

CHAPTER II

LITERATURE REVIEW

Literature review is divided into two parts including the development of potassium-based catalyst for transesterification of palm oil to biodiesel and development of Ni and Cu catalysts in hydrogenation of methyl levulinate to gamma-valerolactone.

2.1 Development of potassium-based catalyst for transesterification of palm oil to biodiesel

2.1.1 Biodiesel production

Biodiesel is produced by transesterification as shown in Figure 2.1. Triglycerides in oil react with alcohol, generally methanol, by using acid or base catalyst to produce fatty acid methyl esters which is also known as biodiesel (Boz et al., 2009).

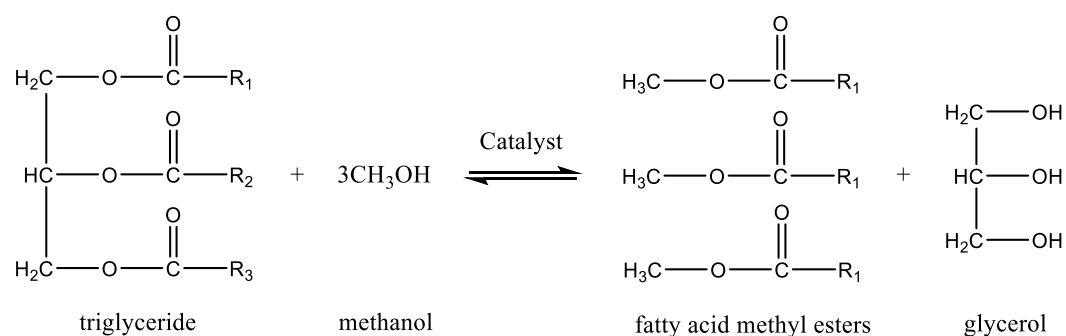


Figure 2.1 Transesterification reaction of the triglycerides to fatty acid methyl esters.

The transesterification reaction can be catalyzed by five distinct types of catalysts. The first category comprises alkali homogeneous catalysts, which are highly active and cost-effective, yet their purification process is notably laborious (Leung et

al., 2010; Vicente et al., 2004). Second, acid homogeneous catalysts are preferable for oils rich in free fatty acids (FFA), albeit characterized by lower reaction rates and challenging separation processes (Marchetti et al., 2007; Liu et al., 2010). Third, alkali heterogeneous catalysts necessitate a high alcohol-to-oil ratio for effectiveness, but these catalysts offer the advantage of being more environmentally benign by minimizing waste emissions (Highina et al., 2011; Zhang et al., 2010). The fourth type, acid heterogeneous catalysts, exhibit reduced corrosiveness and toxicity; however, they are more expensive and pose greater diffusional challenges compared to their homogeneous counterparts (Wan Omar et al., 2011). Lastly, enzymatic catalysts facilitate straightforward separation, regeneration, and reuse, despite their slower reaction rates and propensity for activity loss (Shimada et al., 2002).

2.1.2 Potassium-based heterogeneous catalyst

The predominant heterogeneous catalysts utilized in biodiesel production include carbonates and oxides of alkali and alkaline earth metals, which are supported on materials with high porosity and surface area, such as SiO_2 , Al_2O_3 , and zeolites (Perego et al., 2017; Refaat, 2011; Romero et al., 2005).

Sanchez et al. (2014) conducted a study where they varied the alkali and alkaline earth oxides on $\gamma\text{-Al}_2\text{O}_3$ supports to investigate the behavior of soybean oil transesterification with different $\gamma\text{-Al}_2\text{O}_3$ -based catalysts. Their findings indicated that $\text{K}/\gamma\text{-Al}_2\text{O}_3$ demonstrated superior performance compared to other catalysts tested. Additionally, Hindryawati et al. (2014) reported that potassium-based catalysts exhibit higher basicity and are more resistant to free fatty acid contamination in triglyceride sources compared to lithium and sodium alternatives.

