UNIVERSITI PUTRA MALAYSIA

CATALYTIC KETONIZATION OF PALMITIC ACID OVER A SERIES OF TRANSITION METAL OXIDES SUPPORTED ON ZIRCONIA-BASED CATALYSTS

SHAMINA BINTI ABDUL ALEEM

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By

SHAMINA BINTI ABDUL ALEEM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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DEDICATION

For Safeerah and Yusuf

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : Professor Datuk Taufiq-Yap Yun Hin, PhD
Faculty : Science

Development of sustainable routes to produce bio-based compounds from renewable feedstock is the most relevant strategy to counterbalance the inevitable depletion of fossil resources in the near future. Therefore, the potential of upgrading of bio-based feedstock to produce value added chemicals are highly sought after where ketonization is one of the reactions to convert fatty acids into value added alkanones, ready for subsequent process to yield lubricants, waxes, and specialty chemicals. Current development in ketonization relies heavily on using diluted short chained carboxylic acid as feedstock and very few literatures with fatty acids are found, furthermore current ketonization with fatty acids results in low to moderate yields of ketone with single metal oxides. This study aims to develop ZrO_2 based catalysts for the ketonization of palmitic acid to produce elongated ketones as the intermediate in producing high performing bio lubricants. In this work, modification of ZrO_2 based catalyst with selected transition metals dopants have shown promising improvement in catalytic activity of palmitic acid ketonization reaction. Small amounts of metal oxide deposition on the surface of ZrO_2 catalyst enhances the yield of palmitone (16-hentriacontanone) as the major product with pentadecane as the largest side product. This investigation explores the effects of carefully chosen metal oxides (Fe_2O_3, NiO, MnO_2, CeO_2, CuO, CoO, Cr_2O_3, La_2O_3 and ZnO) addition as a dopant on bulk ZrO_2. The catalysts are prepared via deposition-precipitation method followed by calcination at 550°C and characterized by XRD, BET-surface area, TPD-CO_2, TPD-NH_3, FESEM, TEM and XPS. The screening of synthesized catalysts was carried out with 5% catalyst loading onto 15g of pristine palmitic acid and the reaction carried out at 340°C for 3h. Screening studies show catalytic activity improvement with addition of dopants in the order of La_2O_3/ZrO_2 < CoO/ZrO_2 < MnO_2/ZrO_2 with the highest palmitone yield achieved using MnO_2/ZrO_2 catalyst. This is attributed to the existence of intermediate acid and basic sites on the catalyst surface that facilitates the activity of ketonization of palmitic acid. Besides, NiO/ZrO_2 exhibits high selectivity exclusively for pentadecane compared to other catalysts with maximum yield of 24.9% and conversion of 64.9% is observed.

Optimisation of ketonization shows that reaction temperature and time significantly influence the overall catalytic activity. In conclusion, under the optimized reaction condition of 3h, 340ºC and 5% of catalyst loading, highest conversion of 92.3% is achieve with obtained palmitone and pentadecane yield of 27.7% and 10.8% respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KETONISASI BERMANGKIN ASID PALMITIK DENGAN SIRI OKSIDA LOGAM PERALIHAN YANG DISOKONG PADA PEMANGKIN ZIRKONIA

