperhatikan bagi sistem $CaO-Nb_2O_5$ apabila campuran bahan tindak balas direfluksikan pada suhu 65 ^oC dengan nisbah metanol kepada minyak bersamaan 12, jangka masa tindak balas selama 2 jam dan amaun pemangkin sebanyak 3 % berat. Manakala, hasil biodiesel bagi pemangkin campuran oksida

$CaO-CeO_2$ dan campuran oksida CaO-NiO masing-masing mencapai 95 % dan 91 % di bawah keadaan optimum di mana amaun pemangkin sebanyak 5 % berat, nisbah metanol kepada minyak sama dengan 12, dan suhu tindak balas 65 ^oC, tetapi jangka masa yang diperlukan adalah 4 jam dan 3 jam masing-masing. Dari segi kestabilan, sistem pemangkin campuran oksida $CaO-Nb_2O_5$, $CaO-CeO_2$ dan CaO-NiO masing-masing boleh digunakan semula sebanyak 6, 6 dan 5 kali tanpa penurunan aktiviti pemangkinan yang ketara (hasil FAME > 70 %) diperhatikan. Pengisian liang-liang pemangkin dan pelesapan kalsium ke dalam medium tindak balas dan hasil tindak balas merupakan faktor utama penyahaktifan pemangkin yang berasaskan kalsium ini.

Penghasilan biodiesel telah dioptimumkan melalui kaedah gerak balas permukaan (RSM) dengan reka bentuk komposit berpusat (CCD). Pemangkin campuran oksida $CaO-Nb_2O_5$ didapati mencapai hasil biodiesel optimum, 97.05 %, dengan jangka masa tindak balas 2.49 jam, amaun pemangkin 3.54 % berat dan nisbah metanol kepada minyak bersamaan 13.20. Manakala, pemangkin campuran oksida $CaO-CeO_2$ mencapai hasil biodiesel optimum 96.39 % di bawah keadaan tindak balas berikut: jangka masa tindak balas: 3.67 jam, amaun pemangkin: 4.03 % berat dan nisbah metanol kepada minyak: 14.17. Selain itu, di bawah keadaan tindak balas: jangka masa tindak balas: 3.73 jam, jumlah pemangkin: 3.34 % berat dan nisbah metanol kepada minyak bersamaan 12.23, hasil biodiesel optimum yang dicapai pemangkin campuran oksida CaO-NiO adalah 92.93 %.

Kesimpulannya, walaupun kalsium oksida tulen mempunyai prestasi yang memberangsangkan sebagai pemangkin dalam proses penghasilan biodiesel, akan tetapi kecenderungannya untuk terlesap ke dalam medium tindak balas dan juga produk. Namun demikian, pemangkin campuran oksida yang disediakan dalam kajian ini telah meningkatkan prestasi dan kestabilan kalsium oksida dengan mengurangkan keterlarutannya ke dalam medium tindak balas dan produk. Antara tiga jenis campuran oksida yang dikaji, $CaO-Nb_2O_5$ dan $CaO-CeO_2$ merupakan pemangkin campuran oksida yang paling bagus untuk proses transesterifikasi, sama ada dari segi hasil biodiesel (≥ 95 %) atau kestabilan pemangkin (kedua-dua boleh digunakan semula sabanyak 6 kali). Oleh hal yang demikian, pemangkin campuran oksida merupakan pengganti berpotensi kepada pemangkin homogen (NaOH, KOH) yang digunakan dalam industri biodiesel. Pemangkin campuran oksida ini juga merupakan pemangkin yang lebih mesra alam di mana tiada rawatan susulan biodiesel diperlukan.