2.1.3 Potassium catalysts on Faujasite (FAU) zeolite

Faujasite zeolites, designated as FAU, are crystalline aluminosilicates characterized by their unique structure, comprising sodalite cages and supercages, with a pore diameter of approximately 0.74 nm. This class of zeolites is divided into two main categories based on their chemical compositions: zeolite X and zeolite Y (Barthomeuf, 1996). The distinction between zeolite X and Y is primarily based on their

silicon to aluminum (Si/Al) ratios, which are in the ranges of 1-1.5 for zeolite X and 2-5 for zeolite Y, respectively. The incorporation of aluminum within the zeolite framework necessitates the presence of an equivalent number of extra-framework cations to maintain charge neutrality. Notably, zeolite NaX exhibits higher basic properties than zeolite NaY, attributed to their differing Si/Al ratios, which consequently influence their basicity and reactivity (Ma et al., 2021). These materials, particularly zeolite X and Y, have found extensive applications in various domains, including the transesterification process for biodiesel production. Their popularity in such applications can be ascribed to their straightforward synthesis, substantial surface area, voluminous pore structure, stability, and well-defined framework (Polisi et al., 2019; Zito et al., 2015).

Numerous studies have investigated catalysts featuring potassium supported on NaX and NaY for the transesterification of diverse oil sources including palm, soybean, sunflower, and *Jatropha*. Noiroj et al. (2009) evaluated the efficacy of KOH supported on Al_2O_3 and NaY zeolites for transesterification of palm oil. The preparation of these catalysts involved varying the KOH loading from 15 to 35 wt% on Al_2O_3 and from 8 to 15 wt% on NaY. Their investigation identified optimal catalyst compositions of 25 wt% KOH/ Al_2O_3 and 10 wt% KOH/NaY, which achieved a biodiesel yield of 91.07% under conditions below 70 °C, within a 2–3 h reaction time, at a molar ratio of 1:15 (palm oil to methanol), and with a catalyst concentration of 3–6 wt%. The study highlighted NaY as a superior support compared to Al_2O_3 , attributable to the optimal potassium loading. Additionally, it was observed that biodiesel yield diminished when KOH loading exceeded 25 wt% on Al_2O_3 and 10 wt% on NaY. This decline in yield was attributed to the agglomeration of the active KOH phase or the occlusion of basic sites by excessive KOH, which in turn reduced the catalyst's surface area and activity. Moreover, the structure of zeolite NaY collapsed with an increase of the K content.

To mitigate the structural collapse of zeolites, Montalbo et al. (2013) prepared potassium catalysts using rice husk silica (RHS) and zeolite NaY, utilizing both acetate buffer (B) and acetate (A) solutions as potassium sources. The study found that K/NaY catalysts exhibited not only higher surface areas, but also greater stability post-impregnation and calcination compared to K/RHS catalysts, which showed structural

collapse during catalyst preparation. Consequently, NaY-supported catalysts demonstrated superior activity over those supported by RHS. Specifically, the 12K/NaY-A, prepared through the impregnation of 12 wt% K on NaY using an aqueous acetate solution, presented a reduced surface area compared to both bare NaY and the 12K/NaY-B. This reduction suggested a more significant collapse within the 12K/NaY-A zeolite structure, correlating with its incomplete conversion of *Jatropha* seed oil into biodiesel. Conversely, the 12K/NaY-B catalyst achieved complete conversion, yielding a biodiesel efficiency of 77.9%.

Another work from Supamathanon et al. (2011), They synthesized potassium-loaded catalysts on zeolite NaY using an acetate buffer solution as a potassium precursor, a strategic approach to preserve the zeolite framework. Their catalysts, tested in the transesterification of *Jatropha* seed oil, found that a 12 wt.% potassium load yielded a notable biodiesel yield of 73.4% under specific conditions. Building on this foundation, Manadee et al. (2017) explored the substitution of NaY with NaX zeolite, varying potassium content for the same process. Their findings revealed an enhanced biodiesel yield of 83% with a 12 wt.% potassium load, suggesting that NaX zeolite's superior basicity and structural integrity significantly contribute to its increased catalytic activity. These works illustrate the pivotal role of zeolite composition and potassium loading in optimizing catalyst performance for biodiesel production, highlighting a promising avenue for future research in the field.

To improve the dispersion of the active species and catalytic performance of the potassium on FAU zeolite, Rakmae et al. (2016) conducted a comparative study on catalysts for transesterification of palm oil into biodiesel. They synthesized 12 wt% potassium-supported zeolite NaY catalysts using both ultrasound-assisted impregnation with acetate buffer (K/NaY-U) and conventional impregnation methods (K/NaY) for comparison. The study revealed that the potassium precursor decomposed between 370–480 °C, forming potassium carbonate. Both catalyst types exhibited moderate to strong basic sites, but K/NaY-U demonstrated superior potassium dispersion. Notably, the K/NaY-U catalyst facilitated a faster transesterification reaction, achieving a 72% biodiesel yield in 2 hours. This finding underscores the effectiveness of ultrasound-assisted impregnation in catalyst preparation.

