PRODUCTION OF RENEWABLE HYDROCARBON FUEL VIA TITANIUM OXIDE-ALUMINA (TiO₂-Al₂O₃) CATALYTIC DEOXYGENATION REACTION

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FACULTY OF ENGINEERING UNIVERSITY OF MALAYA KUALA LUMPUR

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ABSTRACT

The renewable hydrocarbon-like biofuel from biomass is crucial to substitute fossil fuel. Catalytic deoxygenation is a biofuel upgrading process to eliminate the high oxygen content in biofuel which will lead to corrosion, instability and lower heating value problems. The choice of support is significant to provide the maximum acid strength for the hydrogenolysis of C-O bonds. Al₂O₃ supported catalyst has drawn attention due to the high acidity. However, the high acidity leads to coke deposition, unstable and deactivation of the catalyst. Thus, it is important to develop methods to improve catalyst performance, reduce catalyst coking and enhance catalyst lifetime. Recently, Al₂O₃-TiO₂ mixed oxide catalyst has drawn increasing attention in deoxygenation process owing to its unique properties which can solve the issues from Al₂O₃. Controlled synthesis method is significant to improve the effectiveness of Al₂O₃-TiO₂ in catalytic reaction since the physicochemical properties of the catalyst are co-related to the processing methodology. A series of mesoporous Al₂O₃-TiO₂ mixed oxide catalysts with different TiO₂ content (0.1Ti-0.9Al, 0.2Ti-0.8Al and 0.3Ti-0.7Al) have been synthesized. The physicochemical properties of the catalysts were characterized by XRD, FESEM-EDX, BET, FTIR, FTIR-Py, NH₃-TPD and TGA. The deoxygenation (DO) of triglyceride (i.e. triolein) was carried out in the absence of hydrogen and solvent. The mesoporous Al₂O₃-TiO₂ catalysts showed high performance on the catalytic activity. It was found that 0.2Ti-0.8Al catalyst exhibited the highest conversion (76.86%), and selectivity (27.26%) toward $n-C_{15} + n-C_{15} +$ C₁₇ at 380 °C for 4 h. The excellence performance of mesoporous Al₂O₃-TiO₂ was attributed to its acidity, mesoporosity and large surface area. The results reveal that the mesoporous Al₂O₃-TiO₂ catalyst is a promising catalyst for the synthesis of hydrocarbonlike biofuel via deoxygenation.

ABSTRAK

Bahan api bio seperti hidrokarbon yang boleh diperbaharui dari biomas adalah penting untuk menggantikan bahan api fosil. Tindak balas menyahoksigenan adalah proses peningkatan bahan api bio untuk menghilangkan kandungan oksigen yang tinggi dalam biofuel yang akan mengakibatkan masalah kakisan, ketidakstabilan dan masalah pemanasan yang lebih rendah. Pilihan sokongan adalah penting untuk memberikan kekuatan asid maksimum untuk hidrogenolisis ikatan C-O. Pemangkin Al₂O₃ yang disokong telah menarik perhatian kerana keasidan yang tinggi. Walau bagaimanapun, keasidan yang tinggi membawa kepada pemendapan kok, tidak stabil dan penyahaktifan pemangkin. Oleh itu, adalah penting untuk membangunkan kaedah untuk meningkatkan prestasi pemangkin, mengurangkan coking pemangkin dan meningkatkan pemangkin seumur hidup. Baru-baru ini, pemangkin oksida campuran Al₂O₃-TiO₂ telah menarik perhatian dalam proses deoxygenation kerana ciri-ciri uniknya yang dapat menyelesaikan masalah dari Al₂O₃. Kaedah sintesis terkawal adalah penting untuk meningkatkan keberkesanan Al₂O₃-TiO₂ dalam tindak balas pemangkin kerana sifat fizikokimia pemangkin adalah berkaitan dengan metodologi pemprosesan. Satu siri katalis campuran oksida Al₂O₃-TiO₂ dengan kandungan TiO₂ yang berbeza (0.1Ti-0.9Al, 0.2Ti-0.8Al dan 0.3Ti-0.7Al) telah disintesis. Sifat-sifat fizikokimia pemangkin dicirikan oleh XRD, FESEM-EDX, BET, FTIR, FTIR-Py, NH₃-TPD dan TGA. Deoxygenation (DO) trigliserida (iaitu triolein) dilakukan tanpa menggunakan hidrogen dan pelarut. Pemangkin Al₂O₃-TiO₂ mesoporous menunjukkan peningkatan prestasi pada aktiviti pemangkin berbanding dengan Al₂O₃ dan TiO₂. Mangkin 0.2Ti-0.8Al menunjukkan penukaran tertinggi (76.86%), dan selektiviti (27.26%) ke arah n-C₁₅ + n-C₁₇ pada 380 $^{\circ}$ C selama 4 jam. Prestasi cemerlang mesoporous Al_2O_3 -TiO₂ disebabkan oleh keasidan, mesoporositi dan luas permukaan yang besar. Hasilnya menunjukkan bahawa pemangkin

mesoporous Al₂O₃-TiO₂ adalah pemangkin yang menjanjikan untuk sintesis bahan api bio melalui menyahoksigenan.

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LIST OF SYMBOLS AND ABBREVIATIONS

ă	:	Anatase
Ä	:	Amorphous
Ag	:	Silver
Al	:	Aluminium
Al ₂ O ₃	:	Aluminium oxide
ATSB	:	Aluminium-tri-sec-butoxide
Au	:	Gold
BET	:	Brunauer-Emmett-Teller
ВЈН	:	Barrett-Joyner-Halender
С	:	Carbon
CeO ₂	:	Cerium (IV) oxide
CNTs	:	Carbon nanotubes
Со	:	Cobalt
СО	: C	Carbon monoxide
CO ₂	2:	Carbon dioxide
СТАВ	:	Cetyltrimethylammonium bromide
Cu	:	Copper
CVD	:	Chemical vapour deposition
deCOx	:	Decarboxylation/decarbonylation
DO	:	Deoxygenation
EtOH	:	Ethanol
FAME	:	Fatty acid methyl ester
Fe	:	Iron
FTIR	:	Fourier transform infrared

GC-MS	:	Gas chromatography-mass spectrometry
Н	:	Hydrogen
HCl	:	Hydrochloric acid
HDO	:	Hydrodeoxygenation
H ₂ O	:	Water
KBr	:	Potassium Bromide
М	:	Metal
Mn	:	Manganese
Мо	:	Molybdenum
N_2	:	Nitrogen
Ni	:	Nickel
NIST	:	National Institute of Standards and Testing
NH ₃ -TPD	:	Temperature-programmed desorption of ammonia
NO ₃	:	Nitrate
0	:	Oxygen
ОН	:6	Hydroxide
P	;	Phosphorus
Pd	:	Palladium
Pt	:	Platinum
РТ	:	Pre-treatment
P/P ₀	:	Relative pressure
Ру	:	Pyridine
R	:	Rutile
Rh	:	Rhodium
RS	:	Raman spectroscopy
Ru	:	Ruthenium

S	:	Sulfur
SBA	:	Santa Barbara Amorphous
SEM	:	Scanning electron microscopy
SiO ₂	:	Silicon dioxide
SMSI	:	Strong metal-support interaction
TBOT	:	Titanium (IV) butoxide
TCD	:	Thermal conductivity detector
TEM	:	Transmission electron microscopy
TGA	:	Thermogravimetric analysis
TiO ₂	:	Titanium dioxide
TPD	:	Temperature programmed desorption/reduction
TPR	:	Temperature programmed reduction
V	:	Vanadium
W	:	Tungsten
XPS	:	X-ray photoelectron spectroscopy
XRD	:6	X-ray diffraction
ZrO ₂	:	Zirconium dioxide
ZSM	:	Zeolite Socony Mobil
α	:	Alpha
θ	:	Bragg angle
λ	:	X-ray wavelength
γ	:	Gamma

CHAPTER 1: INTRODUCTION

1.1 Background

The demand of hydrocarbon fuel is growing worldwide, leading to the incapability to meet the requirement for power generation and transportation sector. Fossil fuel is well-known to be the main energy resources. However, the World Energy Forum has predicted that fossil fuel will be exhausted in less than 100 years as shown in Figure 1.1 because the rate of natural production is 10⁵ slower than fossil fuel consumption (Banković–Ilić, Miladinović, Stamenković, & Veljković, 2017). Hence, it has attracted many researchers to develop renewable energy that can replace fossil fuels by using the resources such as solar, wind and biomass which are available on the Earth (Kaygusuz & Sarı, 2003; Toklu, 2013). The usage of solar and wind oriented energy are hindered due to the unpredicted weather and high cost (Chang & Starcher, 2019; Olaofe, 2018). Besides, the solar and wind energy are still limited in the transportation sector. Therefore, the renewable biomass energy is the most promising alternative to substitute fossil fuel (Demirbas, 2011).



Figure 1.1: The exhaustion of biofuel (Banković–Ilić et al., 2017).

Biofuel is the future energy market because it has low greenhouse gas emission, security of supply and sustainability. Conventionally, the biodiesel derived via transesterification from biomass-based triglycerides such as microalgae, sunflower oil, palm oil, *etc.* has been widely used as alternative to fossil fuel in automobile (Vo et al., 2017). Nevertheless, there are many unfavourable issues such as low volatility, high viscosity, high acidity, low heating value and immiscibility (Ly et al., 2016). This will cause severe engine problems namely carbon deposits, engine coking, *etc* (Ashraful et al., 2014). These issues are mainly due to the high oxygen content in the biofuel produce via transesterification that led to low quality fuel. The presence of oxygen molecules in biofuel has also resulted more negative impacts such as corrosiveness, low heating value, low chemical and thermal stability (Ambursa, Sudarsanam, Voon, Hamid, & Bhargava, 2017; Musa, 2016). Hence, the biodiesel namely fatty acid methyl ester (FAME) produced from transesterification has its limitation.

In order to improve the biofuel properties to be comparable with petro-based hydrocarbon fuel, the oxygen content should be removed. Deoxygenation and hydrodeoxygenation processes are capable of producing hydrocarbon like biofuel by removing the oxygen content (Asikin-Mijan, Lee, Marliza, & Taufiq-Yap, 2018). Unfortunately, the hydrodeoxygenation requires the usage of hydrogen which is the main disadvantage (W. Li, Gao, Yao, Ma, & Yan, 2015). In addition, the hydrodeoxygenation process needs to be conducted under high pressure in the presence of hydrogen. Therefore, the production of renewable hydrocarbon fuel from triglycerides without any consumption of hydrogen has become an interesting research topic. There are a numbers of catalysts including transition metal (i.e. Ni, Mo, Cu, Mn) and noble metals (i.e. Pd, Ru, Pt, Ag) has been used in the deoxygenation reaction (Ambursa et al., 2016b; Arun, Sharma, & Dalai, 2015; Ayodele, Togunwa, Abbas, & Daud, 2014; Lungang Chen et al., 2011; Tavizón-Pozos, Suárez-Toriello, del Ángel, & de los Reyes, 2016). Noble metals

such as Pt or Pd are not suitable to be used for large scale industry because they are expensive (Cheng, Wei, Julson, & Rabnawaz, 2017). The deoxygenation process through decarboxylation and decarbonylation in hydrogen-free atmosphere over inexpensive solid acid or base catalysts (Abd Hamid, Ambursa, Sudarsanam, Voon, & Bhargava, 2017; Ambursa et al., 2016b; Ambursa et al., 2017; Choo et al., 2019; Zulkepli et al., 2018). According to the previous literatures, mesoporous acidic metal catalysts (i.e. SBA-15, SBA-16, zeolite) have been broadly utilized for deoxygenation process (Baharudin et al., 2019; Feliczak-Guzik, Szczyglewska, & Nowak, 2018; Horáček, Šťávová, Kelbichová, & Kubička, 2013). On the other hand, Al₂O₃ material with acidic active sites favour the elimination of oxygenated compounds (Rogers & Zheng, 2016) but easily deactivated. Generally, the occurrence of coke deposition on the Al₂O₃ has led to the deactivation (Cheng et al., 2017).

Recently, binary Al₂O₃-TiO₂ found to be possessed remarkable properties such as high surface area, high reducibility, high acidity, and more active phase for oxygen removal as compared to that of pure Al₂O₃ or TiO₂ alone (Ramírez, Rayo, Gutiérrez-Alejandre, Ancheyta, & Rana, 2005; K. Segawa, M. Katsuta, & F. Kameda, 1996). Vo et al. (Vo, Kim, Kim, Yoo, & Kim, 2018) reported that the hydrodeoxygenation of palmitic acid over Mo/Al₂O₃-TiO₂ catalyst was much higher than Mo/Al₂O₃ or Mo/TiO₂ catalysts. This demonstrated that binary Al₂O₃-TiO₂ mixed oxide is more effective than that of Al₂O₃ or TiO₂. Mesoporosity plays a dominant role in liquid-phase catalysis (Linares, Silvestre-Albero, Serrano, Silvestre-Albero, & García-Martínez, 2014) because of the high surface area and large pore structure against diffusion problem (Lestari, Beltramini, & Lu, 2008). Therefore, the development of mesoporous Al₂O₃-TiO₂ has attracted great interest.

In the present study, the mesoporous Al₂O₃-TiO₂ mixed oxide catalysts were synthesized and characterized. They showed a good catalytic activity for the

deoxygenation of triolein to produce a green hydrocarbon like biofuel in the absence of hydrogen. The reaction temperature, time, catalyst loading and reusability were also discussed.

1.2 Gap of knowledge

There is no specific study reported on the application of mesoporous Al₂O₃-TiO₂ mixed catalyst for deoxygenation reaction of triglycerides in the absence of solvent and hydrogen. Moreover, there is only little research has been focused on the design and synthesis of mesoporous Al₂O₃-TiO₂ mixed catalyst.

1.3 Problem statement

Fossil fuels are depleting and alternative biofuel is required to replace it. The biofuel produced from transesterification has high oxygen contents which will lead to corrosive problem, low heating value, high viscosity. Alternatively, the catalytic deoxygenation is able to eliminate the oxygen contents in order to improve the quality of biofuel. Conventionally, the catalytic deoxygenation was performed by using sulfided NiMo and CoMo supported on Al₂O₃ catalyst. However, the catalytic deoxygenation using sulfided NiMo and CoMo supported on Al₂O₃ catalyst led to problems such as low degree of deoxygenation, contaminated biofuel with sulfur, coke formation as well as deactivation. Moreover, the deoxygenation reaction is carried out in hydrogen condition which is high cost in production. Therefore, it is important to develop methods to improve catalyst performance, reduce catalyst coking and enhance catalyst lifetime. Mesoporous Al₂O₃-TiO₂ mixed oxide catalyst has drawn increasing attention for deoxygenation reaction in the absence of hydrogen and solvent due to its unique physicochemical properties which can solve the issues from Al₂O₃.

1.4 Objectives

- i. To synthesize and characterize the physicochemical properties of different ratio of mesoporous Al₂O₃-TiO₂ mixed oxide catalysts (0.1Ti-0.9Al, 0.2Ti-0.8Al and 0.3Ti-0.7Al) as compared to that of Al₂O₃ and TiO₂ catalysts.
- ii. To determine the deoxygenation reaction of triglyceride model compound (triolein) in the absence of H_2 and solvent by using different ratio of mesoporous Al_2O_3 -TiO₂ catalysts as compared to that of Al_2O_3 and TiO₂ catalysts.
- iii. To optimize the reaction conditions (temperature, time and catalyst loading wt. %) and determine its reusability by using mesoporous Al₂O₃-TiO₂ catalyst.

1.5 Thesis organization

The present thesis has five chapters comprising of this first chapter which is introduction. Chapter 2 provides comprehensive literature review on recent deoxygenation process using metal oxide supported catalyst such as TiO₂, Al₂O₃, SiO₂, ZrO₂, CeO₂, and Al₂O₃-TiO₂ supported catalyst. The choice of support is significant to provide the maximum acid strength for the hydrogenolysis of C-O bonds. The deoxygenation of phenolic-based, furan-based and fatty acid feedstock using Al₂O₃-TiO₂ supported catalyst are also comprehensively reviewed. Moreover, the synthesis of Al₂O₃-TiO₂ supported catalyst is discussed because controlled synthesis method is significant to improve the effectiveness of catalyst in catalytic reaction since the physicochemical properties of the catalyst are co-related to the processing methodology. Next, chapter 3 describes the details of raw materials, instrument for analysis and experimental setup. Chapter 4 provides the results obtained from experiments and discussion about the results. A series of mesoporous Al₂O₃-TiO₂ mixed oxide catalysts with different TiO₂ content (0.1Ti-0.9Al, 0.2Ti-0.8Al and 0.3Ti-0.7Al) have been synthesized. The physicochemical properties of the catalysts were characterized by XRD, FESEM-EDX, BET, FTIR, NH₃-

TPD, FTIR-Py, and TGA. The mesoporous Al_2O_3 -TiO₂ has higher acidity, mesoporosity and larger surface area as compared to that of Al_2O_3 and TiO₂ catalyst. The deoxygenation (DO) of triglyceride (i.e. triolein) was carried out in the absence of hydrogen and solvent. The mesoporous Al_2O_3 -TiO₂ catalysts showed high catalytic activity performance as compared to that of Al_2O_3 and TiO₂ catalyst. Lastly, chapter 5 gives conclusion and suggests recommendation for future studies.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

2.1.1 Biofuel

Fossil fuel consumption and environmental issue are triggering research interest in the area of renewable and sustainable alternatives (Matayeva, Basile, Cavani, Bianchi, & Chiaberge, 2019). Biofuel, as a substitute for traditional petroleum liquid fuel, has been widely used in recent years (M. Guo, Song, & Buhain, 2015). Conventionally, biodiesel also known as fatty acid methyl ester (FAME) is produced via transesterification for renewable fuel (Nicodème, Berchem, Jacquet, & Richel, 2018; A. S. Silitonga et al., 2018). Compared with fossil fuels, biodiesel is environmentally friendly, economical and technically feasible. Moreover, the synthetic sources of biodiesel are readily available (S. X. Tan, Lim, Ong, & Pang, 2019). Vegetable oil is extracted from triglyceride-based plant and further processed to biodiesel. However, the biodiesel enrichment caused an increase in viscosity and reduces the volatility of the blend (A. Silitonga, Masjuki, Mahlia, Ong, Chong, et al., 2013). Besides, severe engine problems such as carbon deposit, lubricant thickening and *etc* are produced owing to the high oxygen contents, low volatility, high unsaturated acid contents and high viscosity of the extracted bio-oil (Ashraful et al., 2014; Demirbas, 2008). Moreover, high O_2 content in biodiesel blends will increase the NO_x emissions (A. Silitonga, Masjuki, Mahlia, Ong, & Chong, 2013). The large consumption of raw material and high production cost of plant oil lead to less cost-effective when compared to the petrochemical industry (Fatih Demirbas, Balat, & Balat, 2011). Many attempts are made to find new and cost-effective technology for better, cleaner, and renewable fuel (Yusuf, Kamarudin, & Yaakub, 2011). As a result, biofuels are rapidly becoming one of the alternative renewable energy to achieve pollution-free properties and cost competitiveness (Sekoai et al., 2019).