Oleh

SHAMINA BINTI ABDUL ALEEM

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Pembangunan laluan lestari untuk menghasilkan sebatian berasaskan bio daripada bahan mentah yang boleh diperbaharui adalah strategi paling relevan untuk menampung kekurangan sumber fosil yang tidak dapat dielakkan. Oleh sebab itu, cara -cara yang berpontensi untuk menaik taraf bahan mentah berasaskan bio untuk menghasilkan bahan kimia bertaraf tinggi amat diperlukan di mana ketonisasi merupakan salah satu tindak balas untuk menukarkan asid lemak kepada alkanon yang menjadi bahan perantara dalam penghasilan minyak pelincir, lilin dan bahan kimia khusus yang lain. Perkembangan semasa dalam ketonisasi sangat bergantung pada penggunaan asid karboksilik rantai pendek yang dicairkan sebagai bahan mentah dan sangat sedikit literatur dengan asid lemak ditemui, tambahan pula ketonisasi semasa dengan asid lemak menghasilkan hasil keton yang rendah hingga sederhana dengan menggunakan oksida logam tunggal. Matlamat kajian ini adalah untuk membangun pemangkin berasaskan ZrO_2 untuk ketonisasi asid palmitik untuk menghasilkan keton berantai karbon panjang sebagai perantara dalam menghasilkan pelincir bio berprestasi tinggi. Dalam penyelidikan ini, pengubahsuaian pemangkin berasaskan ZrO_2 dengan dopan logam peralihan terpilih telah menunjukkan peningkatan yang yang memberangsangkan dalam aktiviti tindak balas ketonisasi asid palmitik. Oksida logam dalam jumlah yang kecil yg dimendapkan pada permukaan mangkin ZrO_2 meningkatkan hasil palmitone (16-hentriacontanone) sebagai produk utama dengan pentadekana sebagai hasil sampingan terbesar. Penyelidikan ini mengkaji kesan penambahan oksida logam terpilih (Fe_2O_3, NiO, MnO_2, CeO_2, CuO, CoO, Cr_2O_3, La_2O_3 dan ZnO) sebagai dopan pada ZrO_2. Pemangkin disediakan melalui kaedah pemendapan-kerpasan diikuti dengan pengkalsinan pada 550°C dan dicirikan oleh XRD, BET-Kawasan permukaan, TPD-CO_2, TPD-NH_3, FESEM, TEM dan XPS. Saringan pemangkin yang disintesis tersebut telah dijalankan dengan 5% pemangkin dimuatkan pada 15g asid palmitik tulen dan tindak balas dijalankan pada 340°C selama 3 jam. Kajian saringan menunjukkan peningkatan aktiviti pemangkin dengan dopan mengikut urutan $La_2O_3/ZrO_2 < CoO/ZrO_2 < MnO_2/ZrO_2$ dengan hasil palmitone tertinggi dicapai menggunakan mangkin MnO_2/ZrO_2. Ini disebabkan oleh kewujudan tapak asid dan bes perantaraan pada

permukaan mangkin yang memudahkan aktiviti ketonisasi asid palmitik. Didapati juga, NiO/ZrO_2 mempamerkan selektiviti tertinggi untuk pentadekana berbanding pemangkin lain dengan hasil maksimum 24.9% dan penukaran sebanyak 64.9% diperhatikan. Pengoptimuman tindak balas ketonisasi menunjukkan bahawa suhu dan masa tindak balas adalah sangat signifikan dalam mempengaruhi keseluruhan aktiviti pemangkin. Kesimpulannya, di bawah keadaan tindak balas yang dioptimumkan iaitu 3h, 340oC dan 5% pemuatan mangkin, penukaran tertinggi sebanyak 92.3% dicapai dengan hasil palmitone dan pentadekana yang diperolehi masing-masing sebanyak 27.7% dan 10.8%.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
CAGR	Compound annual growth rate
DFT	Discrete Fourier transform
DP	Deposition-precipitation
EDX	Energy dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
FFA	Free fatty acid
GC-MS	Gas chromatography mass spectroscopy
GC-FID	Gas chromatography flame ionisation detector
HDO	Hydrodeoxygenation
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
LAO/PAO	Linear alpha olefins/ Poly alpha olefins
PFAD	Palm fatty acid distillate
POME	Palm oil mill effluent
SDG	Sustainable development goals
SPO	Sludge palm oil
TEM	Transmission electron microscopy
TPD-NH_3	Ammonia-temperature programmed desorption
TPD-CO_2	Carbon dioxide-temperature programmed desorption
XRD/XRF	X-Ray Diffraction Analysis/ X-Ray Fluorescence
XPS	X-Ray Photoelectron Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 The background of lubricants industry