While previous literature indicates the effectiveness of K/NaX and K/NaY catalysts in transesterification of various oils, the catalysts in these studies were often prepared using different methods or evaluated on different oil substrates. Furthermore, there is a notable absence of studies detailing the preparation of K/NaX catalysts using ultrasound-assisted impregnation. Therefore, Kosawatthanakun et al. (2022) seeks to address this gap by comparing the physicochemical properties of K/NaX and K/NaY catalysts prepared via ultrasound-assisted impregnation from a potassium acetate buffer solution. Subsequently, their catalytic performance in the transesterification of palm oil will be evaluated under identical conditions. The results from carbon dioxide (CO₂-TPD) and the catalytic decomposition of 2-methylbut-3-yn-2-ol (MBOH) revealed that the calcined K/NaX had higher basicity than K/NaY. Both K/NaX and K/NaY are active in transesterification of palm oil, producing more than 94% of the biodiesel yields. However, the results from the second run indicated that K/NaX was a better catalyst due to the less leaching of potassium species into the produced glycerol and biodiesel.

Previous research highlights zeolite NaX as a promising support material for the transesterification reaction in biodiesel production. Consequently, this study aims to deepen the understanding of support properties by examining how the crystallinity of zeolite NaX affects the transesterification process of palm oil. The insights information are anticipated to significantly contribute to the design and improvement of catalytic performance in biodiesel production.

2.2 Development of nickel and copper catalysts in hydrogenation of methyl levulinate to gamma-valerolactone

2.2.1 Gamma-valerolactone production

Gamma-valerolactone (GVL) is an organic compound with the formula C₅H₈O₂. It is stable in water and in the presence of air, safe, biodegradable, and nontoxic chemical which can be utilized as a food additive; it can also be used as a green solvent for processing biomass, and as an efficient fuel additive (Choi et al., 2015; Manzer, 2014; Yan et al., 2015). Therefore, GVL has drawn considerable attention in

the last decade as a value-added chemical synthesized from lignocellulosic biomass (Dutta et al., 2019).

In general, GVL is primarily synthesized from levulinic acid (LA) and its esters using two main hydrogenation technologies: direct hydrogenation and transfer hydrogenation (Alonso et al., 2013; Kasar et al., 2019). The former traditionally utilizes various metal catalysts (Tan et al., 2015; Tian et al., 2015), such as palladium, ruthenium, rhodium, platinum, and rhenium (Abdelrahman et al., 2014; Galletti et al., 2012; Jones et al., 2016; Upare et al., 2011; Yan et al., 2009), in the presence of molecular hydrogen (H_2). The conventional approach for the production of GVL comprises the catalytic hydrogenation of LA followed by instantaneous lactonization of the γ -hydroxypentanoic acid (HPA) to GVL (Chen et al., 2017) as shown in Figure 2.2.

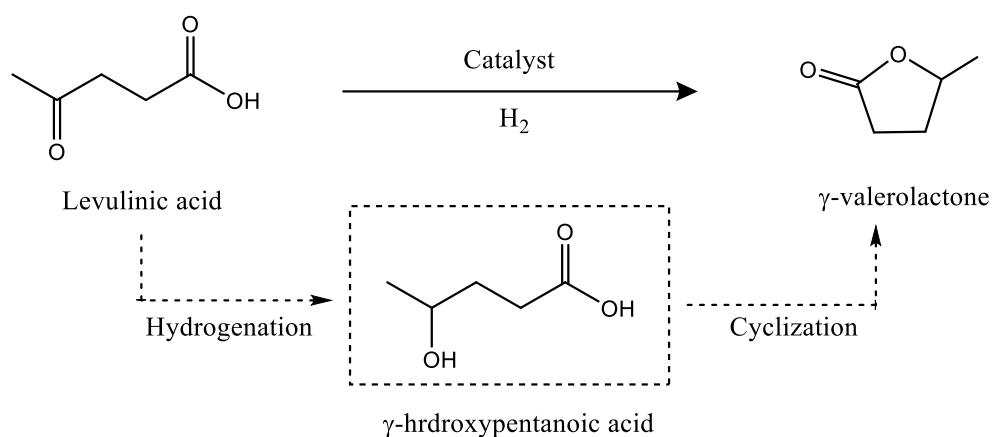


Figure 2.2 Production of GVL from LA by hydrogenation and subsequent cyclization of HPA to GVL.