Recently, biofuel produced via deoxygenation has drawn attention from researchers. Biofuel has many advantages after deoxygenation, and its composition is similar to that of petroleum fuel, which can be directly used in the fuel industry. Deoxygenation is a process where oxygenated compounds are being eliminated from a molecule typically in the form of H₂O, CO₂ or CO. Deoxygenation reaction can be completed by using either hydrogen or ambient condition. The possible mechanisms of deoxygenation pathways are decarboxylation, decarbonylation, hydrodeoxygenation and hydrogenolysis as shown in Table 2.1. Decarboxylation/decarbonylation (deCOx) reaction is the typical deoxygenation (DO) process that removes oxygen in the form of CO₂/CO through direct C-C bond cleavage under mild conditions (Grilc, Likozar, & Levec, 2014). Decarboxylation process targets carboxylic acids whereas decarbonylation process targets aldehydes, carboxylic acid and ketones for oxygen removal. On the other hand, hydrodeoxygenation (HDO) is also a cracking of C-C bond process which is carried out under high or low hydrogen pressure that forms water (H₂O) as by-product. Moreover, hydrogenolysis where it involves cleavage of C-C or C-heteroatom bond when adding hydrogen (Snåre, Kubičková, Mäki-Arvela, Eränen, & Murzin, 2006). Therefore, they are classified as deoxygenation process because the precedent reaction involves oxygen removal, just that the by-product and pathways differ from each other only.



Table 2.1: Possible types of deoxygenation pathways (Oi et al., 2016).

Therefore, the oxygen content in the vegetable oil can be eradicated either as H_2O or CO_x via deoxygenation to produce hydrocarbon biofuel (Kubička, Šimáček, & Žilková, 2009). The properties of biofuel produced via catalytic deoxygenation of vegetable oilbased feeds possess similarity to petroleum fuel allowed them to replace transesterification technology (Shan, Lu, Shi, Yuan, & Shi, 2018).

2.1.2 Source of feedstock

Vegetable oil-based feeds, containing C_8 – C_{24} fatty acids are regarded as an alternative source for hydrocarbon fuel production (Gosselink et al., 2013). In general, biofuel feedstock can be divided into four main categories such as edible vegetable oil, non-edible vegetable oil, waste oil and animal fats (A. Silitonga et al., 2011). In the first generation feedstock, edible oil crops such as sunflower, coconut, palm, rapeseed *etc* are used to produce biofuel (Rahimi, Mohammadi, Basiri, Parsamoghadam, & Masahi, 2016). However, the first-generation biofuel leads to food competition and ecosystem imbalance

owing to the demand of large arable land to cultivate these crops (Parmar, Singh, Pandey, Gnansounou, & Madamwar, 2011). Thus, second generation feedstock, non-edible feedstock such as agricultural waste and waste cooking oils are used to convert into biofuel (Kusumo et al., 2017). However, jatropha, rapeseed, rubber trees and other nonedible feedstock are usually have higher free fatty acids and need for pretreatment process, thus, non-edible feedstock are hard to meet global energy demands (A. Silitonga et al., 2016). Microalgae are currently being promoted as third generation biofuel feedstock (C.-Y. Chen et al., 2013). Microalgae have high cell lipid content and high photosynthetic rate, and are ideal raw materials for the production of biofuels (Galadima & Muraza, 2018). Algae biomass can capture about 3-8% of the incident solar energy, and terrestrial plants can only convert 0.5%. The oil content of 3-5 parts of microalgae dry biomass was greater than 60%, and the average oil content was about 20-50% wt.%. The amount of Nissan oil per unit volume of microalgae broth is related to the growth rate of algae and the oil content of biomass. Compared with traditional oil-producing terrestrial plants such as rapeseed and sunflowers, microalgae grow 12 times faster and yield 30 times higher per hectare (Zhao, Brück, & Lercher, 2013). In addition, it does not require arable land, as microalgae cultivation will compete with food production, which can use wastewater to provide nitrogen sources and industrial carbon dioxide (flue gas) to promote the formation of algal biomass (Mathimani & Mallick, 2019). Therefore, the cultivation of microalgae has a synergistic effect with the recycling of biological wastewater, and it is an active CO₂ reservoir. These characteristics make microalgae a promising green energy biological resource (Mathimani & Pugazhendhi, 2019). However, the third generation has drawback which is low lipid content due to high growth rate. For instance, the lipid content of most of the microalgae are around 20 - 50 %, (w/w), thus the efficiency is lower compared to other sources (Mofijur, Rasul, Hassan, & Nabi, 2019). Therefore, the engineered microalgae (so called fourth generation) is emerged to

solve that particular problem (C. H. Tan, Show, Chang, Ling, & Lan, 2015). Microalgae contain high-value biological products such as pigments, vitamins and antioxidants that can be extracted and utilized. In order to maintain the sustainable development of microalgae based biofuel production, the cultivation of biomass should be induced by lipid culture, efficient harvesting, as well as the combination of lipid extraction and ester exchange reaction of biofuel synthesis (Goh et al., 2019). Palmitic acid, oleic acid, palmitoleic acid, lionoleic acid and stearic acid are common and general fatty acids found in microalgae cell. The vegetable oil-based model compounds such as fatty acids, fatty acid esters and specific triglycerides (i.e. triolein) can be used to investigate the fundamentals of deoxygenation reaction for biofuel production owing to their structural carbon chain similarity (Gosselink et al., 2013).

Bio-oil can be produced via pyrolysis process of lignocellulosic biomass such as lignin, cellulose and hemicellulose (Kay Lup, Abnisa, Daud, & Aroua, 2017). Lignin is the hardest component to be converted into high quality liquid fuels due to its easy coking property in biomass pyrolysis process (Huiyan Zhang, Wang, Shao, & Xiao, 2016). The liquid fuels can be obtained by lignin biomass pyrolysis. However, the liquid fuels obtained from lignin pyrolysis are bio-oil with rich oxygen contents (10–45 wt%) due to the depolymerisation and fragmentation reactions of ligno-cellulosic biomass that eventually leads to issues such as high viscosity, low heating value, low stability and cannot mix with conventional hydrocarbon fuels (Boullosa-Eiras et al., 2014). Thus, these bio-oils obtained from pyrolysis are needed to undergo chemical upgrading process which is deoxygenation to lower the oxygen content and produce high quality liquid fuel (Ansari & Gaikar, 2019). The pyrolysis oils obtain from wooden-based raw are complex chemical polymeric mixtures consisting of different molecules with high oxygen contents such as carboxylic acids, phenols, alcohols, ketones, furfurals, aldehydes or carbohydrates (Bu et al., 2012). Different pyrolysis conditions such as pyrolysis temperature, heating rate,

residence time, low-temperature pretreatment of biomass and reaction time will determine the product yields of that particular model compound in the pyrolysis bio-oil (Lyu, Wu, & Zhang, 2015; Mohan, Pittman, & Steele, 2006). This complex nature of pyrolysis oil will cause difficulty in deoxygenation upgrading process because detrimental side reactions such as thermal pathways may happen if the parameter conditions are not taken into account for some high reactive oxygen-rich molecules (Boullosa-Eiras et al., 2014). Pyrolysis is a promising option for sustainable development for bio-oil. However, pyrolysis technology is also faced with a lot of critical challenges such as the development of new cost-effective and efficient reactors, novel catalyst and post-pyrolysis treatment is needed to improve the process and oil properties (Uddin et al., 2018). The nature complexity of the bio-oil which contain more than 300 compounds has limited the application and further processing (Choudhary & Phillips, 2011).

2.2 Deoxygenation process using metal oxide supported catalyst

This section summarized and discussed the deoxygenation process of the selected metal oxide such as TiO₂, Al₂O₃, SiO₂, ZrO₂, CeO₂ and Al₂O₃-TiO₂ supported catalysts to produce hydrocarbon-graded biofuel. Deoxygenation of biologically derived molecules has evolved into a promising synthetic tool for the synthesis of fuels and chemicals (Ansari & Gaikar, 2019). The development of homogeneous and heterogeneous catalysts with good chemical stability and high activity are the main support of deoxygenation reaction (Roldugina, Naranov, Maximov, & Karakhanov, 2018). In essence, deoxydehydration process with a homogeneous catalyst can be utilized to produce many fine chemicals, such as benzene, alkenes, phenol, furans and acrolein extracted directly from biomass, while HDO strategy is mainly used to produce diesel series alkanes (Cheng et al., 2017). However, non-precious metals are good alternatives catalyst and support for cost-effective processes. Currently, the deoxygenation process demonstrates that biomass conversion synthesis has entered the next frontier, deriving

products from other sources that are not available from biomass (Cao et al., 2018). The future development strategies to remove oxygen from biofuel molecules will help to prepare block chemicals and fuels with specific properties. There is no doubt that the implementation of catalytic deoxygenation technology will be the main key to develop biomass based economy (Romero et al., 2016).

2.2.1 TiO₂ supported catalyst

Titanium dioxide (TiO₂) is a reducible oxide with good chemical stability, zero toxicity, low cost, non-hazardous, hard and dense polymorphs (anatase, brookite and rutile) (Hengzhong Zhang & Banfield, 2000). TiO₂ is famous for its strong metal-support interaction (SMSI) properties (Tauster, Fung, & Garten, 1978). The catalytic performance, adsorption geometry, electronic structures, dispersion of metal catalyst on the support and metal size growth can be affected and controlled by the SMSI (Oi et al., 2016). In deoxygenation process using TiO₂ supported catalyst, high hydrogen pressure was commonly used for different feedstocks. The presence of unsaturated biofuel products can be reduced and the stability of the catalyst can be improved by using high H₂ pressure (Hengst, Arend, Pfützenreuter, & Hoelderich, 2015). An overview for the deoxygenation of different feedstock using TiO₂ supported catalyst under different reaction conditions and respective selectivity is shown at Table 2.2.

Catalyst	Metal (w/w)	Reactant	Rea	ction cor	ditions	Conv. (%)	Selectivity	Remark	Ref.
			T (°C)	t (h)	H2 (MPa)				
Ru-Fe/TiO ₂	1% Fe 4% Ru	Anisole	350	3	1	98	60% benzene 20% cyclohexane 5% methoxycyclohexane	Adding the Fe increase the selectivity of the catalyst and conversion	(Phan & Ko, 2018)
Pt-Mo/TiO ₂	1% Pt 0.5% Mo	Guaiacol	285	1	4	97	73.4% cyclohexane 12.5% cyclohexanol ~3% phenol ~3% methane	Mo favor hydrogenolysis while suppress dehydration to cyclohexane	(He, Hu, & Wang, 2018)
Ni-Cu/TiO ₂	N/A	Dibenzo- furan	260	6	10	96	53% bicyclohexyl-1-ene 45% bicyclohexyl	Cu–Ni/TiO ₂ has highest selectivity to Bicyclohexane	(Ambursa et al., 2016a)
NiMo/TiO ₂	15% Mo 3.3% Ni	Rapeseed oil	300	4	3.5	100	~8% n-heptadecane ~54% n-octadecane	NiMo/TiO2 catalyst increased selectivity to HDO	(Kubička et al., 2014)
AuRh/TiO2	1.58% Au 0.68% Rh	Guaiacol	280	6	4	94	~62% cyclohexane ~10% methylcyclohexane ~14% phenol	Most selective catalyst toward O-free (naphthenic) compounds.	(Nguyen, Laurenti, Afanasiev, Konuspayeva, & Piccolo, 2016)
Mo/TiO ₂	30% Mo	Palmitic acid	280	4	4	~90%	~10% hexadecanal ~20% hexadecane ~35% pentadecane ~35% hexadecane	Facilitate the dehydration process of alcohol and an increase in hydrocarbon selectivity.	(Vo et al., 2018)
Mo ₂ C/TiO ₂	6.8% Mo	Phenol	350		2.5	65	~90% cyclohexene	Active for phenol HDO and 15 wt% Mo ₂ C/TiO ₂ showed the highest activity	(Boullosa-Eiras et al., 2014)

Table 2.2: Overview of deoxygenation reaction under different conditions using TiO₂ supported catalyst.

It was found that TiO₂ supported catalyst showed particular deoxygenation activity. Kubička et al. (Kubička et al., 2014) investigated the effect of nickel and molybdenum interactions on the catalyst activity, pore size distribution, active phase cluster size and the deoxygenation performance using rapeseed oil as a feedstock in details. They found that the conversion was 100% with increased selectivity to hydrodeoxygenated products. Recently, He et al. (He et al., 2018) investigated the hydrodeoxygenation reaction of guaiacol on Pt-Mo/TiO₂ and Pt-Mg/TiO₂ catalyst. The Pt-Mo/TiO₂ gave a conversion over 97% with mainly hydrodeoxygenation pathway to produce 73.4% cyclohexane yield, indicated metal sites and metal-support interface showed superior active hydrogen. However, the dehydration and hydrogenolysis pathways were inhibited by Mg, resulting unfavorable system for hydrodeoxygenation.

In terms of storage, titanium dioxide can be extracted by acid decomposition by rutile or decomposed by titanium tetrachloride (He et al., 2018). Titanium dioxide is stable in nature and is widely used as a white pigment in paint (Oi et al., 2016). It has good covering ability and is similar to lead white, but it does not turn black like lead white(Gómez et al., 2016); it has the same persistence as zinc white. It is easy to store.

 TiO_2 supported with transition metals or noble metals can deoxygenate various feedstocks and produce hydrocarbon-graded biofuel. Transition metals are preferable owing to its cheaper price and almost-like activity compared to noble metals. However, although it has good chemical stability, zero toxicity, low cost, non-toxic, the main drawback is the high consumption of hydrogen to maintain its activity since TiO_2 is a reducible oxide (He et al., 2018). Therefore, the deoxygenation reaction with high conversion rate should be selected when the cost permits, so as not to consume excessive hydrogen energy (Rodseanglung, Ratana, Phongaksorn, & Tungkamania, 2015).

2.2.2 Al₂O₃ supported catalyst

Aluminum oxide (Al₂O₃) is a refractory oxide with high hardness, strength and chemical inertness (Osman et al., 2012). Alpha (α) and gamma (γ) are the different phases of Al₂O₃. Extremely high calcination temperature typically over 1000°C will produce α -Al₂O₃ with high temperature resistant, low specific surface area, inert and nearly zero catalytic activity (Lamouri et al., 2017). On the contrary, γ -Al₂O₃ has high catalytic activity, specific surface area, purity, temperature resistant and superior dispersion. Moreover, γ -Al₂O₃ has good porosity parameters and this property provides large surface area, very uniform channels and narrow pore size distribution (Sifontes et al., 2010). Therefore, various researchers used γ -Al₂O₃ as catalyst or catalyst support for catalytic reaction. Table 2.3 shows an overview for the deoxygenation of different feedstock using Al₂O₃ supported catalyst under different reaction conditions and corresponding selectivity.

Catalyst	Metal (w/w)	Reactant	Reaction conditions		Conv. (%)	Selectivity Remark		Ref.		
	× ,		T (°C)	t (h)	H2 (MPa)					
NiMoS/Al ₂ O ₃	15% Mo 3.3% Ni	Rapeseed oil	300	4	3.5	100	~22% n-heptadecane ~56% n-octadecane	NiMoS/Al ₂ O ₃ catalyst is more efficient in hydrogenation.	(Kubička et al., 2014)	
Pd/Al ₂ O ₃	5% Pd	Stearic acid	350	3	1.4	100	91% heptadecane 9% octadecane	1w% Pd/Al ₂ O ₃ has the highest activity of catalytic oxidation of adjacent xylene after H ₂ reduction.	(Berenblyum, Podoplelova, Shamsiev, Katsman, & Danyusheysky, 2011)	
Ni/γ-Al ₂ O ₃	15% Ni	Stearic acid	270	6	0.8	100	90.3% heptadecane 5.8% hexadecane 2.4% pentadecane 1.5% octadecane	The acidity of the carrier depends on the nickel content of the oxidation catalyst, and with the increase of nickel content, the acidity of the carrier increases with the increase of nickel content.	(Kumar, Yenumala, Maity, & Shee, 2014)	
Co/γ-Al ₂ O ₃	10% Co	Palm oil	300	N/A	5	88.6	~33% n-C ₁₈ ~30% n-C ₁₇ ~20% n-C ₁₆ ~17% n-C ₁₅	The catalyst has good catalytic activity (>90% yield) and remains stable in the continuous operation of the H.	(Srifa, Viriya-empikul, Assabumrungrat, & Faungnawakij, 2015)	
Mo/Al ₂ O ₃	30% Mo	Palmitic acid	280	4	4	~62	~7% hexadecanal ~61% hexadecanol ~6% hexadecane ~26% hexadecane	Lower palmitic acid conversion compared with Mo/Al ₂ O ₃ -TiO ₂ catalysts	(Vo et al., 2018)	
Ni ₂ P/Al ₂ O ₃	11.2% Ni ₂ P	Guaiacol	300	N/A	0.1	99.6	30.9% benzene 13.7% phenol 1.5% cresol	The largest clusters appear on the Al ₂ O ₃ , indicating a weak association between Ni and P. Ni ₂ P/Al ₂ O ₃ enhances the DME synthesis route of phthalates.	(SK. Wu et al., 2013)	
CoMo/Al ₂ O ₃ sulfided	9.2%Mo 4.2% Co	Decanoic acid	340	7	4	46.2	17.5% decene 3.8% nonane 5.5% decane	The additive Co is added to the CoMo/γ-Al ₂ O ₃ catalyst. The formation of CoMoS phase can increase the number of active bits of catalyst and increase the activity of hydrogenation desulfurization (HDS) of catalyst.	(Brillouet, Baltag, Brunet, & Richard, 2014)	

Table 2.3: Overview of deoxygenation reaction under different conditions using Al₂O₃ supported catalyst.

Berenblyum and co-workers (Berenblyum et al., 2011) used palladium impregnated on Al₂O₃ catalyst to convert stearic acid into hydrocarbons. The conversion was 100% and heptadecane was the main reaction product followed by low concentrations of octadecane. However, decarbonylation reaction was dominating compared to decarboxylation in the presence of Pd/ Al₂O₃ catalyst in a H₂ condition. The intermediate product which was formic acid also decomposed catalytically to carbon monoxide at high temperature 300–350°C. On the other hand, Kumar et al. (Kumar et al., 2014) investigated the stearic acid conversion using 15% Ni dispersed on γ -Al₂O₃ as catalyst in a hydrogen atmosphere. The conversion was 100% and Ni/ γ -Al₂O₃ catalyst showed remarkable selectivity toward heptadecane (90.3%). The incorporation of nickel into the γ -Al₂O₃ as support increased their acidity owing to the strong interrelated nickel oxide in the catalyst.

The activity and stability of metal supported catalyst is strongly affected by the support acidity and interaction between metal and support (Iino, Cho, Takagaki, Kikuchi, & Ted Oyama, 2014). Al₂O₃ supported with noble metals or transition metals showed excellent deoxygenation owing to the presence of acidity in Al₂O₃ support that provides additional reaction sites for hydrogen adsorption or disassociation of the oxygenated compounds (Rogers & Zheng, 2016). However, the high acidity caused high tendency for coke deposition on the Al₂O₃ supported catalyst that eventually leads to unstable and deactivation (Cheng et al., 2017). The possible optimized solution would be mixing Al₂O₃ and TiO₂ which will be discussed in next section. And, it should be sealed dry and preserved (C. Yang et al., 2016).

