CHAPTER I
INTRODUCTION

1.1 Introduction

Global energy demand is projected to increase by 2% annually, with consumption predicted to double that of 2001 by 2050 (Li et al., 2016). The gradual decline in fossil fuels has prompted a shift towards biomass valorization as an alternative to secure energy and chemical supplies (Zhang et al., 2016). Liquid biomass, such as edible and non-edible oils, can be converted into biodiesel to replace fossil fuels (Lee et al., 2014). Solid biomass, such as lignocellulose, can be converted into high-value chemicals such as 5-hydroxymethylfurfural (HMF), levulinic acid (LA), dimethylfuran (DMF), and gamma-valerolactone (GVL) (Ennaert et al., 2016; Teong et al., 2014). Therefore, biomass conversion to value-added chemicals and fuels using heterogeneous catalysts is a key concern in green chemistry (Chen et al., 2017). This thesis focuses on the development of solid catalysts for producing two prominent bio-based chemicals: biodiesel or fatty acid methyl ester (FAME) from liquid biomass, and GVL from solid biomass. The first part examines the impact of zeolite NaX crystallinity on the catalytic performance of K/NaX catalysts in the transesterification of palm oil. The second part investigates the catalytic behavior of nickel (Ni) and copper (Cu) mono/bimetallic (NiCu) catalysts in the hydrogenation of methyl levulinate (ML) to GVL.

Biodiesel or FAME, is typically synthesized through the transesterification process of triglycerides present in liquid biomass, including vegetable oils or animal fats. This procedure involves the utilization of alcohol and a catalyst (Meher et al., 2006). Heterogeneous catalysts play a pivotal role in this process, where carbonates and oxides of alkali and alkaline earth metals are predominant. These catalysts are frequently supported on materials characterized by high porosity and surface area,

such as SiO_2, Al_2O_3, and zeolites (Perego et al., 2017; Refaat, 2011; Romero et al., 2005). Numerous studies have investigated the use of potassium-supported zeolite catalysts for transesterification reactions, highlighting the notable properties of Faujasite (FAU) zeolites like NaX and NaY, which possess large surface areas and exhibit high thermal stability. These characteristics make them particularly intriguing for biodiesel production processes (Kosawatthanakun et al., 2022; Rakmae et al., 2016; Supamathanon et al., 2011; Verboekend et al., 2016).

Previous studies have compared various support materials for their efficacy in catalyzing transesterification reactions, revealing that zeolite NaX serves as a highly efficient catalyst for this process. Therefore, the first part of this research aims to develop and enhance understanding of the K/NaX catalyst by investigating how the crystallinity of zeolite NaX influences the transesterification process of palm oil.

Solid biomass, lignocellulose, presents an avenue for the production of biofuels and valuable chemicals through biorefinery processes (Alonso et al., 2012; Huber et al., 2006; Kumar et al., 2009). Among these chemicals, GVL has garnered significant attention due to its renewable, non-toxic, and biodegradable properties, serving various roles as a solvent, fuel additive, and precursor for bio-based polymers (Fegyverneki et al., 2010; Horváth et al., 2008; Liguori et al., 2015). GVL is conventionally synthesized via hydrogenation, where LA or its ester undergoes transformation in the presence of H_2 gas (Serrano-Ruiz et al., 2010). However, this method presents significant drawbacks, including the necessity of noble metal catalysts and the requirement for high-pressure H_2, leading to economic challenges. Conversely, an alternative transfer hydrogenation method, employing alcohols and formic acid (FA) as hydrogen donors instead of H_2, has gained widespread adoption (Deng et al., 2009; Hengne et al., 2012). While this method addresses the challenges associated with corrosive FA, the use of alcohols as hydrogen sources in catalytic transfer hydrogenation (CTH) of LA and its esters to GVL has emerged as a prominent trend (Tang et al., 2014; Yang et al., 2013).

Various solid heterogeneous and homogeneous metal catalysts have been developed for LA reduction, particularly noble metals like ruthenium, platinum, and palladium (Galletti et al., 2012; Yan et al., 2009; Upare et al., 2011). To reduce

operational costs, alternative non-noble metals such as Cu and Ni have been explored (Shimizu et al., 2014; Zhang et al., 2015). In a study by Cai et al. (2017), the CTH of ethyl levulinate (EL) to GVL, utilizing 10Cu-5Ni/Al_2O_3 as a catalyst, yielded a 97% GVL yield in 12 hours at 150 °C. While the bimetallic catalysts of Ni and Cu showed high catalytic activity and stability, it's essential to note that Cai et al. focused exclusively on metal-supported catalysts and pure support materials, neglecting the performance of pure nickel or copper catalysts. Consequently, the second part of this research aims to investigate the catalytic activity and selectivity of Ni and Cu during the CTH process of ML to GVL. Utilizing a sole NiCu alloy catalyst without support materials, the catalyst was prepared, characterized, and tested using 2-propanol as a hydrogen donor.

1.2 References

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