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I certify that a Thesis Examination Committee has met on 18 December 2014 to conduct the final examination of Wong Yong Chen on his thesis entitled "Calcium-Based Mixed Oxide Catalysts for Transesterification of Palm Oil to Biodiesel" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

h	hour
min	minute
^{o}C	Degree Celsius
wt. %	weight percent
g	gram
nm	nanometers
Å	Angstrom
θ	theta
2θ	2-theta
λ	wavelength
E_0	Ground state
E_1	Excited state
rpm	Revolutions per minute
RSPO	Roundtable on Sustainable Palm Oil
NGO	Non-governmental Organisations
MPOB	Malaysian Palm Oil Board
LCA	Life Cycle Analysis
GHG	Greenhouse Gases
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Esters
^{13}C NMR	Carbon-13 Nuclear Magnetic Resonance
TGA	Thermal Gravimetric Analysis
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
BET	Brunauer-Emmett-Teller
TPD	Temperature Programmed Desorption
FT-IR	Fourier-transform Infrared
ATR	Attenuated Total Reflection
SEM	Scanning Electron Microscopy
GC	Gas Chromatography
AAS	Atomic Absorption Spectroscopy
FID	Flame Ionization Detector
RSM	Response Surface Methodology
CCD	Central Composite Design
ANOVA	Analysis of Variance
ICDD	International Center for Diffraction Data
FWHM	Full width at half maximum
JCPDS	Joint Committee on Powder Diffraction Standard

CHAPTER 1

INTRODUCTION

1.1 Energy

Energy is defined as the potential or the ability to do work. Energy can exist in various forms such as potential energy, kinetic energy, heat energy, electrical energy and sound energy. Energy cannot be created or destroyed. However, it can be transformed from one form to another like from potential energy to kinetic energy or from kinetic energy to heat energy (Lim and Lim, 2012). In general, there are two main groups of energy which are non-renewable energy and renewable energy.

1.2 Non-renewable Energy

Non-renewable energy is the energy in which its resources cannot be re-produced, re-grown, regenerated or even reused in order to fulfill the consumption and demand. Thus, these resources will be depleted continuously and it is very hard to be replaced once it is used. As a consequence, the availability of these resources is decreasing from time to time. Resources of non-renewable energy are nuclear power and fossil fuel (coal, petroleum and natural gas) (Chiras, 2006).

Until today, the energy is mainly derived from non-renewable energy such as nuclear, coal, petroleum and natural gas. Among these energy resources, fossil fuels comprise more than 80 % of the total world energy consumption (EIA, 2008). It shows that the mankind is still greatly relied on the coal, petroleum and natural gas to preserve economic growth and maintain standard of living. Fossil fuels are extensively used as fuels in automotive and in electricity generation especially in industry.

The World Energy Forum has predicted that coal, petroleum and gas reserves will be diminished in less than 10 decades (Sharma and Singh, 2009). On the other hands, World Energy Outlook 2006 estimated the reserves depletion time for petroleum is between 39 to 43 years, while for coal and natural gas are 164 and 64 years respectively (IEA, 2006). According to Khan *et al.* (2008), fossil fuels, uranium and energy mix would be possible to sustain world energy till the end of 21st century but eventually new energy sources would be required to volte-face global warming and meet the increased population demand. The new energy in this context may refer to renewable energy.

1.3 Renewable Energy

Renewable energy is the energy that can be produced and regenerated continuously. This renewable source of energy includes wind energy, tidal energy, hydropower, solar energy, geothermal energy and others. Renewable energy is widely used in generating electricity as well as in producing heat and fuel (Quaschning, 2005).

Nowadays, there is worldwide research carried out by the global community in looking for other reliable energy resources to replace fossil fuel resources due to their uncertainty in future supply and the potential one is the energy produced from biomass. According to Demirbas (2008), biomass represents a secure domestic source of energy that is not subject to the price fluctuations and supply uncertainties of imported petroleum and natural gas. Demirbas also claimed that Turkey as one of the major agricultural country in the world, increasingly produced biomass energy and this energy would be the potential energy to substitute fossil fuels.

Advantage of using renewable energy is that this type of energy does not produce any greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide, chlorofluorocarbons (CFCs) and others. Therefore, it would not lead to greenhouse effect and is environmental friendly. In addition, less maintenance is required for the facilities of renewable energy compared to conventional energy generators. As a result, operation costs for renewable energy is much cheaper than non-renewable energy (Smith and Taylor, 2008).