2.2.3 SiO₂ supported catalyst

Silicon dioxide (SiO_2) is a refractory oxide with white and colorless appearance. SiO_2 support is stable and has been used as a good support for metal loaded catalyst in catalytic

reaction. The coke deposition is low owing to the very weak acidity present in SiO_2 (He & Wang, 2012). Moreover, many research studies focus on SiO_2 because the catalyst deactivation can be avoided owing to the weak acidity. SiO_2 is generally inert towards deoxygenation and it is suitable to be used in hydrogen-free or low hydrogen pressure system. This is because SiO_2 does not require hydrogen for activation and able to perform deoxygenation process to upgrade bio-oil into hydrocarbon-graded biofuel (Rogers & Zheng, 2016). Table 2.4 summarized the deoxygenation process of different feedstock to produce green biofuel using SiO_2 supported catalyst.

Catalyst	Metal	Reactant	Reaction conditions			Conv.	Selectivity	Remark	Ref.
	(w/w)		Т	t	H_2	(%)			
			(°C)	(h)	(MPa)				
NiMoS/SiO ₂	15% Mo 3.3% Ni	Rapeseed oil	300	4	3.5	100	~55% n-heptadecane ~25% n-octadecane	NiMoS/SiO ₂ catalyst exhibited smaller ext hydrogenation reactions and a larger ext decarboxylation.	ent of (Kubička et al., 2014) ent of
Fe-Co/SiO ₂	10% Fe 10% Co	Pipe sawdust bio oil	300	5	3.45	N/A	22.4% hydrocarbon 8.72% phenol 61.47% ester 3.38% alcohol 2.42% aldehydes	The modification effect of medium acidic Fe-Co/SiO ₂ catalyst on biological oil is good.	(Cheng et al., 2017)
Ni/SiO ₂	15% Ni	Methyl laurate	300	N/A	2	95.1	4.1% C6~C10 93% C11 2.5% C12	In the deoxygenation reaction, the selectivity of the Ni/SiO ₂ to the cracking product is higher and the product is mainly the desorption produ	(J. Chen, Shi, Li, & Li, c, 2014) ct.
Co/SiO ₂	20% Co	Guaiacol	300	1	1	100	53.1% aroma 39.7% naphthene	The reduced Co/SiO ₂ catalyst has high HDO activity and aromatic selectivity.	(Mochizuki, Chen, Toba, & Yoshimura, 2014)
Fe/SiO ₂	17% Fe	Guaiacol	400	N/A	0.1	74	38% (benzene, toluene, xylene)	Fe/SiO ₂ has good selectivity to BT production, but it cannot catalyse aromatic ring hydrogenat	(Olcese et al., 2012) ion.
Ni/SiO ₂	5% Ni	Phenol	275	5	10	80	~40% cyclohexane ~32% cyclohexanol	When using cyclohexanol and phenol as the main raw materials, Ni/SiO ₂ catalyst should be	(Peter M. Mortensen, used. Grunwaldt, Jensen, & Jensen, 2016)
Ni ₂ P/SiO ₂	11.2% Ni ₂ P	Guaiacol	300	N/A	0.1	99.5	71.9% benzene 1.9% phenol	The Ni ₂ P grain size of the SiO ₂ load is the small which indicates that Ni and P have strong inter in the active phase, it has a good ability of I transfer.	llest, (SK. Wu et al., 2013) action H atom

Table 2.4: Overview of deoxygenation reaction under different conditions using SiO₂ supported catalyst.
Olcese et al. (Olcese et al., 2012) studied the use of Fe/SiO₂ catalyst at low H₂ pressure (0.1 MPa) and temperature of 400°C for the deoxygenation of guaiacol. They reported that the conversion was 74% and the selectivity was mostly towards the production of benzene, toluene, and xylene (38%) without catalysing the hydrogenation of aromatic ring. On the other hand, the hydrodeoxygenation of guaiacol in low H₂ pressure (0.1 MPa) was also demonstrated by Wu et al. (S.-K. Wu et al., 2013), they showed that Ni₂P/SiO₂ was more active and effective to deoxygenate guaiacol. The conversion was 99.5% and the selectivity was 71.9% benzene. This was attributed to the small Ni₂P particles dispersed on SiO₂ that acted effectively in H-transfer, accumulated low amount of coke and excess phosphorus which maintained Ni₂P in fully phosphided state.

The researches on deoxygenation process using SiO_2 supported catalyst were carried out in high and low H₂ atmosphere as shown in Table 2.4. However, more researches should be focused on deoxygenation of vegetable oils or bio-oils in low H₂ or inert atmosphere (without H₂) owing to the high cost consumption. Storage is easy to absorb moisture, so when not used must be sealed and preserved, and stored in dry environment conditions, around should not exist volatile substances (Cheng et al., 2017). Biofuel is a sustainable and renewable energy and it should not rely massively on H₂ which is a nonrenewable source and most of the H₂ in the world are produced from fossil-fuel reforming (Rogers & Zheng, 2016).

2.2.4 ZrO₂ supported catalyst

Zirconium dioxide as known as zirconia is a reducible oxide with white crystallite appearance. ZrO₂ is an acidic support. It requires a reducing agent (i.e. H₂) to maintain its activity since it is a reducible oxide (Rogers & Zheng, 2016). This has been proved by Peng et al. (Peng, Zhao, Kasakov, Foraita, & Lercher, 2013) who investigated the deoxygenation of palmitic acid using Ni/ZrO₂ under two different atmospheres. They compared the deoxygenation under H₂ atmosphere (1.2 MPa) and inert N₂ atmosphere at identical temperature 260°C. The results showed that the conversion was 100% with a 90% pentadecane selectivity under H₂ atmosphere (1.2 MPa) whereas the conversion was only 3.5% with a 16% pentadecane selectivity under inert N₂ atmosphere. Hence, most of the deoxygenation processes using ZrO₂ supported catalyst were carried out in H₂ condition. Table 2.5 summarized the deoxygenation process of different feedstock to produce hydrocarbon-grade biofuel using ZrO₂ supported catalyst.

Catalyst	Metal (w/w)	Reactant	React	tion cond	ditions	Conv. (%)	Selectivity	Remark	Ref.
			T (°C)	t (h)	H2 (MPa)	(,,,)			
Ni-Cu/ ZrO ₂	N/A	Dibenzo- furan	260	6	10	68.0	71% bicyclohexyl-1-ene 29% bicyclohexyl	Ni-Cu/ZrO ₂ catalysts have the highest selectivity at 260 °C and 270 °C.	(Ambursa et al., 2016a)
Ni-Cu/ ZrO ₂	15.71% Ni 6.29% Cu	<i>Chlorella</i> bio-oil	350	3	2	82.0	N/A	In HDO, Ni-Cu/ZrO ₂ catalysts are more attractive than Ni/ZrO ₂ catalysts because the addition of copper facilitates the reduction of nickel oxide.	(Q. Guo, Wu, Wang, Zhang, & Xu, 2015)
Ni/ZrO ₂	10% Ni	Stearic acid	260	8	4	100.0	96% <i>n</i> -heptadecane	A novel route for the transformation of microalgae oil to alkanes has been developed by selectively cleaving C–C and C–O bonds with ZrO ₂ -supported Ni catalysts.	(Peng, Yuan, Zhao, & Lercher, 2012)
Ru/ZrO2	1% Ru	Propanoic acid	200	N/A	6.4	93.6	56.1% C ₂ H ₆ 28.1% CH ₄ 10.4% C ₃ H ₈ 4.5% propanol	High temperature and high Ru load catalyst Ru load is beneficial to the cracking of C-C bond, while the combination of acidic carrier and metal is beneficial to the hydrogenation of carboxyl group.	(Lungang Chen et al., 2011)
Ni ₂ P/ZrO ₂	11.2% Ni ₂ P	Guaiacol	300	N/A	0.1	96.5	32.4% benzene 25.5% phenol 1.3% cresol	Ni ₂ P/ZrO ₂ enhances the DME synthesis route of phthalic phenol.	(SK. Wu et al., 2013)
RhPt/ZrO ₂	10% Rh 3.4% Pt	Guaiacol	100	5	8	98.7	~92% 1-methyl-1,2- cyclohexanediol ~5% cyclohexanol	Under high and low temperature conditions, the catalysts containing RhPt have good HDO and hydrogenation properties respectively.	(A. Gutierrez, Kaila, Honkela, Slioor, & Krause, 2009)
Ni/ZrO ₂	5% Ni	Phenol	275	4	10	99.8	83% cyclohexane	Nickel was found to be practically inactive for HDO of phenol on a carbon support but more active than the carbon-supported noble metal catalysts when supported on ZrO ₂ .	(Peter M. Mortensen, Grunwaldt, Jensen, & Jensen, 2013)

Table 2.5: Overview of deoxygenation reaction under different conditions using ZrO2 supported catalyst.

Ambursa et al. (Ambursa et al., 2016a) used Ni-Cu/ZrO₂ catalyst to deoxygenate dibenzofuran into bicyclic hydrocarbons at high H₂ pressure (10 MPa) and temperature of 260°C. The conversion was 68% and the major selectivity were bicyclohexyl-1-ene (71%) and bicyclohexyl (29%). The conversion was moderate owing to the bimetallic CuNi agglomerated on the ZrO₂ surface and covered the acidic sites, leading to ineffective hydrodeoxygenation reaction. Interestingly, the selectivity of bicyclohexyl-1-ene was high (71%) because of the surface of ZrO₂ provided available adsorption sites for furanic oxygen to have proper orientation as well as effective activation of C-O and C=O bonds due to the high acidic sites on ZrO₂ surface. On the other hand, Peng and his co-workers (Peng et al., 2012) used Ni/ZrO₂ catalyst to convert stearic acid to diesel-range alkanes under 4 MPa H₂ pressure at 260°C. The conversion was 100% and high selectivity (96%) heptadecane was obtained. And Ni nanoparticles facilitated the cleavage of the C-O bonds, resulting to the hydrogenolysis of stearic acid. In addition, oxygen vacancies of ZrO₂ support facilitated the adsorption of the carboxylic groups to eventually decarbonylated on Ni nanoparticles.

Zirconium dioxide (ZrO₂) has high temperature resistance, chemical corrosion resistance and resistance (Q. Guo et al., 2015). Oxygenation, wear resistance, high coefficient of thermal expansion and low heat capacity and thermal conductivity determine that it is a very ideal high temperature refractory, abrasive material and high temperature insulation material. Zirconium dioxide also has martensitic transformation characteristics, which is an important basis for improving the toughness of ceramic materials and thermal shock stability of refractories (M. Zhang et al., 2019). But at the same time, it has a strong corrosive, irritating and almost insoluble in water. At the time of storage, it should be stored in a dry storeroom, not with strong alkali items to store mixed transport (Titus et al., 2016)

2.2.5 CeO₂ supported catalyst

Cerium (IV) oxide, also known as ceria or ceric dioxide, is a reducible oxide similar to TiO_2 and ZrO_2 . In this case, CeO_2 also requires a reducing agent such as H_2 to maintain its activity and hence, either high or low H_2 pressure is needed for deoxygenation process. Table 2.6 summarized the deoxygenation process of different feedstock to produce green biofuel using CeO₂ supported catalyst.

Shen et al. (Shen et al., 2018) investigated the deoxygenation of octanoic acid at 3 MPa H_2 pressure and 280°C using NiMo/CeO₂ catalyst. The conversion was 100 % with high selectivity of octane (75%) and heptane (22%). The Ni dopant facilitated the formation of C₇ alkane via deoxygenation process while the Mo dopant favoured the formation of C₈ alkane via dehydration-hydrogenation process. The Mo prevented the reduction and strengthened the interaction of metal-support, resulting to higher metal dispersion. Besides, Yang et al. (Y. Yang et al., 2014) used Ni/CeO₂ catalyst to selectively deoxygenate anisole to aromatics under low H₂ pressure (0.3 MPa) and 310°C. Hexane (30%), benzene (49%) and cyclohexane (17%) were the main products owing to the hydrogenation capacity of the aromatic ring by the reducible oxide, CeO₂.

Cerium compounds have many applications due to factors such as purity, physical property and impurity content (Shen et al., 2018). In the distribution of rare earth elements, cerium accounts for about 50% of light rare earth resources (G. Zhou et al., 2017). With the increasing application of high purity cerium, the non-rare earth content index of cerium compounds is more demanding. CeO₂ is the most stable oxide of rare earth element cerium (H. Liu, Zou, Wang, Lu, & Ding, 2012). It is a pale-yellow solid at room temperature, and the yellow is deepened when heated. CeO₂ was widely used in luminescent materials, catalysts, polishing powder, shielding ultraviolet rays *etc* (X. Fan,

Li, Jing, Li, & Chu, 2018). The disadvantage is toxic (Q. Zhou, Zarei, De Girolamo, Yan,& Zhang, 2019). It can be sealed and saved when stored.

Catalyst	Metal	Reactan	Reac	tion cor	nditions	Conv.	Selectivity	Remark	Ref.	
	(w/w)	t	T (°C)	t (h)	H2 (MPa)	(%)				
Ni-Cu/CeO ₂	N/A	Dibenzo- furan	260	6	10	98	~56% bicyclohexyl-1-ene ~43% bicyclohexyl	Ni-Cu/CeO ₂ catalyst was found to be active at 250 °C.	(Ambursa et al., 2016a)	
Ni/CeO ₂	10% Ni	Stearic acid	260	8	4	100	00 93% <i>n</i> -heptadecane High efficiency is achieved by using Ni-based catalysts.		(Peng et al., 2012)	
Ni/CeO ₂	5% Ni	Phenol	275	4	10	100	~88% cyclohexanol Nickel was found to be practically inactive for HDO of phenol on a carbon support		(Peter M. Mortensen et al., 2013)	
Ni-Cu/CeO ₂	28.5% Ni 9.5% Cu	Anisole	250	2	1	100	~100% cyclohexane CeO ₂ are most effective in the target processes.		(Yakovlev et al., 2009)	
Ni/CeO ₂	20% Ni	Anisole	310	6	0.3	98	30% hexane 17% cyclohexane 49% benzene	Remarkable yield in selective production of benzene is achieved by using Ni-based catalysts.	(Y. Yang et al., 2014)	
NiMo/CeO2	1Ni:3Mo	Octanoic acid	300	7	3	100	~75% octane ~22% heptane	Ni were beneficial for the deoxygenation reaction to form C_7 alkane, while the doping of Mo favored the HDO path to C_8 alkane.	(Shen et al., 2018)	
Pt/CeO2	1% Pt	Guaiacol	180	5	5	30	1% cyclohexane 8% cyclohexanol 89% methoxycyclohexanol	The reducibility of Pt in the catalysts have a significant influence on the HDO ability of guaiacol,	(Hellinger et al., 2015)	

Table 2.6: Overview of deoxygenation reaction under different conditions using CeO₂ supported catalyst.

2.2.6 Al₂O₃-TiO₂ supported catalyst

The subsection 2.2.1 to 2.2.5 discussed the TiO₂, Al₂O₃, SiO₂, ZrO₂ and CeO₂ supported catalysts. The acidity order is Al₂O₃ > TiO₂ > ZrO₂ > CeO₂ > SiO₂ (Kay Lup, Abnisa, Wan Daud, & Aroua, 2017). The highest acidity possessed by Al₂O₃ has attracted attention from researchers. However, the high acidity of Al₂O₃ supported catalyst leads to coke deposition that eventually causes unstable and deactivation of the catalyst. Recently, the combination of Al₂O₃-TiO₂ has prominently attracted much attention from researchers to cope with the problems come from Al₂O₃. Many noble metals such as Pd, Ru, Pt, Ag (J. Li, Zhu, Ke, & Hao, 2008; Núñez, Escobar, Vázquez, Reyes, & Hernández-Barrera, 2011; Xu et al., 2016; C. Yang et al., 2016) and transition metals such as Co, Ni, Mo, Mn (Escobar, De Los Reyes, Viveros, & Barrera, 2006; Tavizón-Pozos et al., 2016; Vo et al., 2018; L. Wang, Wang, Cheng, Ning, & Lin, 2018) are well dispersed on Al₂O₃-TiO₂ and they displayed superior catalytic properties for many reactions such as deoxygenation, hydrodesulfurization, oxidative dehydrogenation, oxidation, methanation, photocatalytic degradation, hydrogenation and others.

Deoxygenation was often carried out in hydrogen pressurized condition and sometimes, under ambient condition. Al₂O₃-TiO₂ possesses higher surface area/volume ratio that ultimately assists in the deoxygenation reaction as in the adsorption and diffusion of reactants are effective owing to the well-defined pore structures (Vo et al., 2018). The catalyzed deoxygenation process will take shorter reaction time to finish owing to the high catalytic, stability properties and function of Al₂O₃-TiO₂ such as: (i) play as active phase role for reactant absorption in hydrogen insertion and oxygen removal, (ii) formation of intermediates to decrease the deoxygenation overall activation energy, (iii) weaken the single or double carbon-oxygen bond by forming provisional metal-reactant bond rate (Kay Lup, Abnisa, Wan Daud, et al., 2017). Table 2.7 shows an overview of the comparison of Al₂O₃-TiO₂ supported catalyst and other catalysts in deoxygenation reaction using phenolic, furan and fatty acid based feedstock.

Catalyst	A-T	Metal	Reactant	React	ion cor	nditions	Conv.	Selectivity	Remark	Ref	
	(w ratio)	(w/w)		T (°C)	t (h)	H2 (MPa)	(70)				
CoMoS/A-T	1A-1T	10% Mo	Guaiacol	300 (PT=H	2 H ₂ S atm	5 osphere)	~95	~4.67% cyclohexene ~32.61% cyclohexanol	After adding CoMo sulfide catalyst, the TiO ₂ of load Al ₂ O ₃ has obvious catalytic activity to HDO and HDN reaction.	(Rodseanglung et al., 2015)	
CoMoS/A-T	2A-1T	79% Mo	Phenol	320	4	5.4	~92	~63.33% benzene ~23.33% cyclohexane ~3.33% cyclohexene	Using mixed Al ₂ O ₃ -TiO ₂ oxides (Al/Ti = 2, AT2) as carriers, catalytic activity was significantly improved in the HDO of phenol	(Tavizón-Pozos et al., 2016)	
				(PT=1 2 h, 4	15% H ₂ 00 °C)	S, H ₂ ,					
CoMoS/TiO2	-	7.4% Mo	Guaiacol	300 (PT=1 4 h, 40	12 15% H ₂ 00 °C)	4 S, H ₂ ,	100	~60% phenol ~20% cyclohexane, benzene & cyclohexene	CoMoS/TiO ₂ catalyst has hydrogenation capacity.	(Dongil, Ghampson, Garcia, Fierro, & Escalona, 2016)	
CoMoS/Al ₂ O ₃	-	79% Mo	Phenol	320 (PT=1 2 h, 40	4 15% H ₂ ; 00 °C)	5.4 S, H ₂ ,	~90	~45% benzene ~41% cyclohexane ~2.2% cyclohexene	CoMo/Al ₂ O ₃ has catalytic activity on phenol HDO.	(Tavizón-Pozos et al., 2016)	
CoMoS/Al ₂ O ₃	-	12-16% Mo	Guaiacol	300 (PT=5 350/4	2 5% H 00 °C)	8 2 S , H ₂ ,	~98	~32% phenol ~30% benzene ~13.33% cyclohexanol	Adding sulfide will reduce the hydrogenation activity of the catalyst.	(Andrea Gutierrez, Turpeinen, Viljava, & Krause, 2017)	

Table 2.7: Comparison of Al₂O₃-TiO₂ supported and other catalysts in deoxygenation process using phenolic, furan and fatty acid based feedstock.