Lubricants are defined as a substance that is used to modify the friction and wear of the surfaces that comes into contact with one that is in relative motion (Harris & Kotzalas, 2006; Uhler et al., 2016). Mostly utilised in the industrial and transport sector, lubricants are currently produced through refineries or petrochemical plant that processes crude oils or natural gas. Lubricants play a pivotal role in engine functions such as controlling friction between surfaces, reducing wear by preventing metal to metal contact and controlling the temperature by reducing the heat from fluid friction and combustion of fuel (Lubrizol, 2015) and the supply for this substance is in huge demand. However, the processing, utilization and disposal of this substance are causing irreparable harm to the environment. It is estimated that about 50% of lubricants sold worldwide end up in the environment via volatility, spills and accidents (Chand & Kumar, 2017). Low biodegradability of mineral based lubricants added to its high ecotoxicity are a threat to the ecosystem, hence, the increased utilization of synthetic lubricants is a step in reducing the resultant environmental impact. Synthetic lubricants have higher performance, resulting in higher efficiency and lower fuel consumption, yet the ever-rising demands of this petroleum derived product only increases its contributions towards environmental harm. According to the United States Environmental Protection Agency (USEPA), greenhouse gas emissions from transportation sector is the largest contributor of U.S. greenhouse gas emissions, totalling to about 27% in the year 2020. (USEPA, 2022).

Lubricants are made of 80 – 90% base oils which are made of petroleum hydrocarbon distillates and 10-20% additives. The base oil portion is primarily made up of saturated long-chain hydrocarbons of 15-30 carbon atoms length (Hutchings & Shipway, 2017). Base oils can be of mineral oils or synthetic hydrocarbons such as poly alpha olefins (PAOs) and esters. PAOs are ethylene-derived polymerized linear α-olefins comprising 30 or more carbon atoms that are widely used in automobiles fluids, turbine gear, and bearing oils (Nikolakopoulos et al., 2018). PAOs are colourless liquid with well-defined isoparaffinic structures and high degree of saturation that offers excellent thermal stability to the substance. The demand for PAOs doesn't show a plateau in the near future. The global PAO market size is estimated to grow at a CAGR of 2.9%, reaching USD 17.5 billion by 2023, as reported by Markets and Markets (MarketsandMarkets, 2019). Although synthetic base oils and lubricants are considered high performance lubricants with less environmental impact than mineral base oils, the adverse effects of these chemicals are very well documented. Ecosystems are interrupted with non-biodegradable lubricants disposal as well as emissions increase as the result of combustion (Singh & Goel, 2018). Hence, it is vital to find alternate sources which are eco-friendly and sustainable to produce lubricants and base oil. Biomass derived products is a potential and viable alternative to produce the intermediates needed.

1.2 Upgrading of bio feed into value added chemicals

Development of sustainable routes to produce bio-based compounds such as alcohols, fatty esters, and ketones from renewable feedstock is the most relevant strategy to counterbalance the inevitable depletion of fossil resources in the near future. Therefore, the potential of bio-lubricants development and its applications has received a wider consideration from researchers. The use of bio-based feedstock to produce fuel and lubricants are currently the most sought after route with the use of heterogenous catalysts being vital in this process (Immer et al., 2010). High oxygen content of biomass feedstock has negative effects on the finished hydrocarbon products, such as low heating value, contributes to high viscosity and often immiscible with conventional fluids, hence the need for oxygen removal. Converting these oxygenated feedstock is regarded as a complex process that requires extensive transformative steps in order to reduce the oxygen content of the bio feed, while keeping the carbon and hydrogen intact (Aranda-pérez et al., 2017).

Figure 1.1 shows a roadmap of how different bio-based feedstock can be converted to value added hydrocarbons. Oxygenated feedstock such as triglycerides, lignocellulosic masses, polysaccharides, fatty acids can be converted via reactions such as pyrolysis, esterification, transesterification, hydrodeoxygenation, hydrogenation and others to yield biofuels, bio oils and other value added compounds (R. Kumar et al., 2018). Pyrolysis is a thermochemical decomposition of a feedstock and convert them to value added products in the presence of a catalyst and the absence of oxygen (Basu, 2018). Biomass, which are a mixture of cellulosic materials, lignin and other organics are usually pyrolyzed at high temperatures to produce bio-oil that consists of polar organics (75-80%) and water with release of vapours (Banks & Bridgwater, 2016). On the other hand, direct esterification of acids and alcohol and ester-ester/ester-alcohol based transesterification are of major importance in the processing of biodiesel and renewable chemicals (Hoydonckx et al., 2004; López et al., 2008). Oxygen eliminating hydrodeoxygenation (HDO) is a reaction that removes oxygen from oxygenated compounds using metal oxide catalysts with nickel-molybdenum and cobalt-molybdenum being the commonly used catalysts (Galadima et al., 2022). In the HDO process, a series of reactions (inclusive of hydrogenation, hydrogenolysis, decarbonylation, and hydrolysis) takes place to yield green fuels and chemicals (Zaiman Zhang & Li, 2022).