However, the disadvantage of using renewable energy is some resources are not available in certain countries and areas. Hence, there is difficulty in generating power at that particular area. Besides, the energy produced from the natural resources is normally in small quantity, hardly to generate power or electricity in large quantity (Abbasi, 2010).

1.4 Global Energy Issues

The main global energy issue is the demand versus supply for the fossil fuels. The demand for non-renewable energy increased with the population growth while the reserves of fossil fuels shrunk with the time. When demand over supply, it resulted in energy crisis. The Energy Information Administration (EIA) has predicted that energy consumption increases at an average rate of 1.1 % per annum, from 500 quadrillion Btu in 2006 to 701.6 quadrillion Btu in 2030 (EIA, 2007a). However, the current growth in world energy consumption is approximately 2 % per annum (Mason, 2007). Therefore, the actual energy consumption figure would be higher than that predicted by EIA.

Figure 1.1 illustrates the consumption of fossil fuels worldwide from 1965 to 2030. Among these fossil fuels resources, oil or more commonly known as petroleum remains the most important primary fuel which accounting for 36.4 % of the world's primary energy consumption. The consumption is expected to grow in the similar trend in the future (BP, 2007; EIA, 2007b). Increase in consumption and decrease in the non-renewable reserves will bring a sequence of adverse effects and the most severe one is price fluctuations of fossil fuels.

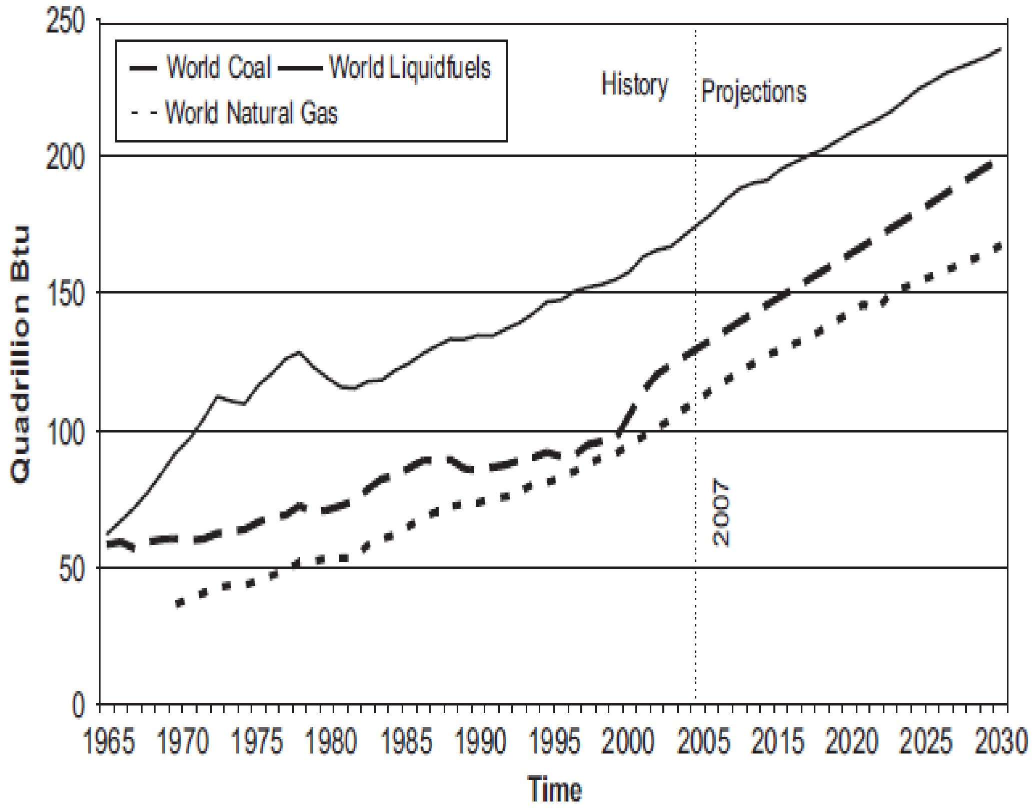

Figure 1.1 Consumption of fossil fuel worldwide from 1965 to 2030 (Data collected from EIA and BP) (Shafiee and Topal, 2009)