								'Table 2.7: continued'		
Catalyst	A-T (w	Metal (w/w)	Reactant	React	tion co	nditions	Conv. (%)	Selectivity	Remark	Ref
	ratio)			Т (°С)	t (h)	H ₂ (MPa)				
Ni ₂ P/A-T	1A-1T	8.8% Ni	Benzofuran	N/A	6	3	95	 71% ethylcyclohexane 12% ethylbenzene 9% methylcyclohexane 5% 2-ethylphenol (2-EtPh) 3% 2,3-dihydrobenzofuran 	Compared with Ni ₂ P/Al ₂ O ₃ , the yield of anaerobic products in Ni ₂ P/A-T increased by 40%.	(Song et al., 2016)
Ni2P/Al2O3	-	8.8% Ni	Benzofuran	N/A	6	3	78	43% ECH 8% EB 8% MCH 25% 2-EtPh 16% 2.3-DHBF	Ni ₂ P/Al ₂ O ₃ has catalytic deoxygenation activity.	(Song et al., 2016)
Ni2P/TiO2	-	8.8% Ni	Benzofuran	N/A	6	3	85	69% ECH 6% EB 8% MCH 10% 2-EtPh 7% 2.3-DHBF	Hydrophobic TiO ₂ shell can enhance water resistance, HDO activity and stability.	(Song et al., 2016)
Ni/Ultrastable Y Zeolite (USY)	Si/Al = 40	5% Ni	Benzofuran	200	2.33	5.171	~77	100% 2.3-DHBF	Ni/USY can improve the hydrogenation reaction rate and is an effective HDO catalyst.	(Gamliel, Karakalos, & Valla, 2018)

'Table 2.7: continued'

Catalyst A-T Metal Reactant **Reaction conditions** Conv. Selectivity Remark Ref (w (w/w)(%) Т H_2 t ratio) (°C) (h) (MPa) 300 5 93.1 The addition of Al to the SBA-15 carrier can Ni₂P/ 10% Ni 3 ~88% ECH (Zhu, Song, Dai, & Benzofuran _ Al-SBA-15 ~4.6% EB promote the formation of more uniform, Song, 2017) ~3.7% MCH smaller, highly dispersed Ni₂P particles on the catalyst. In addition, the inclusion of Al can ~1.8% 2.3-DHBF ~0.8% EtPh increase the strength of the acid. The Ni₂P/Al-SBA-15 shows a higher HDO activity. Mo/A-T 0.8A-30% Mo Palmitic 280 4 4 100 ~93.18% hexadecane The Mo/A-Tcatalyst has good catalytic (Vo et al., 2018) 0.2T acid ~6.82% hexadecene properties for the HDO of palmitic acid. (L. Zhou & Lawal, S-Ni-Mo/y-4.03% Ni Nannochlor 360 N/A 3.447 98.7 ~56.2% C₁₃ - C₂₀ The activity of the catalyst can be maintained Al_2O_3 13.2% Mo -opsis salina HDO:DCO = 6:1by adding sulfide to the Ni-Mo/ γ -Al₂O₃ 2015) in the hydrogenation deoxygenation reaction. 2 Co/H-ZSM-22 Si/Al = 4% Co Palmitic 260 ~99 ~51.1 iso-C₁₆ The dual-function Co/H-ZSM-22 catalyst (Cao et al., 2018) 4 37.5 acid ~15.8% n-C₁₆ has good stability and good catalytic properties for palmitic acid. ~22.3 iso-C₁₅ ~9.6% n-C₁₅ ~1.2% n-C14 MoO₂/CNTs 5% MoO₂ Palmitic 220 100 ~92.2% hexadecane MoO₂/CNTs shows excellent low temperature (Ding et al., 2015) ~7.6% pentadecane activity and 16 alkane selectivity. acid Co-doped 5% MoO₂ Palmitic 180 100 ~89.3% hexadecane The catalyst can be catalyzed by Mo₂C alone (Ding et al., 2016) MoO₂/CNTs 1.5% Co acid ~5.2% pentadecene or by co-catalyzed by Mo₂C and MoO₂. ~4.9% hexadecanol

'Table 2.7: continued'

Coking, the formation of carbonaceous materials on the surface of catalyst due to high acidity present in Al₂O₃ can hinder the catalyst performance due to the blockage of active sites (Qi, Wei, Zong, & Wang, 2013). Coking occurs due to the agglomeration of unsaturated hydrocarbon products consisting double or triple bond and intermediates that are partly oxidized. The use of hydrogen in the process can increase the stability of catalyst and prevent the existent of unsaturated hydrocarbon compound (Kubička et al., 2014). However, it is less environmental friendlier on account of consuming quite weighty amount of hydrogen gas to perform hydrogenation reaction (Asikin-Mijan, Lee, Juan, et al., 2018). Moreover, the high reaction temperature in deoxygenation reaction results huge challenges in hydrocarbon cracking and coke deposition, leading to weakening of cooling passages, catastrophic structural failure, poor selectivity and less catalyst stability (Y. Zhang et al., 2006). For Al₂O₃ supported catalyst, the initial coke build-up occurs rapidly and the coke formation is increased due to the catalyst acidity (Nederlof et al., 2014). Based on the study by Lisovskii et al. (Lisovskii & Aharoni, 1994), the acidity is a factor that increases the formation of coke, resulting in a significant amount of coke on an Al₂O₃ catalyst which is the covering of catalyst surface by a monolayer. In contrast, TiO₂ exhibited low coke formation owing to its weak acid property with Lewis acid sites (Qi et al., 2013). Hence, the addition of TiO₂ into Al₂O₃ will prevent the amount of coke formed at alumina site. According to Zhang et al. (Y. Zhang et al., 2006), they found that the introduction of TiO₂ into Al₂O₃ had a significant effect on the catalyst performance as in the dispersion of TiO_2 leads to better support acidity and increase the strong acid centre. Moreover, they also indicated that the excessive of TiO₂ will cause more coke deposition and lead to serious deactivation. For instance, the addition of 10 wt % of TiO₂ into Al₂O₃ supported Pt catalyst showed high selectivity than 20 wt % addition. This result indicated that the proper amount adjustment

of incorporation TiO_2 into Al_2O_3 is significant in order to cope with coke formation. By using Al_2O_3 -TiO₂ as catalyst or support, it is able to prevent coke formation and promote better catalyst activation as well as deoxygenation process. Therefore, Al_2O_3 -TiO₂ is a potential catalyst or support for catalytic deoxygenation in producing high quality biofuel.

2.2.6.1 Deoxygenation of phenolic-based feedstock using Al₂O₃-TiO₂ supported catalyst

Generally, sulfided catalyst shows high catalytic activity and consequently produces hydrocarbon with increased fraction of superior qualities such as higher heating value, satisfactory acid value and water content (Parapati et al., 2015). However, it has some disadvantages such as the biofuel is contaminated with sulfur. Al₂O₃-TiO₂ is a potential support for sulfided CoMo catalyst to transform bio-oil into useful hydrocarbon fuel owing to its excellent properties via mutual incorporation. It was evidently showed that the conversion rate was high and the selectivity was ideal when Al₂O₃-TiO₂ was used as a support compared to the single Al₂O₃ or TiO₂. Guaiacol is commonly utilized as model compound for lignin in HDO process owing to its –OH and –OCH₃ groups which are the most representative for phenolic monomers derived from lignin (Roldugina et al., 2018). The deoxygenation reactions of guaiacol were carried on via demethylation, demethoxylation, hydrogenation, dehydroxylation and hydrodeoxygenation (Nguyen et al., 2016; Sankaranarayanan et al., 2018).

In the hydrodeoxygenation process of guaiacol by using CoMoS supported on Al_2O_3 -TiO₂, it indicated that the major selectivity was cyclohexanol (Table 2.7). However, the major product was phenol when using CoMoS supported on TiO₂ (Table 2.7). These results showed that the HDO reaction by TiO₂ was in the primary step since phenol was the major selectivity. The better tendency of Al_2O_3 -TiO₂ towards HDO is feasible owing

to the higher reducibility, better metal dopant dispersion as well as larger active phase cluster size compared to TiO₂ or Al₂O₃ (Ramírez et al., 2005; K. Segawa et al., 1996). Other than that, Gutierrez et al, who worked on hydrodeoxygenation of guaiacol using CoMoS/Al₂O₃ also showed that the selectivity was not feasible as in the saturated compound formed was lesser (Table 2.7) compared to the one using Al₂O₃-TiO₂. These results affirmed that Al₂O₃-TiO₂ plays a dominant role in HDO process of phenolic compounds as in it has been demonstrated that the product selectivity can be tuned by mixing both Al₂O₃ and TiO₂. On the other hand, Tavizón-Pozos et al. (Tavizón-Pozos et al., 2016) reported that the use of Al_2O_3 -TiO₂ (molar ratio Al/Ti=2) support for bimetallic CoMoS catalyst was able to tune the support-metal interaction and promote octahedral coordination oxide phase via the dispersion of MoO_x and reducible CoO_x . The catalyst displayed high active sites, enhanced catalytic performance and product selectivity during hydrodeoxygenation of phenol owing to the higher formation of active phase. However, the aromatic carbon-heteroatom bonding cannot be directly cleaved when using CoMoS/Al₂O₃ catalyst (Studentschnig, Schober, & Mittelbach, 2013), leading to unfavourable selectivity (Table 2.7). Apart from that, as discussed before by Wang et al. (W.-y. WANG et al., 2011), the hydrodeoxygenation of phenol using NiMoS/Al₂O₃-TiO₂ was superior as in the process resulted in high conversion, deoxygenation reaction rate and total oxygen-free compound which were 81.9%, 79.4% and 100% respectively owing to efficient specific surface area and acidity properties of the support. It has been evidently demonstrated that Al₂O₃-TiO₂ supported metal sulphide catalyst exhibited excellent properties, better catalytic as well as selectivity towards HDO. However, the draw back in the metal sulphide catalyst is that the reaction has to take place in hydrogen condition which means that the consumption of hydrogen is high as well as quite weighty amount of sulphur source is required to maintain the catalyst in sulfided states (Oi et al., 2016).

Implementing metal sulphide catalyst in industry at a large scale has to take environmental and economical issues into account before carrying out in a large scale. With the better performance and efficiency of Al_2O_3 -TiO₂ supported metal sulphide catalyst, it has the potential to replace the conventional Al_2O_3 or TiO₂ supported metal sulphide catalyst in the industry.

2.2.6.2 Deoxygenation of furan-based feedstock using Al₂O₃-TiO₂ supported catalyst

Furans are heterocyclic organic compounds with four carbon atoms and one oxygen, forming a five-membered aromatic ring (Kay Lup, Abnisa, Daud, et al., 2017). The deoxygenation of benzofuran model compounds can take place via one major reaction pathway. Hydrogenation takes place at the heterocyclic ring to form 2,3-dihydrobenzofuran, and then further converts to octahydrobenzofuran at the benzene ring. The major deoxygenated hydrocarbon products are ethylcyclohexane and methylcyclohexane (Chunyan Liu, Shao, Xiao, Williams, & Liang, 2012).

The hydrodeoxygenation performance of Ni₂P/Al₂O₃-TiO₂ for benzofuran using two different feeds (decalin solution and decalin water mixture) conversion was study by Song et al. (Song et al., 2016). The authors found that the conversion of benzofuran model compound in decalin solution yielded up to 95% with higher oxygen-free selectivity. Moreover, the hydrodeoxygenation of benzofuran in decalin using Ni₂P/Al₂O₃ and Ni₂P/TiO₂ was found lower (78% and 85% respectively) and lesser oxygen-free selectivity compared to Ni₂P/Al₂O₃-TiO₂ (Table 2.7). On the other hand, they also analysed and compared the hydrodeoxygenation performance of benzofuran in decalin water mixture. The HDO conversion of benzofuran in water feed over Ni₂P/A-T was 84%. However, the conversion using Ni₂P/Al₂O₃ showed 58% whereas Ni₂P/TiO₂ showed

79%. The hydrodeoxygenation effectiveness of benzofuran using Ni₂P/A-T was superior owing to the hydrophobic nature of the TiO₂. As discussed before by Moon et al. (Moon & Lee, 2015), they also reported the similar finding related to the usage of hydrophilic and hydrophobic supports. The stability of the Ni₂P catalysts in the presence of H₂O could be improved by utilizing support with hydrophobic nature. In contrast, the hydration of the catalyst surface in hydrodeoxygenation reaction could be increased by using support with hydrophilic nature. Therefore, the stability of catalyst and better hydrodeoxygenation reaction can be achieved through the incorporation of TiO₂ in Al₂O₃-TiO₂. In addition, Zhu et al. (Zhu et al., 2017) investigated the hydrodeoxygenation performance for benzofuran in decalin solution by using Ni₂P/Al-SBA-15 catalyst. They found that the conversion of benzofuran in decalin solution was 93.1% with excellent oxygen-free selectivity (Table 2.7). This result demonstrated that the addition of Al in Al-SBA-15 catalyst can produce smaller and uniform catalyst structure. The Ni₂P/Al-SBA-15 managed to produce O-free product up to 90.3% (Zhu et al., 2017) compared to the 87% deoxygenated products produced by using Ni₂P/A-T catalyst (Song et al., 2016). According to Zhu et al. (Zhu et al., 2017), the better dispersion of the Ni₂P active phase and smaller Ni₂P crystallites were the main contribution to the superior hydrodeoxygenation performance. Same goes to the finding by Song et al. (Song et al., 2016), they identified that no additional phase containing Ni and P was presence and Ni₂P was highly dispersed on the prepared catalyst. Thus, both Ni₂P/A-T and Ni₂P/Al-SBA-15 showed good performance on deoxygenation of benzofuran model compound with slightly difference in conversion percentage.

Apart from that, Gamliel et al. (Gamliel et al., 2018) reported the hydrodeoxygenation of benzofuran using Ni supported on USY zeolite. The authors found that the conversion percentage was about 77% with 100% selectivity on 2,3-dihydrobenzofuran (Table 2.7).

This indicated that the Ni-USY zeolite catalyst showed inefficient performance owing to incapability of the catalyst to perform ring-opening the reactions during hydrodeoxygenation of benzofuran, despite having the zeolite acid sites that usually facilitate cracking reactions. In the catalytic hydrodeoxygenation of benzofuran, the first step of the reaction is the hydrogenation of the O₂-containing ring resulting the formation of 2,3-dihydrobenzofuran. The second step is proceeded by the ring-opening and hydrogenation of remaining double bond resulting the formation of major products which are ethylbenzene, ethylcyclohexane and ethylcyclohexene (C.-L. Lee & Ollis, 1984). As discussed previously by Song et al. (Song et al., 2016), Ni₂P/A-T catalyst converted the benzofuran model compound with superior selectivity (3% 2,3-dihydrobenzofuran and 71% ethylcyclohexane), indicating that the ring opening second step reaction was effective compared to Ni-USY zeolite catalyst that stopped the reaction at the first step. Therefore, Al₂O₃-TiO₂ is definitely an alternative catalyst in performing the deoxygenation process of pyrolysis oil.

2.2.6.3 Deoxygenation of fatty acid feedstock using Al₂O₃-TiO₂ supported catalyst

In a recent published paper, Vo et al. (Vo et al., 2018) recently studied the HDO of palmitic acid over Mo supported on Al₂O₃-TiO₂. They reported that the conversion reached 100% and produced high hexadecane selectivity up to 93.18% and hexadecane up to 6.82% (Table 2.7). In the literature, Zhou et al. (L. Zhou & Lawal, 2015) reported that the hydrodeoxygenation process of *Nannochloropsis* using presulfided NiMo/ γ -Al₂O₃ reached almost complete conversion (98.7%) at reaction conditions (360 °C and 3.447 MPa in H₂), resulting in ~56.2% C₁₃ – C₂₀ hydrocarbon yield and HDO:DCO ratio of 6 (Table 2.7). However, in the sulphided catalyst, a large amount of hydrogen and sulphur-containing agent such as CS₂ or H₂S are required to add into the HDO process to prevent the deactivation of catalyst owing to the formation of oxygenated intermediates.

Ultimately, it raises up the possibility of contamination in liquid products as well as production cost of renewable hydrocarbon (Şenol, Ryymin, Viljava, & Krause, 2007). Referring back to the work done by Vo et al. (Vo et al., 2018), the HDO process was carried out without any sulfided condition. In other words, the contamination issue was avoided and the utilization of Mo supported on Al₂O₃-TiO₂ displayed a better conversion as well owing to the better oxygen vacancies in the catalyst through modification of Al₂O₃ by using TiO₂ with higher oxygen content. The olefin (hexadecene) formed as an intermediate product indicated that the reaction pathways of palmitic acid by using Al₂O₃-TiO₂ followed the major routes of conversion to hydrocarbons in the liquid phase which are HDO to form hexadecane: $C_{15}H_{31}COOH \rightarrow C_{15}H_{31}CHO \rightarrow C_{16}H_{33}OH \rightarrow C_{16}H_{34}$ and, decarboxylation/decarbonylation to form hexadecene: $C_{15}H_{31}COOH \rightarrow [C_{15}H_{31}CHO] \rightarrow$ $C_{15}H_{32}$ (Peroni, Mancino, Baráth, Gutiérrez, & Lercher, 2016). Thus, Al₂O₃-TiO₂ has the tendency to replace sulfided NiMo/ γ -Al₂O₃ in catalytic conversion of palmitic acid.

As discussed previously, the common fatty acids such as palmitic acid, oleic acid, palmitoleic acid, lionoleic acid and stearic acid are found in vegetable oil. Zeolites has been extensively used for deoxygenation of lipids owing to its versatility, acid function of the supports, stability and activity (Schreiber, Rodriguez-Niño, Gutiérrez, & Lercher, 2016). Moreover, the active components can access the porous channel at internal surface more easily due to the improved load capacity when the zeolite is used as a support (Nana Li, Bi, Xia, Chen, & Hu, 2017). From the recent study, Cao et al. (Cao et al., 2018) studied the hydrodeoxygenation of palmitic acid over bifunctional Co/H-ZSM-22 catalysts (Table 2.7). It was found that the HDO of palmitic acid using Co/H-ZSM-22 reached about 99% conversion at reaction conditions (260 °C. 4 h and 2 MPa H₂) resulting in ~51.1% iso-C₁₆, ~15.8% n-C₁₆, ~22.3 iso-C₁₅, ~9.6% n-C₁₅ and ~1.2% n-C₁₄. The conversion of palmitic acid over Mo/Al₂O₃-TiO₂ was 100% and the selectivity of

hexadecane and hexadecene were 93.18% and 6.82% respectively (Table 2.7). Compared to ZSM-22 supported catalyst, Al₂O₃-TiO₂ supported catalyst also provides high conversion and selectivity to C₁₆. Even though Al₂O₃-TiO₂ supported catalyst resulted high conversion and selectivity towards C_{16} , but the n-alkanes products have high freezing point and not effective for fuel especially jet fuel. For instance, the freezing point of n-C16 is 20 °C while the freezing point of multi.iso-C₁₆ is -70 °C (Cao et al., 2018). Hence, isomerization of n-alkanes is necessary for producing bio-fuel. The zeolites such as ZSM-22 are costly due to the use of expensive organic templates in the production or synthesis process (Cui et al., 2018; Meng & Xiao, 2013; Q. Wu et al., 2017). The costly manufacturing process of zeolite has constrained their production in large-scale as well as applications. This has prompted the investigation of cheaper catalyst. Al₂O₃ mixed with appropriate amount of TiO₂ is definitely a potential catalyst or support owing to the high conversion and superior selectivity via hydrodeoxygenation of palmitic acid (model compound of vegetable oil). The cost of Al₂O₃ catalyst is cheaper (Awadallah, Mostafa, Aboul-Enein, & Hanafi, 2014). However, more analysis on isomerization effect of Al₂O₃-TiO₂ has to be studied in order to become an alternative of zeolite for biofuel production.