These bio feedstock can also be upgraded to produce sustainable base oils and PAOs as part of bio-lubricant production. Figure 1.2 shows multiple pathways of upgrading fatty acids and fatty esters into bio-PAO as reported by Yusop and Hong, 2013. Both fatty acids and esters can undergo hydrogenation reaction to produce alkanes or fatty alcohols respectively. In hydrogenation, the unsaturated double bonds react with hydrogen over catalysts, usually nickel based catalysts.

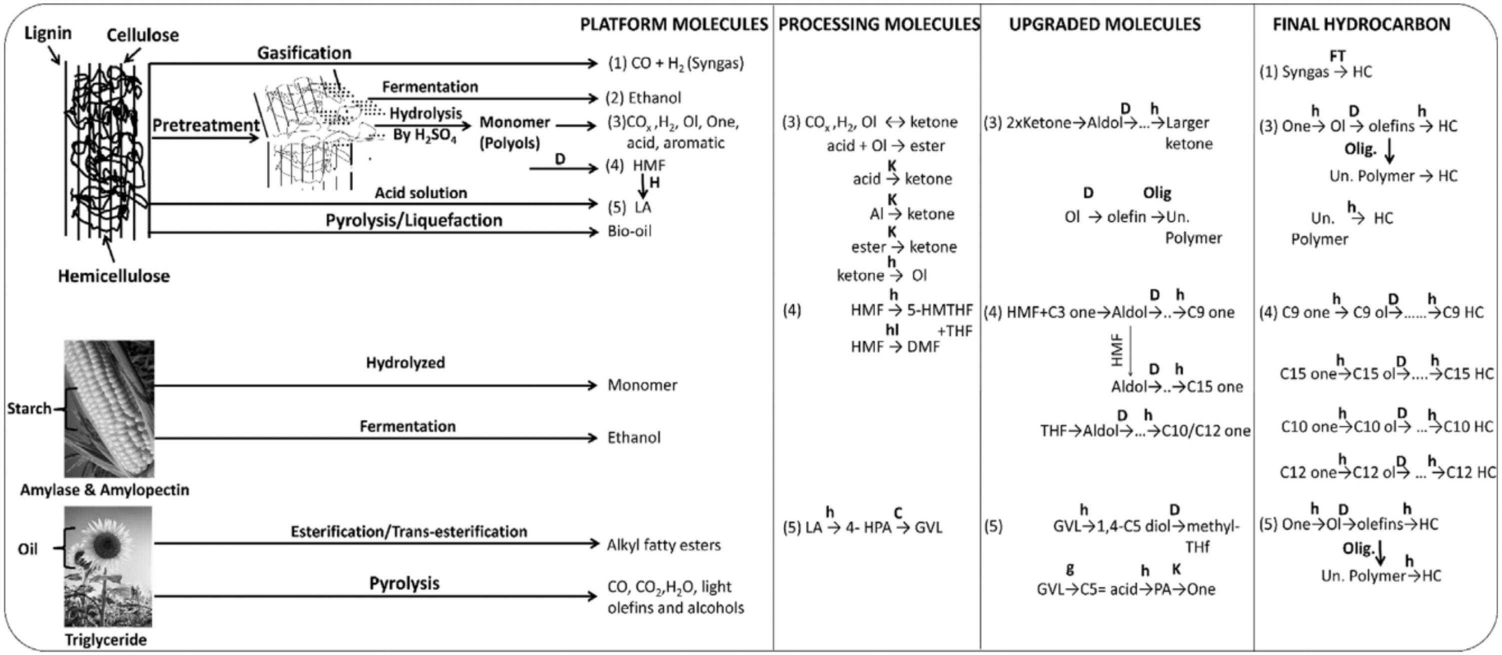

Figure 1.1 : Roadmap of biomass to fuel range hydrocarbon conversion (R. Kumar et al., 2018)
Aldol = aldol condensation product, D= dehydration, K= ketonization, H= hydration, h = hydrogenation, hl = hydrogenolysis, C = cyclization, g = ring opening, Olig.=oligomerization, FT = Fischer-Tropsch, inter.=intermediate, C#= hydrocarbon with # number of carbons, HC= Hydrocarbon, Ol = alcohol, One = ketone, Al = aldehyde, PA = Pentanoic acid, 5-HMTHF = 5-hydroxymethyltetrahydrofurfural, THF = Tetrahydrofurfural, DMF= Dimethyl furan, Un. polymer = Unsaturated polymer, 4-HPA = 4-hydroxypentanoic acid, GVL= γ-valerolactone, HMF= Furfural, THf= tetrahydrofuran, and LA = Levulinic acid

These compounds further undergo selective dehydrogenation and dehydration to produce olefins, which is the starting material for the production of bio PAO (Ray et al., 2011; Yusop & Hong, 2013). Another pathway shown in Figure 1.2 (Route 2) is via the decarboxylation of fatty acids, where the carboxyl group is removed, leaving an olefin to be converted to bio-PAO (Yusoff, I, Yusop, N. M., Basar, J., Belhocine, T., Saleh, 2013).