The availability of reserves and consumption rate of petroleum greatly influence its price in global market. From year 1980 to 2006, the price of petroleum has unexpectedly increased from about 20 dollars per barrel to 60 dollars per barrel. In 2008, the petroleum price even reached over 138 dollar per barrel (Shafiee and Topal, 2009). The sharp increase in petroleum price was due to the high demand of continuously growing population and industry while the number of petroleum reserves increased in a more constant rate. In other words, when demand over supply, the petroleum price will increase.

Besides, extensive generation energy by combusting fossil fuels has created several environmental concerns which can threaten the sustainability of our ecosystem. The main concern would be emission of greenhouse gases (carbon dioxide, methane, nitrous oxide) and other types of air pollutants (sulphur dioxide, hydrocarbons and volatile organic compounds). Huge accumulation of greenhouse gases in the atmosphere will absorb energy from the sun, slowing or preventing the loss of heat to space. Eventually, the earth becomes warmer and this phenomenon is known as "greenhouse effect". Each of greenhouse gases can remain in the atmosphere for different period of time, ranging from a few years to thousands of years.

Carbon dioxide, CO_2 was identified as the primary greenhouse gases that play important role in climate changes. Figure 1.2 shows the total carbon dioxide emitted from combustion of fossil fuels from 1900 to 2008. Global carbon dioxide, CO_2 emission from fossil fuels has significantly increased since 1900. Emission of CO_2 has increased by over 16 times between 1900 and 2008 and by about 1.5 times between 1990 and 2008 (Boden *et al.*, 2010). The main contributors to such high CO_2 emissions would be intensive development of industry and huge number of vehicles.

