Catalytic Process Development of Bio-BTX from Lignocellulose Derived Product: Preliminary Study Using Transition Metal Catalysts

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Abstract. Lately, the increase in biofuel production has simultaneously led to lignocellulose material disposal activities. As a waste produced by the biofuel industry, lignocellulose materials are not utilized fully yet due to their complex polymeric structure. As one compound of lignocellulose, lignin possesses the lowest economic value due to its recalcitrant nature. In this work, guaiacol as one of monomeric substance originated from lignin is used as a representative molecule to be valorized due to the existence of both hydroxyl and methoxy moiety groups in it. One important reaction of lignin monomeric substance (phenolic compounds) valorization is oxygen removal. Aromatic substances such as Benzene and Toluene are produced through oxygen removal from the guaiacol molecule. Hydrodeoxygenation of guaiacol is aimed to remove oxygen atoms from it. Though conventionally hydrogen for the Hydrodeoxygenation process is supplied by external molecular hydrogen, in this work it is supplied from hydrogen atom abstraction of methylcyclohexane. Therefore, in a one-pot catalytic reaction system, methylcyclohexane dehydrogenation is the sole hydrogen provider for subsequent hydrodeoxygenation of guaiacol and this novel concept of a circular hydrogen economy has been proven its feasibility through heterogeneous catalytic reaction schemes conducted in this work. Metal supported on zeolite beta is selected as heterogeneous catalysts to evaluate the feasibility of one-pot hydrodeoxygenation and dehydrogenation reaction. Of every catalytic reaction attempt, multiple products consist of alkylated phenol, phenol itself, and toluene are observed proofing the feasibility of this concept. Possible interaction of catalyst surface acidity and metal contents are also probed through the distribution of byproducts. Overall, sequential dehydrogenation and hydrodeoxygenation have been proven through a catalytic reaction catalyzed by metal-supported zeolite beta catalyst and this work can potentially pave the way for further application. Keywords: heterogeneous catalyst, Hydrodeoxygenation, dehydrogenation

1. Introduction

The race of biomass utilization has been affecting mankind dominantly. These days, the utilization of biomass-derived compounds such as sugar-based compounds, lignocellulose, and vegetable oils has attained significant attention from many governments and research groups[1]. There have been multiple attempts to use vegetable oils as substituents for fossil fuel. In this case, vegetable oils are being used as Fatty Acid Methyl Ester (FAME) and hydrodeoxygenation one[2, 3]. In particular, several tropical
countries have been pushing forwards their utilization of vegetable oils as fuel substituents including Indonesia. Based on data from the Indonesia Bureau of Statistics report in 2018, as one of the biggest palm oil producers, Indonesia has been capable of producing around 35 million tons of crude palm oil per year and will still be increased in the future[4]. This huge production rate of course has also increased the burden on the environment due to empty fruit bunch disposal.

Palm oil plantation empty fruit bunch itself can be categorized as lignocellulose material[5]. As a polymeric material, it consists of cellulose, hemicellulose, and lignin as three dominant polymeric materials [6]. Among the three aforementioned polymeric materials, only cellulose and hemicellulose have been utilized widely these days. For lignin polymeric material, even though its utilization has been researched widely until this day, its utilization is still hindered by its recalcitrant nature [7]. Typically, among numbers attempt lignin utilization, ones always start it by depolymerization and ended with monomer utilization.

For monomer utilization, some previous research results have shown several options for phenolic monomers utilization by removing their oxygen atoms through a catalytic hydrodeoxygenation (HDO) reaction scheme [8]. HDO reactions of lignin-derived compounds are well catalyzed either by noble metals [9] and transition metals [10]. Both types of metals have been reported to be capable of removing oxygen atoms by using molecular hydrogen supplied externally. Even though this scheme has been well-proven, several improvements related to its hydrogen supply can still be discovered.

Lately, some alternative hydrogen sources such as formic acid and alcohols have been discovered as promising ones[11]. Their utilization might reduce the operating pressure of hydrogenation thus benign reaction conditions can be achieved. Formic acid utilization is reported to be well-catalyzed by transition and noble metals whilst alcohol ones are well catalyzed by Lewis acid-base pair catalysts [12]. However, using both formic acid and alcohols produce side products such as carbon dioxide and ketones. Thus, the further discovery of different hydrogen sources is still viable until this day.

In this work, another attempt of using in-situ transfer hydrogenation is attempted through dehydrogenating selected hydrocarbon. One promising option is to conduct methycyclohexane (MCH) dehydrogenation in a one-pot reaction system simultaneously with hydrodeoxygenation of guaiacol. Guaiacol (GUA) itself is selected as a representative of monomers due to its hydroxyl and methoxyl functional groups. For methycyclohexane dehydrogenation, several noble metals and transition metal catalysts have been proven as good options[13, 14]. In a typical paraffin dehydrogenation, metal active sites are known to abstract hydrogen from corresponding paraffin [15]. Subsequently, those hydrogen atoms must be detached from metal active sites to reactivate catalyst metal active sites. Hydrogen atoms are then released from the reaction mixture. By considering the requirements of both paraffin dehydrogenation and hydrodeoxygenation, the later reaction might utilize abstracted hydrogen from dehydrogenated paraffin. Putting it into a simpler line, this research is aimed to investigate the feasibility of one-pot methycyclohexane dehydrogenation and guaiacol deoxygenation by utilizing abstracted hydrogen from methycyclohexane to cleave oxygen from the latter molecule. Effects of metal contents towards catalyst structure are probed through XRD and N2 physisorption techniques whilst product distribution of each reactions is used to probe effects of catalyst composition towards their performances. Thus in the end, optimum catalyst composition and plausible mechanism can be investigated for one-pot MCH dehydrogenation and GUA deoxygenation reactions.