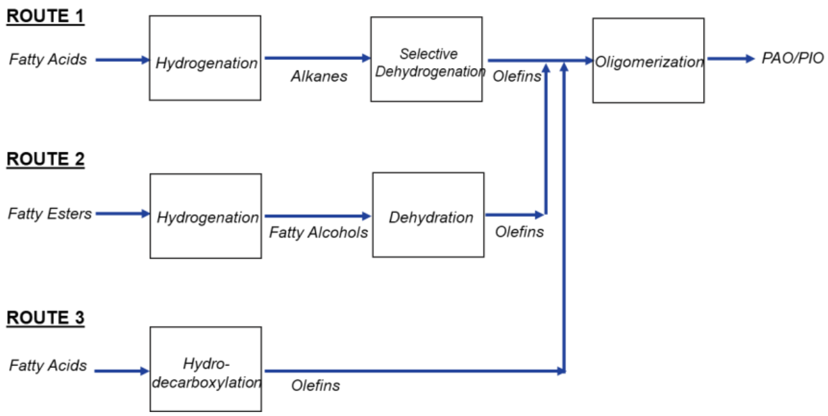

Figure 1.2 : Pathways to produce bio-PAO (Yusop & Hong, 2013)

Apart from these aforementioned pathways, one other catalytic reaction pathway that can convert these bio feedstocks into base oil for lubricants is shown in Figure 1.3. Fatty acids and triglycerides undergo a two-stage reaction process, ketonization followed by hydrogenation, to yield base oil (bio-PAO) for lubricant production. Ketonization, or ketonic decarboxylation is a carbon coupling reaction of fatty acids with a release of CO_2 and water yielding a corresponding ketone (Murzin et al., 2019).

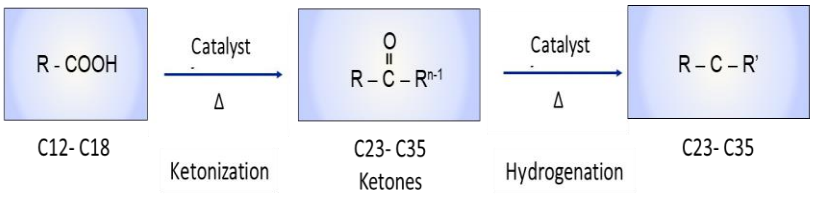

Figure 1.3 : Two-step pathway to bio-base oil (bio-PAO)

The first stage of the pathway shown in Figure 1.3 is ketonization of fatty acids where catalysts are employed in converting oxygenated compounds like fatty acids (Gaertner et al., 2010). Ketonization converts the carboxylic acids to form new C-C bonds via decarboxylative carbon coupling to yield alkanones, carbon dioxide (CO_2) and water (H_2O) (Wang & Iglesia, 2017):

$$2R_1COOH \rightarrow R_1C(=O)R_1 + CO_2 + H_2O \quad (R_1 = \text{alkyl}) \qquad \text{(Eq. 1.1)}$$

This reaction proves to be an attractive pathway in upgrading bio-derived feedstock in that three oxygen atoms are removed, and the carbon chain is elongated to yield heavier carbon components (Wang & Iglesia, 2017). The produced alkanones are ready for subsequent process to yield waxes, lubricants and specialty chemicals (Gaertner et al., 2010).