However, this approach is associated with significant drawbacks, including the necessity of noble metal catalysts and the requirement for high-pressure H_2 , introducing economic challenges (Osatiashtiani et al., 2017). Conversely, an alternative transfer hydrogenation method, employing alcohols and formic acid (FA) as hydrogen donors instead of H_2 , has gained widespread adoption. While this approach mitigates the issues of corrosive formic acid (Chia et al., 2011), the utilization of alcohols as

hydrogen sources in catalytic transfer hydrogenation (CTH) of levulinic acid and its esters to GVL has emerged as a prevailing trend.

2.2.2 Alcohol as hydrogen donors

Alcohol serves as widely employed hydrogen donors in metal catalyzed CTH reactions. Secondary alcohols typically exhibit superior activity compared to primary alcohols in the dehydrogenation process over metal surfaces, facilitating efficient hydrogen transfer to the substrate. This heightened activity can be attributed to the enhanced stabilizing effect resulting from the presence of two alkyl groups, compared to one, which leads to inductive electron donation to the alpha-carbon of the alcohol during the dehydrogenation process (Aramendía et al., 2001; Panagiotopoulou et al., 2014; Scholz et al., 2013; Yang et al., 2013). Moreover, primary alcohols may irreversibly adsorb onto the metal surface. Thereby, the active sites become blocked by alkoxide species. In contrast, the adsorption of secondary alcohol, such as 2-propanol, breaks the $C_{\alpha}H$ and O-H bonds releasing of acetone (Geboers et al. 2014), as shown in Figure 2.3. Therefore, 2-propanol was chosen for this research.

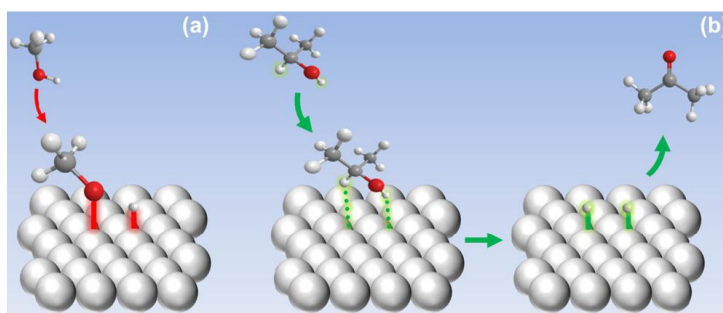


Figure 2.3 Interactions of (a) primary and (b) secondary alcohol with a Ni. Reprinted (adapted) with permission from (Geboers et al., 2014) Copyright 2013 Elsevier B.V.

2.2.3 Nickel and copper catalysts for hydrogenation of LA to GVL

There has been a notable development of solid heterogeneous and homogeneous metal catalysts for the reduction of levulinic acid, particularly focusing on noble metals such as ruthenium, platinum, and palladium. Within the category of

noble metal catalysts, Ruthenium catalysts have demonstrated exceptional performance and selectivity, achieving a 97% yield in the hydrogenation of LA in dioxane as a solvent at 423 K with 5 wt% Ru/C (Manzer, 2004; Upare et al., 2011). To reduce operational costs, non-noble metals like copper (Cu) and nickel (Ni) have been explored for this reaction (Shimizu et al., 2014; Upare et al., 2011; Zhang et al., 2015). These metals are of particular interest for catalytic applications, in the quest for the use of more earth-abundant elements, as well as for their activity in hydrogenation processes.

2.2.4 GVL production from the hydrogenation of methyl levulinate

Although, LA is the most common building block for GVL production. Ding et al. (2015) studied cellulose conversion to methyl levulinate (ML) via alcoholysis. They mentioned that when compared with LA, ML is a non-corrosive biomass derivative with a lower boiling point and viscosity. This makes ML more applicable for its separation from acidic media and more feasible for its use in further reactions. Li et al. (2017) demonstrated the production of ML with promising yields from various biomass-derived components, including cellulose, starch, sucrose, and monosaccharides, using heterogeneous zirconia-zeolite hybrid catalysts.

Alonso et al. (2013) showed their review on GVL production from ML. They mentioned that levulinate esters could be produced from hemicellulose or cellulose. For the first one, hemicellulose can be hydrolyzed to xylose and xylose can be further hydrolyzed to furfural. The hydrogenation of furfural can provide furfuryl alcohol. The alcoholysis of furfuryl alcohol can then give levulinate ester product. While the starting material is cellulose, glucose can be obtained from cellulose hydrolysis. The glucose can be hydrolyzed to hydroxymethylfurfural. It can be converted to LA via hydrolysis. Later, the esterification of LA can give levulinate ester product. After that, GVL can be produced from the CTH process which ML or its ester is hydrogenated to GVL.