The MoO_x is an efficacious and low cost catalyst for scission of the C-O and C=O bonds in many oxygenated bio-oil owing to their excellent properties such as high stability, enough lattice defects as well as good mixed oxidation state (Lei & Chen, 2012; Prasomsri, Shetty, Murugappan, & Roman-Leshkov, 2014). Ding and his research team (Ding et al., 2015) reported the transformation of palmitic acid to alkanes by selectively cleaving C–O bonds with carbon nanotubes (CNTs)-supported MoO₂ catalysts. They found that 5% MoO₂ of dopant into CNTs achieved superior conversion (100%) and product selectivity (~92.2% hexadecane and ~7.6% pentadecane) in the catalytic hydrodeoxygenation of long-chain palmitic acid in reaction conditions i.e. 220 °C, 4 h

and 4 MPa (Table 2.7). However, the nature of the active site(s) of MoO₂/CNTs was not identified (Ding et al., 2016). On the other hand, indeed, the active site(s) of Al₂O₃-TiO₂ was determined as in the Lewis acid sites was improved through the addition of TiO₂ (Huang et al., 2008; Oi et al., 2016), producing better hydrodeoxygenation performance (Ding et al., 2016). In addition, Ding et al. also reported the catalytic hydrodeoxygenation of palmitic acid over a bifunctional Co-doped MoO₂/CNTs catalyst (Ding et al., 2016). They found that the dopant of Co ions into MoO₂/CNTs catalyst improved the catalytic deoxygenation of palmitic acid effectively that reached 100% conversion and selectivity about 89.3% hexadecane, 5.2% pentadecene and 4.9% hexadecanol at 180 °C, 4 h and 4 MPa (Table 2.7). As reported earlier, the conversion of palmitic acid using Mo/Al₂O₃-TiO₂ reached 100% and produced high hexadecane selectivity up to 93.18% and hexadecene up to 6.82% (Table 2.7). Therefore, the role of support plays a dominant role in the hydrodeoxygenation process and product selectivity with their own properties. For instance, the diffusion of substrates is effective in the cylindrical nanostructure of carbon nanotubes (CNTs) catalyst owing to their uniform and larger pore diameter (Ding et al., 2015). On the other hand, Al₂O₃-TiO₂ has mesoporous spherical structure typically with pores ranged from 2 nm to 18 nm that facilitates in the deoxygenation process (Vo et al., 2018). It showed that both spherical shape of Al₂O₃-TiO₂ and cylindrical nanostructure of carbon nanotubes (CNTs) catalyst can provide similar high conversion of palmitic acid with excellent selectivity of hexadecane and they are low cost, high activity, and stability. Hence, it can be concluded that Al_2O_3 -TiO₂ provides a new protocol to decrease the O₂ content of vegetable oil in a lower cost, least contamination, superior conversion rate and selectivity compared to other catalysts, for their utilization in the future.

2.3 Synthesis of Al₂O₃-TiO₂

Al₂O₃-TiO₂ supported catalyst exhibits high surface area, excellent reducibility and metal dispersion, superior catalytic activity and thermal stability (A. Duan et al., 2009; Saih, Nagata, Funamoto, Masuyama, & Segawa, 2005; Vo et al., 2018). It is an established fact in the previous studies that active metals dispersed on Al₂O₃-TiO₂ produced higher catalytic activities compared to the one supported on single Al₂O₃ or TiO₂ (A. Duan et al., 2009; Ramírez et al., 2005; K. Segawa et al., 1996). These results confirm that Al₂O₃-TiO₂ is a promising support material for catalyst as in it can solve the coking problem due to high acidity of Al₂O₃. Correspondingly, the catalyst synthesis method is significant owing to the fact that it will produce superior physicochemical property and consistent quality of the catalyst which is a prerequisite for efficient catalytic performance.

The formation of Al–O–Ti linkages through chemical bonding is the primarily combination between Al_2O_3 and TiO₂. The physicochemical and catalytic performance of Al_2O_3 -TiO₂ will change compared to the single oxide owing to the strong interaction presents in chemical bonding of mixed oxides. The synthesis method will significantly affect the degree of homogeneity as well as dispersion of the Al_2O_3 -TiO₂. Various preparation methods have been studied and used throughout the years from1993 to 2018 to synthesize Al_2O_3 -TiO₂ and employ as catalyst or support for various reactions as shown in Table 2.8.

The systematic and precise preparation method is an essential beginning for developing any feasible catalytic material. As visualized in Table 2.8, the most frequent methodology to synthesize Al₂O₃-TiO₂ is sol-gel. The sol-gel process is a wet-chemistry process to prepare tailored solid materials starting from molecular precursors. The Al₂O₃-

TiO₂ sol-gel reactions are suggested as shown in Eqs. (1) and (2), consisting the hydrolysis and condensation reactions of both alkoxides. The kinetics of hydrolysis and polycondensation reactions are rather complex as in these reactions are started at multitudinous sites. The interconnected Al–O–Ti combines conjointly to form a sol after adequate number of Al–O–Ti bonds are structured in a specific region. After that, a 3-D network is formed by linking the sol or colloidal particles together (Singh et al., 2014).

Hydrolysis:

$$Al-(OR)_4 \cdot Ti-(OR)_4 + 8 H_2 O \rightleftharpoons Al(OH)_4 \cdot Ti(OH)_4 + 8 ROH$$
(2.1)

Condensation:

 $nAl(OH)_4 \cdot Ti(OH)_4 + nAl(OH)_4 \cdot Ti(OH)_4 = (Al-O-Ti-O-Al-O-Ti)_n + nH_2O$ (2.2)

Catalyst	Preparation method	Reactions	Ref.		
NiW/Al ₂ O ₃ -TiO ₂	Co-precipitation/impregnation	Hydrodesulfurization of thiophene	(Ramírez & Gutiérrez- Alejandre, 1998)		
Mo/Al ₂ O ₃ -TiO ₂	Co-precipitation/incipient wetness	Hydrodesulfurization of thiophene	(Ramirez et al., 1993)		
Mo/Al ₂ O ₃ -TiO ₂	CVD/impregnation	Hydrodesulfurization of dibenzothiophene	(K Segawa, M Katsuta, & F Kameda, 1996)		
NiMo/Al ₂ O ₃ -TiO ₂	Impregnation/incipient wetness	Hydrotreatment of Maya heavy crude oil	(Ramírez et al., 2005)		
NiMo/Al ₂ O ₃ -TiO ₂	Impregnation, co-precipitation , sol-gel/incipient wetness	Hydrotreating of heavy gasoil fluid catalytic cracking (FCC) feed	(Santes et al., 2005)		
NiW/Al ₂ O ₃ -TiO ₂	Impregnation	Hydrodesulfurization of 4,6-dimethyldibenzothiophen	(Gutiérrez-Alejandre et al., 2005)		
NiW/Al ₂ O ₃ -TiO ₂	Precipitation/incipient wetness	Hydrodesulfurization of dibenzothiophene	(Cruz-Perez et al., 2011)		
Al ₂ O ₃ -TiO ₂	Self-assembly	Oxidation and hydrolysis of HCN to N ₂	(Ma, Wang, Ning, Cheng, & Hu, 2017)		
Al ₂ O ₃ -TiO ₂	Sol-gel	Photocatalytic degradation of imazapyr	(Adel A. Ismail et al., 2015)		
Al ₂ O ₃ -TiO ₂	Sol-gel	Photocatalytic NO oxidation	(Polat et al., 2015)		
V2O5/Al2O3-TiO2	Sol-gel	Selective oxidation of methanol to dimethoxymethane	(Z. Fan, Guo, Fang, & Sun, 2015)		
•					

Table 2.8: Overview of various synthesis methods and reactions using Al₂O₃-TiO₂ supported catalyst.

'Table 2.8: continued'

Catalyst	Preparation method	Reactions	Ref.		
Al ₂ O ₃ -TiO ₂	Sol-gel	Photocatalytic degradation of 2,4-dichloro-phenoxiace-ticacid	(SW. Lee, Paraguay- Delgado, Arizabalo, Gómez, & Rodríguez-González, 2013)		
Ag/Al ₂ O ₃ -TiO ₂	Sol-gel	Reduction of NO with propene	(J. Li et al., 2008)		
Mn/Al ₂ O ₃ -TiO ₂	Sol-gel	Hydrolysis and oxidation for hydrogen cyanide (HCN) removal	(L. Wang et al., 2018)		
Al ₂ O ₃ -TiO ₂	Sol-gel	Synthesis of rare-earth $(Yb^{3+}-Er^{3+} and Yb^{3+}-Tm^{3+})$ co-doped nanocomposite powder phosphors	(Mokoena et al., 2017)		
V2O5/Al2O3-TiO2	Sol-gel, co-precipitation, mechanical mixing, precipitation, ball milling/wetness impregnation	Oxidation of methanol to dimethoxymethane	(T. Wang, Meng, Zeng, & Gong, 2015)		
Ni ₂ P/Al ₂ O ₃ -TiO ₂	Sol-gel/co-impregnation	Hydrodesulfurization of dibenzothiophene	(Wei, Zhu, Han, Guan, & Li, 2015)		
Ni ₂ P/Al ₂ O ₃ -TiO ₂	Sol-gel/impregnation	Hydrodeoxygenation of benzofuran	(Song et al., 2016)		
Mo/Al ₂ O ₃ -TiO ₂	Sol-gel/impregnation	Hydrodeoxygenation of guaiacol, hydrodenitrogenation of quinoline	(Rodseanglung et al., 2015)		
CoMoS/Al ₂ O ₃ -TiO ₂ & NiMoS/Al ₂ O ₃ -TiO ₂	Sol-gel/impregnation	Transalkylation of isopropylbenzene, hydrogenation of naphthalene, hydrodesulfurization of 4,6-dimethyldiben-zothiophen	(Lecrenay, Sakanishi, Nagamatsu, Mochida, & Suzuka, 1998)		
MoO ₃ /Al ₂ O ₃ -TiO ₂	Sol-gel/impregnation	Oxidative dehydrogenation of ethylbenzene to styrene.	(Kainthla, Babu, Bhanushali, Rao, & Nagaraja, 2017)		

		'Table 2.8: continued'	
Catalyst	Preparation method	Reactions	Ref.
CoMoNi/Al ₂ O ₃ -TiO ₂	Sol-gel/incipient wetness	Hydrodesulfurization of thiophene	(Chao Liu, Zhou, Huang, Cheng, & Yuan, 2014)
Pd/Al ₂ O ₃ -TiO ₂ & Pt/Al ₂ O ₃ -TiO ₂	Sol-gel/incipient wetness	Hydrodesulfurization of 4,6-dimethyl-dibenzothiophene	(Núñez et al., 2011)
NiW/Al ₂ O ₃ -TiO ₂	Sol-gel/incipient wetness	Hydrodesulfurization of diesel oil to ultra clean diesel	(A. Duan et al., 2009)
Ni ₂ P/Al ₂ O ₃ -TiO ₂	Sol-gel/incipient wetness	Hydrodesulfurization of 3-methylthiophene	(K. Wang, Yang, Liu, & Yi, 2009)
Mo/Al ₂ O ₃ -TiO ₂	Sol-gel/incipient wetness	Hydrodemetallation kinetics of Ni-tetraphenylporphyrin (TPP)	(García-López et al., 2005)
Mo/Al ₂ O ₃ -TiO ₂	Sol-gel/spray pyrolysis	Hydrodeoxygenation of palmitic acid to hexadecane	(Vo et al., 2018)
Pd/Al ₂ O ₃ -TiO ₂	Sol-gel/wet-impregnation	Oxidation of ethanol	(C. Yang et al., 2016)
CoMoS/Al ₂ O ₃ -TiO ₂	Sol-gel/wet-impregnation	Hydrodeoxygenation of phenol	(Tavizón-Pozos et al., 2016)
Ni/Al ₂ O ₃ -TiO ₂	Sol-gel/wet impregnation	Dehydrogenation of cyclohexane	(Escobar et al., 2006)
Ru/Al ₂ O ₃ -TiO ₂	Wet-impregnation /incipient wetness	CO ₂ methanation	(Xu et al., 2016)

Sol-gel method allows the catalytic formulation design especially in heterogeneous catalysts synthesis. This method involves the network development via colloidal suspension arrangement (sol) as well as continuous liquid phase system formed by gelation (gel) (Yano, Iwata, & Kurita, 1998). Sol is defined as a colloidal particles ranged 1-100 nm dispersed in a liquid whereas gel is a firm network formed by interconnecting polymeric chains and sub-micron dimensions pores (Singh et al., 2014). Sol-gel route is regularly utilized owing to its low cost, simple operation and possible ability in manipulating the surface and textural properties in order to produce a more promising oxide nanoparticles with higher porosity, large open pores and high purity (Ning Li et al., 2012). This method generally involves hydrolysis and condensation of precursors and drying (Hench & West, 1990). The material properties such as composition and morphology can be controlled by manipulating the parameters of the process (Hench & West, 1990). For the sol-gel synthesis of Al₂O₃-TiO₂, the commonly used precursor for Al₂O₃ includes organic compounds like aluminium-tri-sec-butoxide (ATSB) and other inorganic precursor (no carbon contents) salts like Al(NO₃)₃ (Pajonk, 1991). The former is the alkoxide, the most widely used precursors in sol-gel process owing to its readily reaction with water (Bhaduri, 1993). Post heat treatment is needed for this water reaction procedure to convert the gel into crystalline oxides and as a result, the hydroxyl groups and organic residuals would be removed (C. Wang, Li, & Wang, 2004). On the other hand, for TiO₂, the common precursors are titanium (IV) butoxide (TBOT) and titanium tetraisopropoxide (TTIP). Othman et al. (Othman, Rashid, Ghazi, & Abdullah, 2013) reported that the particle size formed by TBOT precursor was smaller and more uniform compared to TTIP precursor. However, the crystalline phase was easier formed by TTIP compared to TBOT. The schematic diagram of sol-gel synthesis of Al₂O₃-TiO₂ using ATSB and TBOT is illustrated in Figure 2.1 (Hench & West, 1990) (Brinker & Scherer, 2013).



Figure 2.1: Sol-gel synthesis, techniques and products of Al₂O₃-TiO₂.

The formation of M(OH)₄ by complete hydrolysis is somehow hard to be realized. On the contrary, bridging for oxygen and a water or alcohol molecule may be formed through condensation of either two –OH or M–OH groups and an alkoxy group. Oxolation is known as the formation of M–O–M bonds with water as by-product through condensation between two hydroxylated metals. Moreover, alkoxolation is also the formation of M–O– M bonds just that the by-product is an alcohol and the condensation process takes place between a hydroxide and an alkoxide (Singh et al., 2014). In sol-gel process which is mainly based on co-hydrolysis of precursors like metal alkoxides, the homogeneous of the solution mixture is significant. The hydrolysis control is essential owing to the

adjustment of better homogeneous molecular oxide networks for efficient nanomaterial. The sol-gel method can be carried out in different parameters and this will affect the properties of final products as shown in Table 2.9. Al₂O₃-TiO₂ with different textural properties can be produced by altering the preparation conditions (Z. Zhou, Zeng, Cheng, & Yuan, 2010). High acidic properties of metal supported catalyst somehow is not always beneficial in deoxygenation process because the main disadvantages are the catalyst coking and tar formation that block the active centers, leading to catalyst deactivation and lower deoxygenation activity (Asikin-Mijan, Lee, Taufiq-Yap, et al., 2017). This problem can be minimized by tuning the acid sites availability in catalyst design and screening. In sol-gel processing, the mixture needs to stir vigorously for a long period of time (i.e. 6 h, 8 h, 24 h) in order to achieve homogeneous solution with greater crosslinking among substances (Betiha, Rabie, Elfadly, & Yehia, 2016). During the synthesis, surfactant can be added to shape the catalyst particles and improve the pore properties owing to the poreforming agent of the surfactant itself (Vichery & Nedelec, 2016). Surfactant acts as templates for synthesis of mesoporous materials (de Ávila, Silva, & Matos, 2016). Mahoney et al. (Mahoney & Koodali, 2014) reported that cationic surfactant cetyltrimethylammonium bromide (CTAB) was typically used in the synthesis of mesoporous nanocomposite compared to non-ionic surfactant Pluronic P123 and F127 owing to the critical micelle concentration of CTAB was more excellent than P123 and F127. In addition, CTAB is readily to be used at room temperature with relatively great dissolution in an aqueous phase (Huo et al., 1994). One of the advantages of using CTAB compared to non-ionic surfactants is that the latter has to deal with the cloud point issue and precise temperature control is needed to dissolve it. The non-ionic surfactant will precipitate out of the solution if the temperature is exceedingly higher than ambient condition (Wan & Zhao, 2007). The synthesis process of Al₂O₃-TiO₂ using surfactant requires the most reliable method to remove it. Soxhlet extraction using ethanol as solvent is one of the methods to remove the surfactant. However, de Ávila et al. found that soxhlet extraction is not effective for the complete removal of template from mesoporous materials (de Ávila et al., 2016). Similar finding was reported by Du et al. (Du, Khieu, & Hoa, 2013), they stated that weight loss of CTAB template after soxhlet extraction in ethanol for 36 h was almost same as the as-synthesized catalyst and this concluded that template removal was not effective. In contrast, the templates removal in the synthesis of Al₂O₃-TiO₂ is more effective and time saving through washing the samples with ethanol and distilled water, followed by calcination (Tang, 2014). Different calcination temperature will produce the final product with different phase combination as shown in Table 2.9. The nature of oxide precipitates derived from sol-gel method is amorphous and thus, air calcination is inescapable to transform the oxides from amorphous to phases for example anatase/rutile/brookite in titania (Adraider et al., 2013; N. Liu, Zhao, Wang, Peng, & Li, 2013), alpha/gamma in alumina (Lamouri et al., 2017) and etc. However, severe particle agglomeration, small surface area, grain growth as well as transformation to undesired phase are the main drawbacks through the calcination process (Z. Li et al., 2005). Thus, proper manipulation of process parameters is required to control the composition and morphology of the oxide products.

Based on Table 2.8, the less widely used methods include co-precipitation, mechanical mixing, impregnation, self-assembly, precipitation, ball-milling and chemical vapour deposition (CVD). As reported by Wang et al. (T. Wang et al., 2015), V₂O₅/Al₂O₃-TiO₂ prepared by sol-gel method provided the most superior catalytic performance compared to ball milling, mechanical mixing, precipitation and co-precipitation owing to the mixed support and active components interacted efficaciously. Therefore, sol-gel processing

using alkoxide precursors with controlled hydrolysis is a promising technique to produce Al₂O₃-TiO₂ with high homogeneity level. Calcination control is significant to produce sample with high surface area. Thus, sol-gel method will promote Al and Ti both disperse homogeneously and eventually produce mixed metal oxide upon calcination.