1.3 Potential of fatty acids from palm industry in bio lubricant value chain

In Malaysia, palm oil and palm-based bio feed is the main source of feedstock for biofuels (biodiesel, green diesel) and other biochemicals in the oleochemical industry. Malaysia currently accounts for 28% of world palm oil production and 33% of world exports. If taken into account of other oils and fats produced in the country, Malaysia accounts for 9.5% and 19.7% of the world's total production and exports of oils and fats (MPOC, 2019). One of the by-products of palm oil extraction is known as Palm Fatty Acids Distillates (PFAD), which accounts for up to 5% of the raw material inputs and considered as an unwanted processing residue (Neste, 2019). Palm fatty acid distillates are composed of several types of fatty acids with carbon chain lengths in the range of C_{12} - C_{18} with C_{16} being the largest fraction of above 45% (Tay et al., 2009). Table 1.1 shows the fatty acid profile of a PFAD feedstock where palmitic acids being the largest saturated fatty acid constituent (Lokman et al., 2014).

Table 1.1 : Fatty acids profile of PFAD feedstock

Fatty Acid	Formula	Carbon Structure	Composition wt.%
Myristic acid[a]	$C_{14}H_{28}O_2$	$C_{14:0}$	1.93 ± 0.12
Palmitic acid[a]	$C_{16}H_{32}O_2$	$C_{16:0}$	45.68 ± 1.52
Stearic acid[a]	$C_{18}H_{36}O_2$	$C_{18:0}$	4.25 ± 0.04
Oleic acid[b]	$C_{18}H_{34}O_2$	$C_{18:1}$	40.19 ± 1.29
Linoleic acid[c]	$C_{18}H_{32}O_2$	$C_{18:2}$	7.90 ± 0.11

[a]Saturated fatty acids; [b]Monounsaturated fatty acids; [c]Polyunsaturated fatty acids

The highly paraffinic structure of PFAD is suitable for conversion to paraffinic hydrocarbon products. However, PFAD's high oxygen containing constituents needs to be upgraded into feasible starting material for production of fuel, lubricants or other oleochemical synthesis.

1.4 Application of heterogenous catalysts in bio-lubricant synthesis

Catalysts are classified as substances that increases the rate of a chemical reaction without itself becoming permanently involved in the reaction (Richardson, 2013). Hence, the catalyst would not be part of the overall stoichiometry of the reaction, but it will be part of the reaction mechanism steps. Catalysts play a role in reducing the activation energy (E_a) of a reaction without disturbing the energy difference between reactant and products as shown in Figure 1.4.

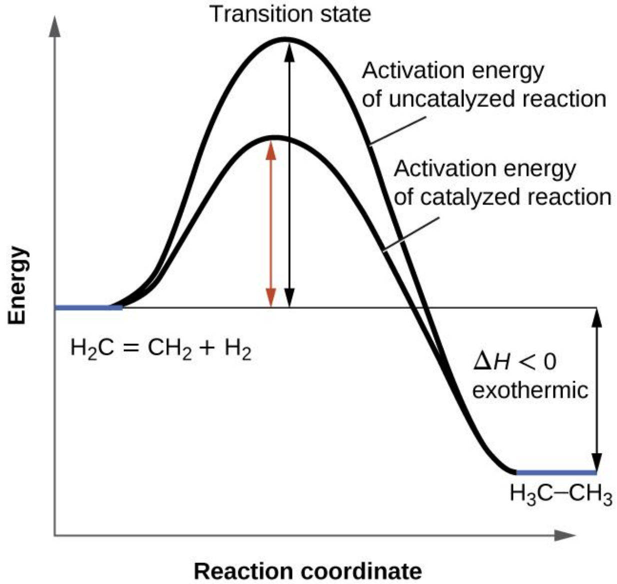

Figure 1.4 : Catalyst lowering the activation energy for a reaction
(Flowers et al., 2022)

Catalysts are usually divided into homogenous, heterogenous and enzymatic catalyst. (Richardson, 2013). Most of the industrial processes employ heterogenous catalysts for ease of handling and separation. Metal oxides catalysts are often employed in the processing of bio-feedstock into value added chemicals, and common catalysts used in these processes are given in Table 1.2.