Yang et al. (2016) investigated the production of GVL from ML using Cu-ZrO₂ catalysts at various temperatures. They observed that the highest GVL selectivity from ML precursor reached approximately 75% at 120 °C after 12 hours of reaction time. Another work by Sato et al. (2017), They also reported that conventional

hydrogenation of ML at 250 °C for 5 hours yielded approximately 82% GVL selectivity over Ni/Al₂O₃ catalysts.

Geboers et al. (2014) prepared alkyl gamma-hydroxypentanoates and gamma-valerolactone from alkyl levulinates by H-transfer catalyzed by Raney Ni and using 2-propanol as an H-donor and solvent. They found that, the reactivity order for the Alkyl gamma-hydroxypentanoates arranged as methyl < ethyl < 2-propyl < butyl levulinates, since a large alkyl residue is a better leaving group than a short one for nucleophilic substitution. Conversely, the results show the longer the alkyl residue, the lower the selectivity to gamma-valerolactone, as shown in Figure 2.4.

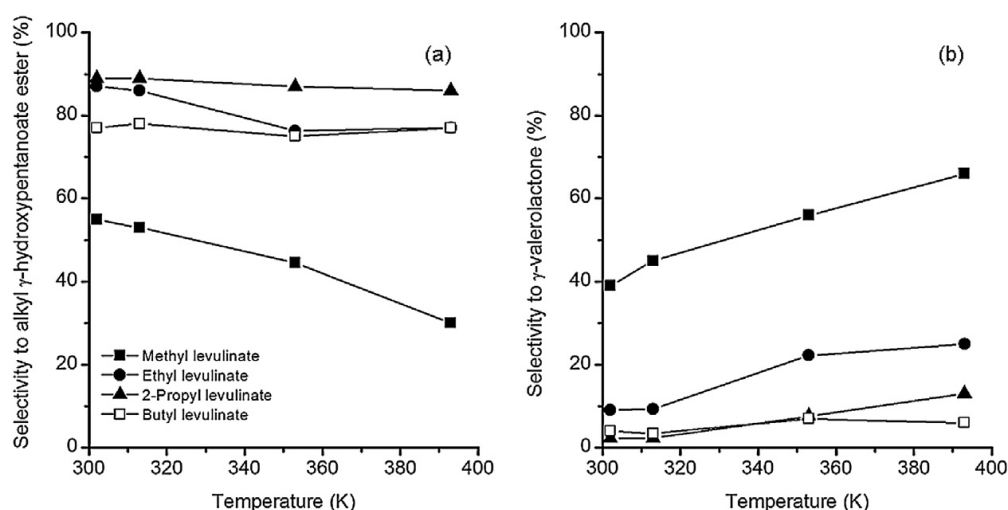


Figure 2.4 Selectivity to (a) alkyl gamma-hydroxypentanoates and (b) gamma-valerolactone in function of reaction temperature (at full conversion of substrate). Reaction mixture: substrate (1.4 mmol), Raney Ni (0.3 g, dry basis), 2-propanol (7 mL). Reprinted (adapted) with permission from (Geboers et al., 2014) Copyright 2013 Elsevier B.V.

Cai et al. (2017) studied the CTH of ethyl levulinate (EL) to GVL with 2-butanol and using 10Cu-5Ni/Al₂O₃ as a catalyst, providing a 97% yield of GVL in 12 h at 150 °C. This work focuses on the utilization of Ni and Cu catalysts for the production of GVL from levulinate esters. The effective synergy observed between Ni and Cu in bimetallic (NiCu alloy) catalysts enhances catalytic activity and stability. Notably, while Cai et al. exclusively investigated metal-supported catalysts and pure support materials, they

did not explore the individual performance of pure nickel or copper catalysts. Therefore, there exists an opportunity to extend the investigation into the promising realm of catalytic transfer hydrogenation within such a system.

Building upon the promising findings in CTH reported in earlier works for the production of valuable biochemicals from biomass (Li et al., 2016; Yang et al., 2016; Cai et al., 2017), this study aims to investigate the distinct roles of Ni and Cu in terms of catalytic activity and selectivity during the CTH process of ML to GVL. The focus is on a sole NiCu alloy catalyst, prepared, characterized, and tested without any supporting materials, utilizing 2-propanol as a hydrogen donor.

2.3 References

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