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Catalyst	Al-Ti	Metal (w/w)	Preparation	BET	Pore	Calcin	ation	Phase	Ref.
	(w ratio)		Method	(m²/g)	size (nm)	°C	h		
Al ₂ O ₃	-	-	Co-precipitation/incipient witness/CVD/	295	3.23	500	3	γ	(Vo et al., 2018)
Mo/Al ₂ O ₃	-	30% Mo	impregnation	281	3.29	500	3	γ	
Mo/Al-Ti	95Al-5Ti	30% Mo		211	3.89	500	3	Ä	
Mo/Al-Ti	90Al-10Ti	30% Mo		193	4.17	500	3	ă	
Mo/Al-Ti	80Al-20Ti	30% Mo		164	4.92	500	3	ă	
Mo/Al-Ti	70Al-30Ti	30% Mo		155	5.57	500	3	ă	
Mo/TiO ₂	-	30% Mo		132	6.39	500	3	MoO ₃	
TiO ₂	-	-		116	5.27	500	3	ă	
CoMoS/Al	-	3% Co, 10% Mo		249.3	3.95	550	4	γ	(Rodseanglung et al.,
CoMoS/Al-Ti	100Al-25Ti	3% Co, 10% Mo	Sol-gel/ impregnation	255.5	4.97	550	4	-	2015)
CoMoS/Al-Ti	100Al-50Ti	3% Co, 10% Mo		231.5	5.15	550	4	-	
CoMoS/Al-Ti	100Al-75Ti	3% Co, 10% Mo		181.5	5.00	550	4	-	
CoMoS/Al-Ti	100Al-100Ti	3% Co, 10% Mo		198.4	5.61	550	4	ă	
CoMoS/Ti	100Ti	3% Co, 10% Mo		67.14	10.62	550	4	ä	

Table 2.9: Sol-gel synthesis of Al₂O₃-TiO₂ under different parameters and resulting characteristics.

							· · · · · · · · · · · · · · · · · · ·		
Catalyst	Al-Ti (w.ratio)	Metal (w/w)	Preparation Method	$\frac{BET}{(m^2/g)}$	Pore size (nm)	Calcination	h	Phase	Ref.
	(* 1410)		Memou	(m /g)	Size (IIII)	C	п		
Al ₂ O ₃	-	-	-	233.3	13.1	500	6	γ	(A. Duan et al., 2009)
Al-Ti	95Al-5Ti	-	Self-assembly	270.1	11.5	500	6	γ	
Al-Ti	90Al-10Ti	-	Sol-gel	264.7	12.0	500	6	ă,γ	
Al-Ti	85Al-15Ti	-	-	262.1	11.9	500	6	ă, v	
Al-Ti	80Al-20iT	-	Impregnation	259.3	11.7	500	6	ă, v	
Al-Ti	70Al-30Ti	-	Precipitation/incipient witness	258.7	10.3	500	6	ă, γ	
TiO ₂	-	-	1 1	5.5	3.91	500	6	ă	
			-						
NiW/Al ₂ O ₃	-	3.5% Ni, 28% W		222.4	9.0	600	5	γ	
NiW/Al-Ti	95Al-5Ti	3.5% Ni, 28% W		218.8	9.5	600	5	γ	
NiW/Al-Ti	85Al-15Ti	3.5% Ni, 28% W		215.3	9.9	600	5	ă, γ	
NiW/Al-Ti	80Al-20Ti	3.5% Ni, 28% W		210.2	9.8	600	5	ă, γ	
NiW/Al-Ti	70Al-30Ti	3.5% Ni, 28% W		205.4	9.2	600	5	ă, γ	
Al ₂ O ₃	-	-	Self-assembly	-	-	500	6	γ	(Huang et al., 2008)
Al-Ti	95Al-5Ti	-	Sol-gel	-	-	500	6	γ	
Al-Ti	85Al-15Ti	-	Impregnation/incipient witness	-	-	500	6	ă, γ	
Al-Ti	80Al-20Ti	-	Impregnation,	-	-	500	6	ă, γ	
Al-Ti	70Al-30Ti	-	Co-precipitation,	-	-	500	6	ă, γ	
			sol-gel/incipient witness					•	
			-						
NiMo/Al ₂ O ₃	-	3.5% Ni, 15.5% Mo		252.3	8.82	500	4	γ	
NiMo/Al-Ti	95Al-5Ti	3.5% Ni, 15.5% Mo		248.7	9.69	500	4	γ	
NiMo/Al-Ti	85Al-15Ti	3.5% Ni. 15.5% Mo		223.9	10.2	500	4	ă. γ	
NiMo/Al-Ti	80Al-20Ti	3.5% Ni, 15.5% Mo		221.0	9.85	500	4	ă, y	
NiMo/Al-Ti	70Al-30Ti	3.5% Ni, 15.5% Mo		231.1	9.28	500	4	ă, γ	

'Table 2.9: continued'

'Table 2.9: continued'											
Catalyst	Al-Ti (w ratio)	Metal (w/w)	Preparation Method	BET (m²/g)	Pore size (nm)	Calcination °C	h	Phase	Ref.		
Al ₂ O ₃	-	-	Impregnation	217	9.5	550	3	γ	(Ramírez et al., 2005)		
Al-Ti	95Al-5Ti	-		215	6.5	550	3	γ			
NiMo/Al-Ti	95Al-5Ti	4.3% Ni, 10% Mo		179	6.0	500	4	γ			
TiO2	_	-	_	63.4		900	2	ă. R	(Ahmed & Abdel-		
Al-Ti	10Al-90Ti	-	Self-assembly	70.3	-	900	2	R	Messih. 2011)		
Al-Ti	20Al-80Ti	-	Sol-gel	77.3	_	900	2	ă. R			
Al-Ti	40Al-60Ti	-		94.6	-	900	2	ă. α. *			
Al-Ti	60Al-40Ti	-		100.2	-	900	2	ă, R,			
Al-Ti	80Al-20Ti	-		123.5	-	900	2	α, *			
Al-Ti	90Al-10Ti	-		130.4	-	900	2	ă, α, *			
								ă, α, *			
Al-Ti	10Al-90Ti	_	Self-assembly	259	-	600	1	Ä	(Sedneva, Lokshin,		
Al-Ti	10Al-90Ti	_	Sol-gel	103	-	700	1	ă	Belikov, & Knyazeva		
Al-Ti	10Al-90Ti	-		8.4	-	900	1	R.a	2013)		
Al-Ti	20Al-80Ti	-		205	-	600	1	Ä	/		
Al-Ti	20Al-80Ti	-		131	-	700	1	ă			
Al-Ti	20Al-80Ti	-		13.4	-	900	1	ă, R, α			
Al-Ti	30Al-70Ti	-		276	-	600	1	Ä			
Al-Ti	30Al-70Ti	-		223	-	700	1	ă			
Al-Ti	30Al-70Ti	-		39.8	-	900	1	ă, R, α			
Al-Ti	40Al-60Ti	-		299	-	600	1	Ä			
Al-Ti	40Al-60Ti	-		147	-	800	1	ă			
Δ1_Ti	40Al-60Ti	-		35.2	-	900	1	ă, R, α			

'Table	2.9:	continued'
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2.4 Physicochemical properties

2.4.1 Al₂O₃-TiO₂

As depicted by previous literatures, the physicochemical properties of Al₂O₃-TiO₂ and metal or metal-oxide supported on Al₂O₃-TiO₂ were characterized by various techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), temperature programmed desorption/reduction (TPD/TPR), N₂ adsorption–desorption isotherms, transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Raman spectroscopy (RS) and etc (A. Duan et al., 2009; Adel A. Ismail et al., 2015; Ma et al., 2017; Polat et al., 2015; Rodseanglung et al., 2015; Song et al., 2016; Tao, Li, Huang, Wang, & Ye, 2016; Tavizón-Pozos et al., 2016; Vo et al., 2018; L. Wang et al., 2018; T. Wang et al., 2015; C. Yang et al., 2016). As mentioned earlier, Al₂O₃-TiO₂ are usually prepared through calcination of Al(OH)₄-Ti(OH)₄ hydroxide gels prepared from respective alkoxide precursors via sol-gel synthesis. The phases formed by different calcination temperature are able to be analysed through X-ray powder diffraction as in samples calcined at low temperature will show X-ray amorphous state. On the other hand, the samples calcined at high temperature (for example 900 °C) will show protruding line, indicating that the rutile phase in TiO₂ is mostly displayed. The rutile phase can be hindered by incorporating suitable amount of Al_2O_3 phase (Z. Zhou et al., 2010). One explanation for this effect was given by Ahmed et al. (Ahmed & Abdel-Messih, 2011), who studied the structure and nature of phases of Al₂O₃-TiO₂. From the X-ray diffraction study of Al₂O₃-TiO₂ samples having dissimilar composition and calcined at 900 °C, they reported that Al₂O₃-TiO₂ possessed rutile phase at 10–20% alumina content whereas anatase phase was prominent at 40%–90% alumina content. The crystallinity of the tialite (Al_2TiO_5) compound was identified in the sample with 40%–90% high alumina content.

In addition, Sedneva et al. (Sedneva et al., 2013) reported that Al_2O_3 -TiO₂ possessed anatase phase prepared at 10–40% alumina content and calcination temperature 700 °C. On the other hand, 10% alumina loading showed rutile phase only when calcined at 900 °C but 20–40% alumina loading displayed anatase and rutile phase. Moreover, Mohammadi (Mohammadi, 2014), who employed the sol-gel method to synthesize Al_2O_3 -TiO₂, reported that the poor crystalline structure (anatase-TiO₂) was displayed by samples calcined at 600 °C whereas good crystalline structures (anatase-TiO₂, rutile-TiO₂ phases) were shown by samples calcined at 800 °C. This result demonstrated that the anatase-TiO₂ phase was stable up to calcination temperature of 800 °C. Therefore, it proved that the proper addition of Al_2O_3 hindered the transformation from anatase to rutile in TiO₂ because the rutile phase was obtained at calcination temperature of 400 °C in TiO₂.

In comparison to the single oxide, Al_2O_3 -TiO₂ exhibits larger specific surface area than that of TiO₂. The mutual interaction between Al_2O_3 and TiO₂ inhibit their individual crystallization when both of them are precipitated. By mixing, the alumina lattice parameters will be modified owing to the larger Ti⁴⁺ ions being partially integrated into Al_2O_3 octahedral sites (Gómez et al., 2016). As reported before by Ismail et al. (Adel A. Ismail et al., 2015), they found that the addition of Al_2O_3 (0–5%) resulted the surface area of TiO₂ increased from 174 m²g⁻¹ to 325 m²g⁻¹. For Al_2O_3 -TiO₂, the surface area will be decreased with increasing TiO₂ content (Rodseanglung et al., 2015). According to Duan et al. (A. Duan et al., 2009), they reported that the specific surface area of Al_2O_3 -TiO₂ decreased from 270.1 m²g⁻¹ to 258.7 m²g⁻¹ with increasing TiO₂ content from 5% to 30%. In fact, TiO₂ was normally a material with a lower pore volume and surface area. Moreover, Al_2O_3 -TiO₂ is a mesoporous material and exhibits advantage over its nano-
sized pore diameter, which is predominantly owing to its morphological characteristics. Hence, it is important to tune the morphological properties of Al₂O₃-TiO₂ such as porosity and size in order to achieve efficacious result for their applications. The surface morphology of Al₂O₃-TiO₂ has obvious difference as compared to that of TiO₂. The crystallite size of TiO_2 is bigger than Al_2O_3 -TiO₂, demonstrating that the crystallite growth of TiO₂ is inhibited by the initiation of intermediate layers. Wetchakun et al. (Wetchakun, Incessungvorn, Wetchakun, & Phanichphant, 2012) prepared TiO₂ calcined at 400 °C and the crystallite size obtained was 9.00 nm for anatase and 11.90 nm for rutile phase. They also synthesized TiO₂ calcined at 500 °C and the result showed 12.79 nm and 25.57 nm for anatase and rutile phase respectively. In contrast, Ismail et al. (Adel A. Ismail et al., 2015) reported that Al₂O₃-TiO₂ prepared at Al₂O₃ contents (0.5 and 2 wt.%) and calcination temperature 450 °C showed TiO₂ particles were formed in mesoporous structure with quite stable size $(10 \pm 2 \text{ nm})$. Thus, the oxides with smaller crystallite size are more easily to be acquired. Moreover, the performance of catalyst is significantly affected by the acid-base properties. The acid-base properties of binary metal oxides were first observed by Tanabe et al. in 1970, they defined the theoretical concept of acidity generation in various binary oxides, which was not exist in single oxides. Moreover, Tanabe el al. reported that the binary oxides exhibited an excellent correlation between the average electronegativity of metal ions and the highest acid strength (Tanabe, 1970). Thus, the surface acidity of properly mixed Al₂O₃-TiO₂ is greater than that of the single Al_2O_3 or TiO₂. The acid-base of Al_2O_3 -TiO₂ was extensively characterized by using temperature-programmed desorption of ammonia (NH3-TPD) and temperatureprogrammed desorption of carbon dioxide (CO₂-TPD). According to Vo et al., the surface acidic properties of Mo/Al₂O₃, Mo/ TiO₂ and Mo/Al₂O₃-TiO₂ were examined by NH₃-TPD. They reported that the calcined Mo/TiO₂ catalyst showed lower amount of weak

acid sites than Mo/Al₂O₃. The incorporation of TiO₂ into Al₂O₃ support increased the strong acid sites of catalyst. The acid density of Mo/(80Al-20Ti) catalyst resulted the highest value of 4.52 μ mol·m⁻² and it was higher compared to the Mo/(70Al-30Ti) (3.17 μ mol·m⁻²), Mo/Al₂O₃ (2.71 μ mol·m⁻²) and Mo/TiO₂ (2.89 μ mol·m⁻²) catalyst (Vo et al., 2018). Therefore, the catalytic reactions are significantly affected by the acidity of catalyst (Seo, Jung, Lee, & Yoo, 2008). There is limited study on mesoporous Al₂O₃-TiO₂ for deoxygenation and thus, the application of mesoporous Al₂O₃-TiO₂ in deoxygenation can be further explored.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

Aluminium-tri-*sec*-butoxide (ATSB) with purity > 97%, titanium (IV) butoxide TBOT with purity > 97% and hexadecyl-trimethylammonium bromide (CTAB) surfactant were obtained from Sigma-Aldrich. The chemical solvents such as absolute ethanol (EtOH) with purity 99.90% and hexane with purity 98% were obtained from Merck. Distilled water was used in this study. Hydrochloric acid (HCl) with purity 37% was obtained from Merck. The triglyceride model compound triolein with purity 65% was obtained from Sigma-Aldrich and used for deoxygenation reaction without further purification and treatment. Analytical grade n-hexane with purity > 98% for GC solvent dilution was bought from Merck.

3.2 Catalyst synthesis

In this study, mesoporous Al_2O_3 -TiO₂ mixed oxide catalysts were synthesized by solgel method. The molar ratio of Al_2O_3 -TiO₂ synthesis was 0.0856EtOH: xTBOT: (1-x) ATSB where x = 0.1, 0.2, 0.3. The mixture was sonicated for 30 min to agitate the particles. Hexadecyl-trimethylammonium bromide (CTAB) was used as a structure directing agent. The molar ratio of surfactant mixture was 0.0011CTAB: 1.9444H₂O: 0.1713EtOH. The pH of the surfactant mixture was adjusted to 1 by 0.5 M HCl. The Al₂O₃-TiO₂ solution was added slowly to the vigorously stirred surfactant mixture. The mixture was stirred for 6 h and then washed several times with distilled water and absolute ethanol until the pH solution 7 was obtained. The samples were dried overnight at 100 °C. After that, the samples were calcined in air at 500 °C for 5 h with the ramping rate of 1 °C/min to remove the CTAB template. For comparison, mesoporous Al₂O₃ and TiO₂ catalysts were also synthesized using the same procedure mentioned above except no TBOT and ATSB was added for Al₂O₃ and TiO₂ preparation, respectively. Figure 3.1 shows the synthesis method.



Figure 3.1: Diagram for catalyst synthesis method.

3.3 Characterizations

3.3.1 Brunauer-Emmett-Teller surface area and porosity analysis (BET)

BET measures specific surface area, pore volume and pore size distribution. The working principle is the solid surface is physically undergo adsorption of a gas, typically from nitrogen sorption isotherm at liquid nitrogen temperature. Then, total amount of nitrogen that has been adsorbed is calculated correlative to the surface monomolecular layer. Adsorption isotherms are determined through the interaction of physicochemical conditions (Sing, 2001). Type II BET isotherm refers to the macroporous solids, it has multilayer adsorption after the monolayer adsorption, resulting in reversible and unrestricted multilayer isotherm. On the other hand, type IV is mainly referring to the mesoporous adsorbent, it has pore filling is performed after the coverage of monolayer surface. The adsorption stops after the pores are fully filled (Naderi, 2015).

The textural properties of the synthesized catalysts (i.e. specific surface area, pore volume and pore size distribution) were determined using N₂ porosity analyser (Tristar II

series; micromeritics) at 77 K. Prior the analysis, the catalysts were degassed at 300 °C for 6 h. The specific surface area was calculated from the adsorption branch of the isotherm in the relative pressure (P/P_0) range of 0.05-0.2. The average pore size was obtained using the Barrett-Joyner-Halender (BJH) method.

3.3.2 Temperature-programmed desorption of ammonia (NH₃-TPD)

The temperature-programmed desorption of ammonia (NH₃-TPD) is broadly utilized to reveal acidity information of a catalyst. The quantity of acid sites of a catalyst is estimated by ammonia through penetration into all pores of the catalyst. The small molecular size of ammonia allows it to access to microporous and mesoporous materials. The ammonia is able to titrate the acid sites of the catalyst, revealing the acidity information (Lin Chen, Janssens, Skoglundh, & Grönbeck, 2019).

Temperature-programmed desorption of ammonia (NH₃-TPD) was performed to investigate the acidity of the catalysts using Thermo-Finnigan TPD/R/O 1100 instrument equipped with thermal conductivity detector (TCD). The adsorbed moisture from the catalyst pores was released by pretreating the catalysts under N₂ gas flow for 30 min at 250 °C. Then, the NH₃ adsorption onto the surface of catalysts were performed by exposing to NH₃ gas for an hour. The excess NH₃ was subsequently removed with N₂ gas flow at the rate of 20 mL/ min for 30 min before the analysis.

3.3.3 Fourier transform infrared spectroscopy (FTIR) and pyridine FTIR

The working principle of FTIR is to use an infrared absorption spectrum to study the molecule chemical bonds. The sample molecules absorb wavelength of light within infrared region, exciting the molecules into a higher vibrational state. Then, the sample profile is produced by the spectra, providing absorbed wavelength for screening of

different bonds present in the molecule (Ashraf A. Ismail, van de Voort, & Sedman, 1997). The FTIR absorption spectra were obtained with a Bruker Vertex 80/80v spectrometer in the range of 4000-400 cm⁻¹ using the KBr pellet method.