Table 1.2 : Common metal oxide catalysts used in bio feed processing

Reaction	Common Catalysts	Ref
Hydrogenation	Pd/Pt catalysts	
Hydrodeoxygenation	Ni–Mo and Co–Mo, Al_2O_3-supported sulphided Ni–Mo and Co–Mo	(Kim et al., 2019)
Decarboxylation	Noble metals such as Pd and Pt, Ni	(Wu et al., 2016)
Gasification	K, Na, Ca, Mg based catalyst	(Arnold & Hill, 2019)
Transesterification	CaO, MgO, SrO	(Borges & Díaz, 2012)
Ketonization	Transition metal oxides like TiO_2, ZrO_2,	(Pham et al., 2013)

1.5 Evolution of catalysts for ketonization of carboxylic acids

Ketonization of carboxylic acids to produce symmetrical ketones is an attractive option for fatty acid conversion as it transforms the feedstock into a longer carbon chain value added product with elimination of three oxygens for every two carboxylic acids. It is also a clean reaction as there are no dangerous by products are formed (Murzin et al., 2019). Ketonization was first reported as dry distillation of calcium acetate to acetone in early 1858 and until 1920s it was the industrially used method to produce acetone (Renz, 2005). Improvements to this process into a semi -continuous process was developed around 1928, around the same time heterogenous catalytic processes for ketonization in the gas phase were reported. The interest in ketonization slowly waned however, before its recent resurgence.

A variety of basic, acidic and amphoteric metal oxide catalysts have been screened in the catalytic ketonization reaction (M. Gliński et al., 2014; R. Kumar et al., 2018; Renz, 2005). Based on those findings, amphoteric reducible metals such as ZrO_2 have been shown to be a more effective catalyst compared to other oxides in ketonization (Simakova & Yu, 2016). Fally et al. (2000) reported that high ketonization activity of ZrO_2 catalyst is due to the formation of a highly defective surface, higher Lewis acid content and oxygen vacancies (Fally et al., 2000). The role of heterogenous catalysts and the mechanisms of the ketonization reaction have been heavily reviewed in the literature, however, there is no collective agreement on the definitive ketonization mechanism (Boekaerts & Sels, 2021). Several possibilities of the mechanism has been put forth to explain ketonization among them being bulk ketonization, roles of α-hydrogen, ketene intermediates and β-ketoacid intermediates and there are compelling evidences in favour of the β-ketoacid intermediate route to produce ketones (Boekaerts & Sels, 2021; Pham et al., 2013). The study by Pham et al. (2013) illustrates the mechanism of the ketonization of carboxylic acids via the β-ketoacid intermediate where coupling of an enolized carboxylate with a carboxylate or an acylium. These β-ketoacids readily decompose at mild temperatures to produce ketone and CO_2.

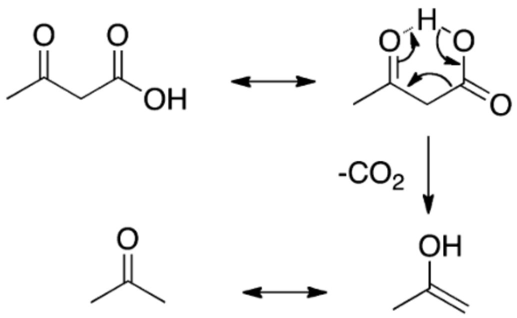

Figure 1.5 : Ketonization mechanism via β-ketoacid intermediate (Pham et al., 2013)

There is only a small amount of published work on the ketonization of fatty acids. Corma et al. (2008) have demonstrated the ketonization of lauric acid at high conversion and selectivity (98%) over MgO catalyst in the gas phase (Corma et al., 2008). In another study that investigated the saturation of fatty acids in the ketonization efficiency, it is found that the ketonization selectivity to ketones decreased with increasing unsaturation due to cracking that leads to production of coke (89% to 75%) (K. Lee et al., 2018).