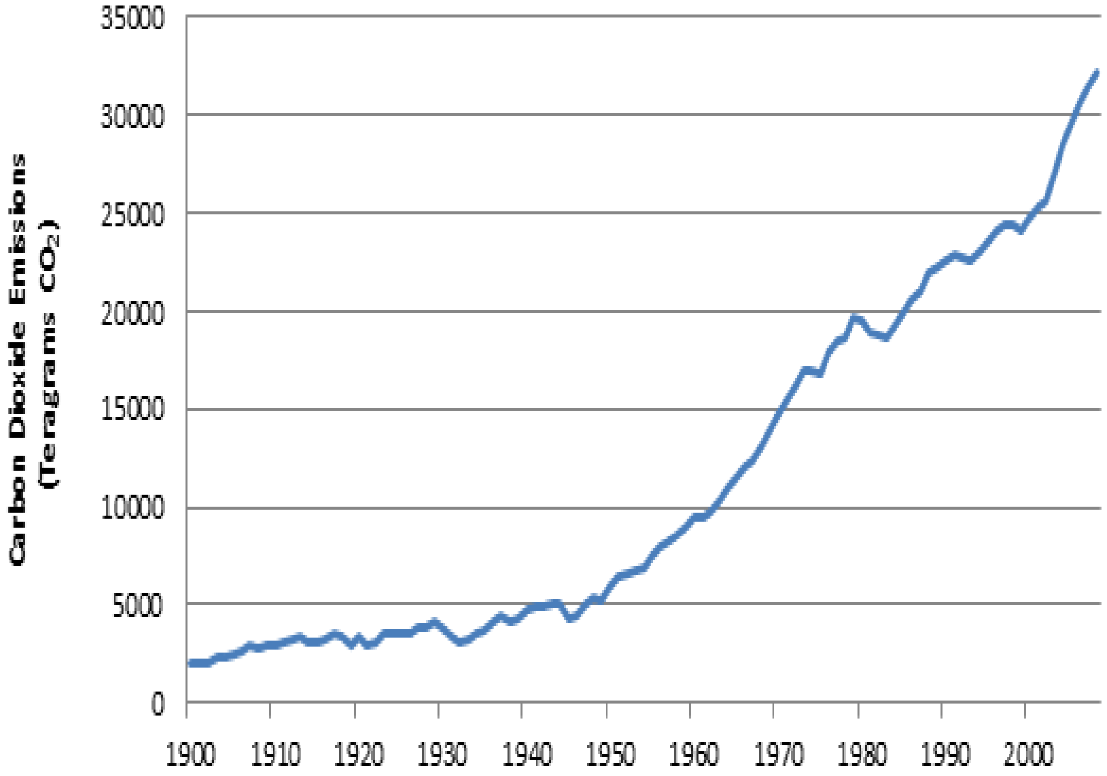

Figure 1.2 Global carbon dioxide (CO_2) emissions from fossil fuels from 1900-2008 (Boden *et al.*, 2010)

1.5 Catalyst

Catalyst is a chemical substance that causes or accelerates a chemical reaction (Silberberg, 2009). It is usually applied in small amount relative to the reactant and only workable in specific chemical reaction. The catalyst lowers the activation energy of the reaction and thus increases the rate of the reaction. It only affects the rate of the reaction instead of the thermodynamic equilibrium of reactants and products (Zumdahl and DeCoste, 2010). In general, the catalyst can be categorized into two groups, which are homogeneous and heterogeneous catalysts.

1.5.1 Homogeneous Catalyst

Homogeneous catalyst is a catalyst that exists in the same phase as the reactants. Phase here refer to solid, liquid or gas (Silberberg, 2009). Commonly, it is co-dissolved in a solvent with the reactants. Homogeneous catalysis system is very popular in industrial catalytic reactions since mid-1980s. The industry that mostly applies this system is pharmaceutical industry. However, the main disadvantage of this catalyst is its poor recovery. More separation and purification steps are required in order to separate the dissolved catalysts from the products (Riegel and Kent, 2007). Hence, nowadays researches are more on heterogeneous catalyst.

1.5.2 Heterogeneous Catalyst

Heterogeneous catalyst is a catalyst that present in different phase with the reactants. In majority heterogeneous catalysis system, the catalysts are normally existed in solid form whereas the reactants are in liquid or gases state (Silberberg, 2009). Heterogeneous catalysis system is prefers due to the ease separation of the catalyst from the products. Additionally, it can be reused for many times without significant loss of catalytic activity. Hence, it helps to minimize the environmental problems that usually encountered in homogeneous catalysis system (Guisnet, 1991). Adsorption is commonly an essential step in heterogeneous catalysis. Adsorption is the process where a molecule in the gas phase or in solution binds to atoms on the solid or liquid surface. After that, some of the bonds of the reactant molecules will be weakened and broken down, results in formation of new molecules. Finally, the product molecules formed will desorb from the active sites of the catalyst. The active sites are now free and ready for new adsorption and desorption process (Whitten and Davis, 2010).

1.6 Palm Oil

Palm oil is derived from the flesh of the fruit of the oil palm species *Elaeis guineensis* (Reeves and Weihrauch, 1979). It is bright-red colour in its virgin form due to high content of carotene. It composes of myristic acid (1.0 %), palmitic acid (43.5 %), stearic acid (4.3 %), oleic acid (36.6 %), linoleic acid (9.1 %) and other (5.5 %). At room temperature, palm oil exists as semi-solid form. Palm oil has good resistance to oxidation and heat at prolonged elevated temperature, making palm oil an ideal ingredient in frying oil blends (Che Man *et al.*, 1999).