The pyridine FTIR spectroscopy is a standard characterization method to identify Lewis and Bronsted of solid acids. Lewis acid accepts electron-pair whereas Bronsted acid donates hydrogen ion during chemical reaction. Pyridine interacts with the acid site of the catalyst, generating two main signal series which are 1455 cm⁻¹ (corresponding to Lewis acid sites) and 1545 cm⁻¹ (corresponding to Bronsted sites) (Damyanova, Centeno, Petrov, & Grange, 2001). The pyridine FTIR spectra were analysed using a Nicolet 2000 FT-IR spectrometer. The samples were pressed to a wafer form before placing into the IR cell. Next, the samples were degassed at 400 °C under vacuum (10⁻³ mbar) for 5 h. After cooling, pyridine was applied to the samples for 1 min. The weakly bound pyridine molecules were removed after evacuation (30min, 200 °C) and the spectra were recorded. Thermal conductivity detector (TCD) detected the ammonia desorption from the acid sites of the catalyst under helium gas flow (30 mL/min) from 50 °C to 900 °C with ramping of 10 °C/min and held for 30 min.

3.3.4 Field emission scanning electron microscopy with energy dispersive mapping analysis (FESEM-EDX)

The electron microscope produced high magnification, in-depth focus and great resolution for better observation. The working principle is the electron gun generates electrons that enter the surface of a sample, thereafter many low energy secondary electrons are generated. The surface topography decides the intensity of the secondary electrons, whereby, the image is constructed by measuring that intensity as a function of scanning primary electron beam position. The morphological change and element composition of the catalyst are revealed by Energy Dispersive X-ray (EDX) as well. The samples emit X-ray characteristics which reveal elemental information of the samples (Restivo, Degano, Ribechini, Pérez-Arantegui, & Colombini, 2014).

The morphology characteristics of the catalysts were determined by field emission scanning electron microscopy (FESEM) with energy dispersive mapping (EDX) using power 30 kV after the samples were coated with gold. The dissemination of mixed catalyst was identified using elemental mapping analysis.

3.3.5 X-ray diffraction analysis (XRD)

The X-ray diffraction (XRD) is an analytical technique to determine the phase identification of a crystalline material by constructive interference of monochromatic X-ray. The cathode ray tube emits X-ray, thereafter filtered to generate monochromatic radiation, concentrate and then directed to the sample. The X-ray scattering from atoms generates diffraction peaks. The peak intensities reveal the periodic atomic arrangement within the crystal of a given material (Kohli, 2012).

The catalyst crystallographic structures were determined by powder X-ray diffraction (XRD). The XRD patterns of catalysts was obtained on X-ray Bruker D8 advance diffractometer equipped with a Cu K α radiation source ($\lambda = 0.1542$ nm) at 40 kV in the two theta (2 θ) range of 20° to 80° with the step size of 0.04° and step time of 1 s. X'pert high score plus software was used to interpret the XRD data.

3.3.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a method to determine the changes in physical or chemical properties of a material. It is measured as function of constant heating rate by increasing temperature. The weight loss of a volatile components that happens provides measurement of thermal stability, moisture, solvent filler content, as well as the percentage of composition in a compound (Groenewoud, 2001).

The thermogravimetric analysis (TGA) with simultaneous thermal analyzer (TGA, Mettler Toledo 990) was used to study the coking tendency of the fresh catalyst and the carbon deposition on the reused catalyst. The samples were heated from 30 °C to 800 °C at the heating rate of 10 °C/min under 20 mL/min of air flow.

3.4 Deoxygenation of triolein

The deoxygenation of triolein was carried out in a 100 mL stirring reactor as shown in Figure 3.2. The chosen model compound for triglyceride was triolein because it is made of three oleic acids and its structure is similar to plant oil (Zulkepli et al., 2018). In a typical experiment, about 10 g triolein and 5 wt.% catalyst were loaded to the reactor. The reactor was linked in a vacuum line to evacuate the air in the system before the deoxygenation reaction takes place. The deoxygenation reaction was performed under temperature 380 °C, time 1 h and stirred at 400 rpm under partial vacuum (10 mbar) condition. The assumption of the test rig is the reactor line is always maintained at partial vacuum condition and the water inlet temperature is always same as room temperature as it is supplied by water pipe at laboratory. The boundary is that pressure built up in vacuum line was adjusted during the reaction by releasing the generated gas in order to maintain the partial vacuum condition. The liquid fuel was collected in the bulb flask by condensing the vapour released from the cracking reaction in the condenser pathway. Afterwards, the reactor was cooled to room temperature and the collected liquid fuel was further analysed by GC-MS. The experiment was repeated three times to obtain the average value, the significant lines were plotted at graph. For reusability study, the catalyst reactivation process was carried out by simply washing with hexane for several

times to remove the adsorbed organics after each deoxygenation experiment. The catalyst was then reused for next experiment under same reaction conditions.



Figure 3.2: Diagram for deoxygenation reactor.

3.5 **Product analysis**

The liquid hydrocarbon products were collected and further analysed qualitatively by gas chromatography–mass spectroscopy (GCMS; Shimadzu GC 2010 Plus) equipped with RTX 5 MS capillary column (length 30.0 m x film thickness 0.25 μ m x inner diameter 0.25 mm). Prior to the analysis, GC grade *n*-hexane was used to dilute the liquid products to 600 ppm. An aliquot of 1 μ L sample was inserted into the GCMS column. The helium flow rate was 35.7 mL/min with 36.9 kPa. The oven temperature was raised

from 40 to 300 °C at a ramping of 5 °C/min and held for 30 min. Based on the GCMS analysis, the alkane and alkene hydrocarbons ($C_8 - C_{20}$) are the main composition in the liquid products. The generated hydrocarbon fraction peaks from GC-MS spectrum was identified via standard mass spectra from the National Institute of Standards and Testing's (NIST) library. The peak area from the GC chromatogram is proportional to the relative percentage of the product (Alsultan, Asikin-Mijan, Lee, Albazzaz, & Taufiq-Yap, 2017; Asikin-Mijan, Lee, Taufiq-Yap, et al., 2017; Zulkepli et al., 2018). Hence, the conversion of triolein, product selectivity and removal of oxygen content were defined as follows:

$$Conversion = \underline{initial \ mass \ of \ triolein \ - \ final \ mass \ of \ triolein \ after \ reaction} \ x \ 100\%$$
(3.1)
initial mass of triolein

Product selectivity =
$$\underline{\text{area of desired organic compound}} \times 100\%$$
 (3.2)
area of all products

Hydrocarbon selectivity = $\underline{\text{area of selected hydrocarbon fraction}} \times 100\%$ (3.3) area of hydrocarbons (C₈-C₂₀)

Removal of oxygen content (%) = $\underline{\text{initial oxygen content}} - \underline{\text{final oxygen content}} \times 100\%$ (3.4) initial oxygen content

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Physicochemical characteristics of catalyst

4.1.1 Brunauer-Emmett-Teller (BET) analysis

The N₂ adsorption-desorption isotherms and pore size distributions of γ -Al₂O₃, TiO₂ and Al₂O₃-TiO₂ catalysts are shown in Figure 4.1 (a) and (b), respectively. All the catalysts showed the presence of a standard type of isotherm IV with H1 hysteresis loops and exhibited mesopore size distribution between 2 nm and 40 nm. This proved that the mesoporous nature of the synthesized catalysts. Indeed, the formation of mesoporous structure will overcome the diffusion limitation of large triolein molecule. Table 4.1 listed the specific surface areas and average pore sizes for all catalysts. The surface areas of mesoporous Al₂O₃ and mesoporous TiO₂ were 352.01 m²/g and 7.83 m²/g, respectively. Interestingly, the mesoporous 0.2Ti-0.8Al catalyst had the largest surface area of 398.60 m^2/g , followed by 384.76 m^2/g for 0.1Ti-0.9Al, providing more active centres compared to Al₂O₃. However, a progressive decrease of surface area to $305.55 \text{ m}^2/\text{g}$ was observed for the 0.3Ti-0.7Al catalyst, then down to the lowest value surface area of 7.83 m^2/g for TiO_2 . When the Al₂O₃- TiO_2 catalysts contain low Ti contents (i.e. 10 wt.% and 20 wt.%), the specific surface area increased (Stakheev et al., 2002) because the TiO₂ were attached to surface of Al₂O₃. The crystalline phase of the TiO₂ began to form by increasing the TiO₂ content in the Al₂O₃-TiO₂ catalyst up to 30 wt.%. The high TiO₂ content reduced the network connectivity, leading to decrease in surface area and smaller pore size. This is concordance with the XRD result that showed the peak characteristic of the anatase phase TiO₂ is prominent for 0.3Ti-0.7Al. The tendency of the relatively low TiO₂ content in Al₂O₃-TiO₂ catalyst to increase the surface area is in a good agreement with the results

reported by Linacero et al. (Linacero, Rojas-Cervantes, & Lopez-Gonzalez, 2000) and Stakheev et al. (Stakheev et al., 2002).



Figure 4.1: Textural properties of Al₂O₃, 0.1Ti-0.9Al, 0.2Ti-0.8Al, 0.3Ti-0.7Al and TiO₂ catalysts: (a) N₂ adsorption and desorption isotherms and (b) pore size distributions.

Catalyst	^a Specific surface area (m ² /g)	^b Pore volume (cm ³ /g)	^c Average pore diameter (nm)	^d Total acid site (μmol/g)
Al_2O_3	352.01	1.64	12.83	1644.65
0.1Ti-0.9Al	384.76	1.53	11.53	1875.35
0.2Ti-0.8Al	398.60	1.26	9.06	2734.63
0.3Ti-0.7Al	305.55	0.76	7.47	1873.68
TiO ₂	7.83	0.02	13.12	439.06

Table 4.1: Textural and acidic properties of Al₂O₃, 0.1Ti-0.9Al, 0.2Ti-0.8Al,0.3Ti-0.7Al and TiO₂ catalysts.

^a Specific surface area was determined by BET analysis.

^{b,c} Pore volume and average pore size were determined by BJH desorption method.

^d Total acid site was determined by TPD-NH₃ analysis.

4.1.2 Temperature-programmed desorption of ammonia (NH₃-TPD) and fourier transform infrared spectroscopy - pyridine (FTIR-Py)

The acidity profile of all synthesized catalysts were determined by using temperature programmed desorption of NH₃. Figure 4.2 shows the NH₃-TPD pattern of mesoporous Al₂O₃, TiO₂ and Al₂O₃-TiO₂ with different TiO₂ content. Table 4.1 summarized the total acid sites of each catalyst. It is known that the acidity is essential to promote the cleavage of C-O bonds during deoxygenation reaction (Asikin-Mijan, Lee, Abdulkareem-Alsultan, Afandi, & Taufiq-Yap, 2017). Two acidic sites of catalyst are present depending on the desorption temperature which are weak-medium sites (T < 500°C) and strong acid sites (T > 500°C) (Widayatno et al., 2016). The cracking process via decarboxylation reaction is facilitated by the weak-medium acidic sites of catalyst (T < 500°C) (Asikin-Mijan, Lee, Taufiq-Yap, et al., 2017). From the NH₃-TPD profile, all synthesized catalysts exhibited weak-medium acidic site. The results showed that Al₂O₃-TiO₂ catalysts rendered higher amount of total acid site than the Al₂O₃ or TiO₂ catalysts. Surprisingly, the 0.2Ti-0.8AI rendered the largest weak-medium acidic site with total acidity (2734.63 μ mol/g) compared to 0.1Ti-0.9AI and 0.3Ti-0.7AI catalysts. The introduction of TiO₂ into Al₂O₃

enhanced the acidic content is due to the distribution of an excess positive or negative charge induced by the bridged hetero metal-oxygen bonds formation, as suggested by Tanabe's model (Tanabe, 1970, 2012). The enhanced acidic content in Al₂O₃-TiO₂ system also can be due to the possible formation of Ti-O-Al bonds which have been proposed in many literatures (Khaleel, 2011; Linacero et al., 2000). In addition, pyridine FT-IR spectroscopy is used to study the type of acid sites of prepared catalysts. The band at 1455 cm⁻¹ is assigned to the pyridine interacting with Lewis acid sites. The band at 1490 cm⁻¹ indicated the total acidity of the catalyst. Based on Figure 4.3, the acid sites of as-prepared catalysts mainly assigned to Lewis acid which has high intensity. The increased intensity of the Lewis acid site and total acidity present in the 0.2Ti-0.8Al catalyst is due to the larger surface area. The reaction through initial binding of the oxygenated substrates and cleavage of the C-O bonding can be facilitated by the Lewis acid sites (H. Duan et al., 2017). Hence, the 0.2Ti-0.8Al catalyst is capable to promote deoxygenation via decarboxylation reaction, indicating that the introduction of proper amount of TiO₂ into Al₂O₃ increased the acidic properties of catalysts. This is also observed by others (M. Yang, Men, Li, & Chen, 2012), in which the acid site enhanced by the introduction of TiO_2 to Al_2O_3 .



Figure 4.2: NH₃-TPD profiles of (a) Al_2O_3 , (b) 0.1Ti-0.9Al, (c) 0.2Ti-0.8Al, (d) 0.3Ti-0.7Al and (e) TiO₂ catalysts.



Figure 4.3: Pyridine FT-IR spectra of (a) Al_2O_3 , (b) 0.1Ti-0.9Al, (c) 0.2Ti-0.8Al, (d) 0.3Ti-0.7Al and (e) TiO₂ catalysts.

4.1.3 Field emission scanning electron microscopy with energy dispersive mapping analysis (FESEM-EDX)

Figure 4.4 shows a series of mesoporous Al_2O_3 -TiO₂ morphology. It was observed that the Al_2O_3 catalyst possessed irregular interconnected mesoporous framework with discontinuity structure. It should be noticed that the formation of mesoporous structures was attributed to the use of CTAB surfactant. The mesoporous structure can facilitate the introduction of TiO₂ into Al_2O_3 . On the other hand, the 0.1Ti-0.9Al and 0.2Ti-0.8Al catalysts show that the small irregular clusters of TiO₂ were attached to surface of Al_2O_3 , which still keeps the Al_2O_3 surface structure. However, 0.3Ti-0.8Al revealed an obvious agglomeration of TiO_2 on the surface of the Al_2O_3 due to high loading of 30 wt.% Ti, resulting in decrease of surface area.

Moreover, the dissemination of Al and Ti inside the Al₂O₃, TiO₂ and Al₂O₃-TiO₂ catalysts were analysed by using elemental dot mapping (EDX) as shown in Figure 4.5. It was clearly demonstrated that the presence of TiO₂ were well-dispersed over the γ -Al₂O₃ phase. Furthermore, the actual loading of Ti:Al in 0.1Ti-0.9Al, 0.2Ti-0.8Al and 0.3Ti-0.7Al calculated from EDX analysis were 9.76:90.24, 19.05:80.95 and 32.59:67.32 wt.% respectively which are comparable to intended theoretical ratio of 10:90, 20:80 and 30:70 wt.% respectively.



Figure 4.4: FESEM (60 kx) of (a) Al₂O₃, (b) 0.1Ti-0.9Al, (c) 0.2Ti-0.8Al, (d) 0.3Ti-0.7Al and (e) TiO₂ catalysts.



Figure 4.5: Elemental mapping (15 kx) of (a) Al₂O₃, (b) 0.1Ti-0.9Al, (c) 0.2Ti-0.8Al, (d) 0.3Ti-0.7Al and (e) TiO₂ catalysts.

4.1.4 X-ray diffraction analysis (XRD)

Figure 4.6 shows the XRD patterns of Al₂O₃, TiO₂ and Al₂O₃-TiO₂ catalysts. The Al₂O₃ catalyst shows several peaks at 36.7°, 45.9° and 67.0° which belong to γ - Al₂O₃ (M. Yang et al., 2012). Meanwhile, the TiO₂ has reflection peaks at 25.3°, 37.7°, 48.0°, 53.8° , 62.6° and 74.9° which are attributed to the anatase phase (Vo et al., 2018). For Al₂O₃-TiO₂ catalysts, they have stable crystalline anatase phase without the presence of rutile phase. The mixed 0.1Ti-0.9Al catalyst containing 10 wt.% TiO₂ and 90 wt.% Al₂O₃ showed no trace of TiO₂ diffraction characteristic peaks, indicating that low TiO₂ content was well mixed with Al₂O₃ (Yanmin, Xingquan, Chunxiang, & Tiansheng, 2010). However, the anatase TiO₂ peak intensity at 25.3° increased with TiO₂ content which signified at 20 wt.% and 30 wt.% of TiO₂. This proved that the TiO₂ are mixed with Al₂O₃ to form Al₂O₃-TiO₂ mixed oxide. The protrusion of TiO₂ anatase phase in Al₂O₃-TiO₂ catalysts suggested that the sol-gel synthesis method stabilized the anatase even it was calcined at 500 °C, which is well agreed with other literature (Ahmed & Abdel-Messih, 2011). Interestingly, 0.3Ti-0.7Al did not show any diffraction peak of γ - Al₂O₃ at 36.7°, 45.9° and 67.0° which obviously demonstrate that the accumulation of TiO₂ (Huang et al., 2008).



Figure 4.6: XRD patterns for (a) Al_2O_3 , (b) 0.1Ti-0.9Al, (c) 0.2Ti-0.8Al, (d) 0.3Ti-0.7Al and (e) TiO₂ catalysts.

4.1.5 Fourier transform infrared spectroscopy analysis (FTIR)

Figure 4.7 shows the FT-IR spectra of mesoporous Al₂O₃-TiO₂ catalysts with different ratio of Al₂O₃ and TiO₂. The bands centered around 3494 cm⁻¹ and 1637 cm⁻¹ resulted from the -OH stretching and bending mode, respectively, of the surface adsorbed water that maintained in the matrix (Ghampson, Pecchi, Fierro, Videla, & Escalona, 2017). For Al₂O₃ as shown at Figure 4.7 (a), the characteristic vibration of the γ -Al₂O₃ lattice structure was observed at 1390 cm⁻¹ (C. Zhang, Liu, Chen, & Dong, 2012). The band region in the range of 400-1000 cm⁻¹ was assigned to the stretching vibration of Al-O-Al bond (Doss & Zallen, 1993). The stretching vibration band of AlO₆ octahedra was indicated at the band region of 500-600 cm⁻¹ while the stretching vibration band of AlO₄ tetrahedra was observed at the band region of 680-900 cm⁻¹ (K. Wang et al., 2009). For TiO₂ as shown at Figure 4.7 (e), the low band region of 400-1000 cm⁻¹ was the Ti-O-Ti bond of a TiO₂ network (Majeed et al., 2015). For mixed Al₂O₃-TiO₂ as shown at Figure 4.7 (b-d), it demonstrated that the peak intensity of AlO₆ octahedra (500-600 cm⁻¹) and AlO₄ tetrahedra (680-900 cm⁻¹) slowly disappeared as the TiO₂ content increases. The stretching vibration of AlO₆ octahedra at 500-600 cm⁻¹ was covered by the Ti-O stretching vibration at 400-600 cm⁻¹, leading to the outer surface γ -Al₂O₃ was wrapped by the TiO₂. There is no obvious peak at 1390 cm⁻¹ in 0.1Ti-0.9Al and 0.2Ti-0.8Al because the low content of TiO₂ can increase the dispersion of the metal oxide in Al₂O₃-TiO₂ (Tavizón-Pozos et al., 2016). In the case of 0.3Ti-0.7Al, the spectrum shows 1390 cm⁻¹ peak of γ -Al₂O₃, suggesting that 30 wt% TiO₂ loading could be beyond the saturated coverage of Al₂O₃-TiO₂ catalyst.