Most of the literature and studies on ketonization investigates the conversion of short chained carboxylic acids such as acetic acids, propionic acids and pentanoic acids (Murzin et al., 2019). A screening study conducted by Gliński et al. (2014) shows the ketonization of propionic acid over 32 metal oxide catalysts at temperatures 350 to 450°C and compared the activity of those oxides. Their findings clearly show there are three groups of catalysts according to its activity; slightly active, fairly active and the highly active where oxides of manganese, zirconium, cerium, thorium, and uranium are placed in the highly active category (M. Gliński et al., 2014). Furthermore, to increase the selectivity and yield, the carboxylic acid feed is often diluted using solvents like hexane, dodecane and xylene (Y. Guo et al., 2020; Maluangnont et al., 2017; Snell & Shanks, 2013a). Overall, it should be noticed that a variety of feedstock has been used in ketonization, although the focus is mostly on diluted short chained carboxylic acids.

1.6 Problem Statement

Fossil fuel-based hydrocarbon products (fuels, lubricants, and chemicals) are large contributors to carbon emission, cause irreparable harm to the environment and a major stumbling block in achieving SDG goals. The shift to utilize readily available renewable and alternative feedstock is a valuable step in producing bio derived products such as bio lubricant and its intermediates. Furthermore, the utilization of these bio-derived feed is a natural progression towards reaching sustainability goals. Ketonization is an attractive pathway to upgrade renewable feedstock into value added sustainable chemicals (fuel, lubricants, wax, and intermediates). Most of the previous studies focuses heavily on ketonization of short chain carboxylic acids (acetic and propionic acid) whereas the requirements for sustainable chemicals like lubricants and its intermediates often require long chain paraffins and isoparaffins (C_{20}-C_{40}). Moreover, acid feeds are often diluted with expensive solvents to increase the activity of ketonization. The acids are diluted 1-50% in solvents like dodecane or xylene, making the process very solvent intensive. Solventless ketonization on the other hand, pose limitations on the reaction in terms of steric hindrance of the long alkyl chain of long chain fatty acid thus reducing the activity of the catalyst. Apart from this , current literature does not elucidate strongly the physico-chemical properties of catalysts suited for ketonization although acid-base amphoteric characteristics of the catalysts are often mentioned as a promoting factor for the reaction.

This study aims to improve the catalyst activity of long chain fatty acid ketonization under in bulk, solventless conditions by developing catalysts and changing the physico-chemical characteristics using transition metal dopants. Based on literatures, we explore the effect of a series metal oxide dopants (Fe_2O_3, NiO, MnO_2, CeO_2, CuO, CoO, Cr_2O_3,

La_2O_3 and ZnO) supported on ZrO_2 for the ketonization of palmitic acid and it is expected that these dopants will influence the physico-chemical characteristics of the base ZrO_2 (i.e., acid/base nature). Therefore, the synergistic effects of these added dopants on ZrO_2 are investigated to convert solvent-free, bulk palmitic acid ($C_{15}COOH$) to palmitone ($C_{31}H_{62}O$). Since most of the previous studies focused on ketonization of diluted short chain carboxylic acids, there is a research gap in application of longer chain fatty acids as a feedstock for solventless ketonization. Hence, this study aims to illustrate the activity of various metal oxide catalysts in palmitic acid ketonization and identify the most active metal oxide dopants and its physico-chemical characteristic to enhance the product yield and selectivity.

1.7 Objectives

The main objective of this study is to identify the best catalyst ZrO_2 based catalyst candidate for the ketonization of palmitic acid. The specific objectives of this research are listed as below:

1. To synthesize and characterise Zirconia supported catalysts with addition of selected dopants via deposition-precipitation method (Fe, Ni, Ce, Cu, Cr, Co, Mn, La, and Zn).
2. To perform catalytic ketonization of bulk palmitic acid using the prepared catalysts.
3. To optimize ketonization reaction parameters, namely the reaction temperature, catalyst loading, and reaction time to achieve highest ketone yield based on the best catalyst candidate from Objective 2.

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