The oil palm tree is originates from West Africa where it grows in the wild (Reeves and Weihrauch, 1979). Later, it was developed into an agricultural crop due to its wide applications such as foods, oleochemical products, as energy and so on. It was introduced to Malaysia by the British in early 1870's as an ornamental plant. Currently, Malaysia is the second largest palm oil producer in the world after Indonesia. Although Indonesia produces more palm oil, Malaysia is the largest exporter of palm oil in the world having exported 18 million tonnes of palm oil products to China, Pakistan, European Union, India and United States in 2011 (Choo, 2012). In Malaysia, the tenera variety (a hybrid of the dura and pisifera) oil palm trees are planted. This variety can yield about 4-5 tonnes of crude palm oil per hectare per year, higher than the dura and pisifera varieties. The oil palm is the most efficient oil-bearing crop in which it produces 3.62 tonnes of oil per hectare of land compare to soybean, sunflower and rapeseed which produce 0.40, 0.46 and 0.68 tonnes of oil, respectively, on the same planted area (Sumathi *et al.*, 2008).

1.7 Problem Statements

In this modern era, the energy is still mainly derived from non-renewable sources such as petroleum, coal and natural gas. Owing to the fast industrial revolution and fast population growth rate, the demand of energy is higher than the supply rate of energy. Besides, extensive burning of petroleum-based fuels has been resulted in an increase in greenhouse gases (such as CO, CO_2, SO_2) concentrations, or more commonly known as global warming. The energy crisis issue combined with environmental awareness has urged the development of cleaner alternative fuels. Biodiesel, a biomass-derived fuel, showed a huge potential as an alternative fuel as it is renewable energy (can be continuously derived from biomass) and environmental benign. Moreover, biodiesel has similar compositions as petroleum, a potential substitute for the petroleum. Biodiesel can be continuously produced from animal fats, palm oil, sunflower oil, soy bean oil, jatropha oil, algal oil and waste oil. Malaysia is the largest exporter of palm oil, making palm oil a best candidate for biodiesel production. Utilization of palm oil as feedstock can reduce the cost of biodiesel production as well as control the price and quality of the biodiesel. Additionally, palm-based biodiesel can reduce the current green-house gases emission rate greater than the rapeseed, sunflower and soy-based biodiesel.

In current biodiesel industry, the biodiesel was produced via homogeneous catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH). These catalysts were consumed in the reaction, cannot be regenerated and reused. Besides, waste water discarded from washing steps resulted in environmental pollution. Recently, CaO with strong basicity strength has been reported as a promising catalyst in biodiesel production, showing high catalytic activity. However, leaching of CaO into methanol medium and products has been observed. This phenomenon greatly reduced the catalytic activity of CaO in the following reactions. Thus, new catalysts with high basicity, great stability, regeneration capability and environmental friendly have been increasingly researched.

In this study, biodiesel was produced via transesterification of palm oil, served as an alternative fuel and to reduce the global warming. In addition, new heterogeneous catalysts have been designed and applied to overcome the drawbacks of homogeneous catalysts. Various calcium-based mixed oxide catalysts were synthesized to improve the basicity and stability of CaO. The results showed that calcium-based mixed oxide catalysts have higher catalytic activity than CaO. Besides, calcium-based mixed oxide catalysts showed better stability than CaO, where calcium-based mixed oxide can be reused in more numbers of reactions without significant loss of catalytic activity. Furthermore, the yield and reaction parameters of the transesterification reaction were optimized by using response surface methodology (RSM) in order to make the catalysts more valuable.

1.8 Objectives

The objectives of this study are as follows:

1. To synthesize CaO-Nb_2O_5 mixed oxide catalysts by solid state method, while CaO-CeO_2 and CaO-NiO mixed oxide catalysts via wet impregnation method.

2. To characterize the catalyst samples by using x-ray diffraction (XRD), thermal gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) surface area analysis, temperature-programmed desorption with carbon dioxide as probe molecule (TPD-CO_2), x-ray fluorescence (XRF) spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM).

3. To evaluate the catalytic activities of calcium-based mixed oxide catalysts in the biodiesel production.

4. To evaluate the effect of various parameters such as reaction period, methanol to oil molar ratio, catalyst loading, reaction temperature and calcination temperatures on the catalytic activity of calcium-based mixed oxide catalysts.

5. To optimize the biodiesel yield by using response surface methodology (RSM).

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