Figure 4.7: FT-IR spectra of (a) Al_2O_3 , (b) 0.1Ti-0.9Al, (c) 0.2Ti-0.8Al, (d) 0.3Ti-0.7Al and (e) TiO₂ catalysts.

4.2 Catalytic deoxygenation activity

The deoxygenation reaction is to cleave the C-O bonding in triolein. Oxygen atom in the triolein undergo cleavage to form hydrocarbon (C_8 - C_{20}) and oxygenated by-products such as carboxylic acid (-COOH), alcohol (-OH) and ketone (RC(=O)R'). Figure 4.8 shows the cleavage of C-O bonding in triolein.



Figure 4.8: Cleavage of C-O bonding in triolein

The deoxygenation reaction of triolein over the synthesized mesoporous Al₂O₃, 0.1Ti-0.9Al, 0.2Ti-0.8Al, 0.3Ti-0.7Al and TiO₂ catalysts was determined. The conversion, removal of oxygen content, product distribution and straight chain hydrocarbon selectivity was summarized in Figure 4.9. According to the GCMS analysis, the range of hydrocarbon distribution for deoxygenated liquid products were comprised of saturated and unsaturated C₈-C₂₀. As shown in Figure 4.9, the triolein conversion over mesoporous Al₂O₃-TiO₂ catalysts was higher than that of Al₂O₃ or TiO₂ catalysts. The conversion and hydrocarbon distribution C₈-C₂₀ of blank test were 40.12% and 38.91% respectively. This result indicated that the catalytic deoxygenation over synthesized catalysts were more reactive in the order of 0.2Ti-0.8Al > 0.1Ti-0.9Al > 0.3Ti-0.7Al > Al₂O₃ > TiO₂ > blank. As expected that 0.2Ti-0.8Al catalyst gave the highest conversion, hydrocarbon distribution of C_{8} - C_{20} and removal of oxygen content up to 53.96%, 66.75% and 91.51% respectively. This can be assigned to the introduction of TiO₂ into Al₂O₃ that enhanced the surface area and acidity. Unfortunately, the 0.3Ti-0.7Al showed lower conversion (51.00%), hydrocarbon distribution (63.77%) and removal of oxygen content (88.93%), indicating that the deoxygenation reaction of triolein was influenced by the amount of acidity.

Theoretically, the triolein mainly possesses C₁₆ and C₁₈ fatty acid derivatives and they tend to convert into $n-C_{15} + n-C_{17}$ hydrocarbon fraction via decarboxylation pathway. Figure 4.9 (c) shows the straight-chain saturated and unsaturated C₈-C₂₀ hydrocarbon selectivity. Based on the GCMS results, it showed that the selectivity of $n-C_{15} + n-C_{17}$ decreases followed the sequence: 0.2Ti-0.8Al (14.51%) > 0.3Ti-0.7Al (11.71%) > 0.1Ti- $0.9A1(10.60\%) > Al_2O_3(9.59\%) > TiO_2(4.50\%)$. The 0.2Ti-0.8Al catalyst has the lowest alcohol intermediates because the TiO₂ has increased the hydrocarbon selectivity through dehydration process of alcohol (Oi et al., 2016). As refer to Figure 4.2, the acid sites of the binary Al₂O₃-TiO₂ catalyst increased with the addition of TiO₂, and thus exhibited higher deoxygenation performance. The better $n-C_{15} + n-C_{17}$ selectivity in 0.2Ti-0.8Al catalyst was due to the highest acidic site (2734.63 µmol/g) that facilitated the cleavage of C–O bonds via decarboxylation reaction. The decarboxylation pathway was suggested to be the main pathway based on the fact that the $C_{17}H_{34}$ from triolein is formed through scission of C–O bond in oleic acid by the removal of oxygenated compound in the form of CO₂. This mechanism pathway was well studied that cleavage of C–O bonds in forming $C_{17}H_{34}$ from triolein proceed with decarboxylation in the absence of hydrogen (Choo et al., 2019). Furthermore, the excellent performance of the 0.2Ti-0.8Al was also due to the large surface area (398.60 m^2/g). The large surface area enables the large triolein molecule to access easily to the acid sites. Moreover, the mesoporous structure and large surface area provide fast diffusion to triolein that enhanced the catalytic performance.

Although the efficiency of decarboxylation reaction using 0.2Ti-0.8Al catalyst is higher, it still undergoes some minor side reactions such as cyclization and polymerization reactions. It can be seen from the minor formation of heavy hydrocarbon fractions (1.11%) and cyclic compounds (15.73%) in the liquid product. This unfavourable reactions could be assigned to the strong acidity in 0.2Ti-0.8Al catalyst. Moreover, small amount of oxygenated intermediates such as carboxylic acid and ketone were also observed using 0.2Ti-0.8Al catalyst. This result implied that the deoxygenation process was complex, consisting the breaking of large triolein molecule to mono-chains, deoxygenation, cyclization and ketonization of oxygenated intermediates. Fig 4.7 (c) shows the percentage of oxygenated intermediates (heavy hydrocarbon + carboxylic acid + cyclic compound + alcohol + ketone) followed the sequence: 0.2Ti-0.8Al (29.83%) < 0.1Ti-0.9Al (33.98%) < 0.3Ti-0.7Al (34.95%) < Al₂O₃ (43.67%) < TiO₂ (44.25%). The catalyst with high acidity strength will reduce these side reactions and thereby, enhance the cracking process of large unsaturated triglycerides molecule (Idem, Katikaneni, & Bakhshi, 1997). The TiO₂ catalyst has the lowest decarboxylation activity (4.50% for n- $C_{15} + n - C_{17}$) compared to other catalysts, showing that the low acid site does not facile the decarboxylation pathway. From the catalytic study, the catalyst acidity rendered the main characteristic for decarboxylation pathway. Overall, the deoxygenation reaction through decarboxylation pathway can be facilitated by the introduction of 20 wt.% TiO₂ into Al₂O₃ that enhanced surface area and acid strength.





Figure 4.9: Comparison study of (a) conversion and removal of oxygen content, (b) product distribution and (c) straight chain hydrocarbon selectivity from deoxygenated reaction. Reaction condition: temperature 380 °C, time 1 h, catalyst loading 5 wt.%, pressure 10 mbar and stirring speed 400 rpm. Error bars show the average of three independent experiments.

4.3 Optimization studies

4.3.1 Effect of temperature

Figure 4.10 shows the conversion, hydrocarbon distribution (C₈-C₂₀), removal of oxygen content and straight chain saturated and unsaturated hydrocarbon selectivity (C₈-C₂₀) influenced by the reaction temperature from 320 to 380 °C. The conversion and hydrocarbon distribution (C₈-C₂₀) increased gradually when the reaction temperature increased from 320 to 380 °C. The highest conversion (53.96%) was obtained at 380 °C with hydrocarbon distribution (C₈-C₂₀) of 64.87% and removal of oxygen content (91.51%). In the view of decarboxylation selectivity, the formation of n-C₁₅ + n-C₁₇ increased followed the sequence: 380 °C (14.51%) > 350 °C (13.08%) > 320 °C (9.47%). The catalyst particles can be dispersed effectively in the viscous liquid at high

temperature, simultaneously increasing the decarboxylation pathways via better mass transfer in the reaction (Alsultan et al., 2017). At the same time, the formation of shorter straight chain hydrocarbon n-C₈–n-C₁₃ showed a gradual increase followed the sequence: 380 °C (50.97%) > 350 °C (45.53%) > 320 °C (33.23%). It can be suggested that the increment of temperature will facilitate the oxygenated intermediates to undergo further thermal cracking via secondary reaction, resulting slight increase in lighter hydrocarbon fractions (Arend, Nonnen, Hoelderich, Fischer, & Groos, 2011; Asikin-Mijan, Lee, Taufiq-Yap, et al., 2017). The temperature higher than 380 °C is not favorable for deoxygenation of triolein because it has been reported that the undesirable side reactions of triolein such as cracking, dehydrogenation and aromatization will occur at high temperature of 400 °C (Choo et al., 2019). Based on this result, it concluded that 380 °C was the optimum deoxygenation temperature since it obtained the maximum conversion (53.96%), hydrocarbon distribution C₈-C₂₀ (64.87%) and n-C₁₅ + n-C₁₇ selectivity (14.51%).





Figure 4.10: Optimization study of (a) conversion, hydrocarbon distribution and removal of oxygen content, (b) straight chain hydrocarbon selectivity from deoxygenation reaction by 0.2Ti-0.8Al. Reaction condition: temperature (320-380 °C), time 1 h, catalyst loading 5 wt.%, pressure 10 mbar and stirring speed 400 rpm. Error bars show the average of three independent experiments.

4.3.2 Effect of reaction time

Figure 4.11 shows the conversion, hydrocarbon distribution (C_8-C_{20}), removal of oxygen content and selectivity. It was found that the conversion, hydrocarbon distribution (C_8-C_{20}) and removal of oxygen content increased progressively to obtain a maximum of 72.67%, 73.62% and 94.56% respectively at 4 h. It was evident that the formation of *n*- $C_{15} + n-C_{17}$ increased with reaction time. This suggested that the longer reaction time facilitated the decarboxylation reaction as the catalyst surface and the large reactant compound can react more effectively. However, the *n*- $C_{15} + n-C_{17}$ selectivity reduced when the reaction time prolonged to 5 h because the deoxygenated liquid product proceeded further thermal cracking, resulting the formation of shorter straight chain hydrocarbon fractions and gaseous products. Based on the result, it was found that the

selectivity of lighter fractions ($C_8 - C_{13}$) for 5 h (64.63%) is higher than 4 h (58.91%). Therefore, 4 h reaction time is the best reaction time for decarboxylation reaction with mesoporous 0.2Ti-0.8Al.



Figure 4.11: Optimization study of (a) conversion, hydrocarbon distribution and removal of oxygen content, (b) straight chain hydrocarbon selectivity from deoxygenation reaction by 0.2Ti-0.8Al. Reaction condition: time (15 min-5 h), temperature 380 °C, catalyst loading 5 wt.%, pressure 10 mbar and stirring speed 400 rpm. Error bars show the average of three independent experiments.

4.3.3 Effect of catalyst loading

Figure 4.12 illustrates the conversion, hydrocarbon distribution (C₈-C₂₀), removal of oxygen content and selectivity influenced by the catalyst loading (1-9 wt.%). Based on the result, the range of catalyst loading from 1 to 7 wt.% increased the deoxygenation reaction. The conversion, hydrocarbon distribution (C_8-C_{20}) and removal of oxygen content increased gradually from 67.89% (1 wt.%) to 76.86% (7 wt.%), 65.75% (1 wt.%) to 79.38% (7 wt.%) and 90.79% (1 wt.%) to 97.44% (7 wt.%) respectively. The active site of the catalyst for the deoxygenation process increased as the catalyst loading increased. It was evident that the formation of $n-C_{15} + n-C_{17}$ increased followed the sequence: 27.26% (7 wt.%) > 22.13% (5 wt.%) > 20.27% (3 wt.%) > 19.93% (9 wt.%) > 16.51% (1 wt.%). The best result was obtained with the 7 wt.% catalyst loading. Over loaded amount of catalyst up to 9 wt.% reduced the efficiency of deoxygenation reaction. It suggested that excessive active site might lead to the cracking of deoxygenated product. In addition, it promoted secondary reaction especially polymerization that caused coking at the surface of catalyst (P. M. Mortensen, Grunwaldt, Jensen, Knudsen, & Jensen, 2011). Therefore, 7 wt.% catalyst loading was the most suitable and economical since it resulted the optimum conversion (76.86%), C₈-C₂₀ hydrocarbon distribution (79.38%), oxygen removal content (97.44%) and $n-C_{15} + n-C_{17}$ selectivity (27.26%). Therefore, it has concluded that the optimum deoxygenation reaction of triolein was achieved at 380 °C, 4 h and 7 wt.% loading by using 0.2Ti-0.8Al catalyst.

As compared to previous study by Suraya and her team (Zulkepli et al., 2018), they carried out deoxygenation reaction of triolein by using nickel supported on mesoporous silica (HMS) catalyst. They obtained the highest conversion of 75.20% for HMS catalyst. The present study using 0.2Ti-0.8Al resulted the highest conversion up to 76.86% which

is slightly higher than that of HMS catalyst (75.20%). On the other hand, Asikin and her team (Asikin-Mijan, Lee, Juan, et al., 2018) performed deoxygenation reaction of triolein by using SiO₂-Al₂O₃ catalyst and they obtained the highest C₈-C₂₀ hydrocarbon distribution up to 46%. The present study using 0.2Ti-0.8Al resulted the highest C₈-C₂₀ hydrocarbon distribution up to 79.38% which is higher than that of SiO₂-Al₂O₃ catalyst. This might due to the surface area of 0.2Ti-0.8Al (398.60 m²/g) is larger than that of SiO₂-Al₂O₃ (382.6 m²/g). In addition, the acidity of 0.2Ti-0.8Al (2734.63 µmol/g) is higher than that of SiO₂-Al₂O₃ (1526.5 µmol/g) as well. Therefore, this revealed that the mesoporous Al₂O₃-TiO₂ is a better catalyst to facilitate deoxygenation reaction of triolein.





Figure 4.12: Optimization study of (a) conversion, hydrocarbon distribution and removal of oxygen content, (b) straight chain hydrocarbon selectivity from deoxygenation reaction by 0.2Ti-0.8Al. Reaction condition: catalyst loading (1-9 wt.%), temperature 380 °C, time 4 h, pressure 10 mbar and stirring speed 400 rpm. Error bars show the average of three independent experiments.

4.4 Reusability study of catalyst in deoxygenation of triolein

The catalyst reusability is a significant study for cost saving purpose in the production of green biofuel. The catalyst reusability study of 0.2Ti-0.8Al catalyst was further investigated at 380 °C, 4 h and 7 wt.% catalyst loading. As shown in Figure 4.13, the catalytic activity of 0.2Ti-0.8Al catalyst was consistent up to fourth run with a slight decrease in conversion from 76.86% to 72.04% (4.82% reduction), hydrocarbon distribution (C₈-C₂₀) from 79.38% to 66.03% (13.35% reduction), removal of oxygen content from 97.44% to 92.17% (5.27% reduction) and n-C₁₅+n-C₁₇ selectivity from 27.26% to 20.17% (7.09% reduction). As compared to previous study by Asikin and her team (Asikin-Mijan, Lee, Taufiq-Yap, et al., 2017), they carried out deoxygenation of triolein by using NiO-CaO₅/SiO₂-Al₂O₃ catalyst. The result showed that the conversion was reduced from 73% to 65% (8% reduction), n-C₁₅+n-C₁₇ selectivity from 47% to 28% (19% reduction) after fourth run. This revealed that the metal oxide supported SiO₂-Al₂O₃ catalyst is not effective than that of Al₂O₃-TiO₂ catalyst in term of catalyst life cycle. The 0.2Ti-0.8Al catalyst was able to perform progressively with mild deactivation happened.

In order to investigate the cause of deactivation, XRD and TGA analysis were used to determine the catalyst stability and coke formation. Based on the XRD results in Figure 4.14 (a), the 4th reactivated catalyst showed same crystallinity patterns at 25.3°, 48.0° and 67.0°, which assigned to characteristic peak of γ - Al₂O₃ and anatase TiO₂. Thus, this suggested that the 0.2Ti-0.8Al catalyst is still stable after consecutive deoxygenation reactions. In addition, TGA analysis was carried out to evaluate the extent of coke deposition. Figure 4.14 (b) displays the amount of carbonaceous deposited on the surface of reactivated and also fresh catalyst. The weight loss stage is the indication to study the variation of fresh and reactivated catalysts. It was observed that the reactivated catalyst. The reactivated catalyst exhibited the weight loss stage of coke decomposition in the ranged 380-560 °C and the weight loss was around 14 wt.%. This would mean the coke deposition on the catalyst surface blocked the access of triolein reactant molecule to the active site, which led to the decrease in deoxygenation activity.



Figure 4.13: Reusability of the 0.2Ti-0.8Al catalyst for deoxygenation of triolein. Reaction condition: temperature 380 °C, time 4 h, catalyst loading 7 wt.%, pressure 10 mbar and stirring speed 400 rpm. Error bars show the average of three independent experiments.



Figure 4.14: (a) XRD diffraction and (b) TGA profiles for fresh and 4th reactivated 0.2Ti-0.8Al catalyst.
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

5.1 Conclusions

All objectives in the present study were successfully achieved. The mesoporous Al_2O_3 -TiO₂ mixed oxide catalysts with different ratio (0.1Ti-0.9Al, 0.2Ti-0.8Al and 0.3Ti-0.7Al) were successfully synthesized and characterized. The mesoporous 0.2Ti-0.8Al catalyst exhibited the best physicochemical properties with larger weak-medium acidity (2734.63 µmol/g) and larger surface area (398.60 m²/g) as compared to that of Al_2O_3 and TiO₂ catalysts.

The mesoporous Al₂O₃-TiO₂ catalysts rendered better performance on the deoxygenation reaction of triolein in the absence of H₂ and solvent as compared to that of Al₂O₃ and TiO₂ catalysts. The 0.2Ti-0.8Al catalyst demonstrated the best deoxygenation activity with conversion (53.96%), C₈-C₂₀ hydrocarbon distribution (66.75%), removal of oxygen content (91.51%) and n-C₁₅ + n-C₁₇ selectivity (14.51%) under reaction conditions of 380 °C, 5 wt.% catalyst loading and 1 h reaction time due to the excellent physicochemical properties. This suggested that the modification of Al₂O₃ by proper amount of TiO₂ significantly facilitated the deoxygenation reaction of triolein by promoting the cleavage of C-O bonds.

In addition, the mesoporous 0.2Ti-0.8Al catalyst resulted optimal catalytic performance with conversion (76.86%), C₈-C₂₀ hydrocarbon distribution (79.38%), oxygen removal content (97.44%), and n-C₁₅ + n-C₁₇ selectivity (27.26%) under optimal reaction conditions of 380 °C, 7 wt.% catalyst loading and 4 h reaction time. Furthermore, the reusability experiment results showed that the deoxygenation reaction of triolein by

using mesoporous 0.2Ti-0.8Al catalyst was consistent for four consecutive cycles with a slight decrease in conversion from 76.86% to 72.04%, hydrocarbon distribution (C_8-C_{20}) from 79.38% to 66.03%, removal of oxygen content from 97.44% to 92.17% and *n*- $C_{15}+n-C_{17}$ selectivity from 27.26% to 20.17%. Therefore, the mesoporous Al₂O₃-TiO₂ catalyst can be applied for the production of hydrocarbon-biofuel.

5.2 **Recommendations for future studies**

Considering that deoxygenation using Al₂O₃-TiO₂ could be proceeded with some opportunities, with no H₂ consumption for current developing trend due to its low cost and environmental friendliness. The following recommendations for future studies are suggested:

- The deoxygenation reaction of different feedstock or model compound using Al₂O₃-TiO₂ catalyst without H₂ consumption could be carried out.
- Metal or metal oxide supported catalysts have good catalytic activity on the deoxygenation reaction. The deoxygenation reaction using metal or metal oxide supported on Al₂O₃-TiO₂ catalyst without H₂ consumption could be emphasized as well in order to serve as high quality catalyst for biofuel synthesis in large scale industry.
- Optimization of the influence of process parameters to investigate the conversion of the product.
- Development of catalyst life cycle by reducing the coking of catalyst.

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