2. Material and Methods

2.1. Catalyst Preparation
Catalyst preparation is started by zeolite beta (Si/Al = 25) impregnation with both Nickel Nitrate hexahydrate and Ammonium para molybdate as both Nickel and Molybdenum actives sites sources respectively. In a typical synthesis, controlled amounts of Nickel Nitrate hexahydrate and Ammonium para Molybdate are being dissolved in 50 ml of Deionized Water. Following precursors’ dissolution, H-Beta Zeolite is suspended to the precursors solution and sonicated briefly to ensure complete dispersion of precursors. The suspension is then moved into a 100 ml Teflon-lined hydrothermal autoclave and
heated at 150 °C for 24 hours for hydrothermal impregnation treatment. Subsequently, the cooled suspension is being dried in a drying oven at 100 °C for 24 hours to remove the water. As the final step, impregnated zeolite is then calcined at 500 °C for 3 hours in a muffle furnace to change the phase of metal precursors into their oxide forms. Prepared catalyst is then denoted as xNi-yMo/H-Beta (x and y stand for %-wt composition of Nickel and Molybdenum respectively) and analyzed with X-Ray Diffraction techniques in Bruker D8 Advance XRD to check its crystal structure. Catalyst porosity is also being analyzed using Quantachrome NOVAtouch series N2-physisorption equipment.

2.2. Catalysts performance test

In this work, MCH as molecular hydrogen source is mixed with guaiacol to form a homogenous solution. Into the previously mentioned solution, certain amount of Ni/Mo impregnated Beta is mixed so that Reactant/Catalyst ratio of 10 wt/wt is achieved. Into a 100 ml-autoclave reactor, reaction mixture is transferred and sealed to prevent it from escaping during elevated temperature reaction period. In order to remove air from sealed autoclave reactor, N2 gas is flown into autoclave reactor, purged for at least three times, and used to pressurized the reactor up to 20 bar. Reaction initiation is then started by heating the autoclave reactor until desired temperature and mixing the reaction mixture by using magnetic stirrer vigorously. After certain time reaction has been reached, reaction mixture is then cooled, filtered, and analyzed by using Shimadzu GC-MS to determine product distribution of each batch. More detailed workflow and product distribution calculation are explained in supporting information.

3. Results and Discussion

3.1. Characterization of Prepared Catalyst

Present crystalline phases of each constituent, either support and active sites, of prepared catalysts are being studied through wide-angle X-Ray Diffraction technique. From figure 1, it can clearly be observed that beta structures of zeolite beta are well preserved, proven by the appearance of double peaks at 7.9 and 22.5° 2θ diffraction angle. These results are well matched with numbers of previous works that use the same type of zeolite [16, 17]. Structure intactness has shown that during all steps of catalysts preparation, none to negligible change is applied to crystal structure of zeolite. As for active sites, NiO peaks at 50 and 70°[18] are not detected. From the same spectra, MoO3 peak at 40° that can be used to distinguished MoO3 [19] from beta structure is not detectable as well. Both NiO and MoO3 peaks absence in X-Ray Diffractogram indicates that both active metal sites are well dispersed so that their crystal structure are not detected [20].
From figure 2, it can be observed that the addition of metal precursors has reduced both specific surface area and total pore volume of zeolite support significantly. This phenomenon can be related to pore filling by metal active sites[21, 22]. In term of the porosity abatement, both 8Ni7Mo and 12Ni3Mo have similar specific surface area and adsorption-desorption isotherms. Aforementioned similarity is mostly caused by similar loading amount of metal precursors, 15%-wt total loading. Thus, porosity analysis of prepared catalysts has proven the existence of impregnated substances, in this case metal active sites. Furthermore, since in this work the total metal loading is fixed at 15%-wt, almost negligible difference between each loading is observed.

**Figure 1.** X-Ray Diffractogram of prepared catalysts (1,2: attributed peaks for beta structure, 3: MoO₃ peak, 4,5: NiO peaks).

**Figure 2.** N₂ adsorption-desorption isotherm of prepared catalysts.
3.2. Catalytic Performance of Prepared Catalysts

Catalytic conversion of both guaiacol (GUA) and methylcyclohexane (MCH) in a one-pot catalytic reaction system primarily consists of two subsequent reactions. The first reaction that happens in this scheme is hydrogen abstraction within the MCH ring so that aromatics compound can be obtained. Subsequently, abstracted hydrogen is used to cleavage either hydroxyl and methoxyl bonds within GUA. Thus, to present a clear and concise discussion, the one-pot reaction scheme is separated into the dehydrogenation aspect, oxygen atoms removal aspect, and synergistic aspect between hydrogenation and oxygen removal.

3.2.1. Dehydrogenation aspect. From the dehydrogenation side, it can be seen from figure 3 that mostly MCH molecules are being converted into methylated products, in this case, alkyl cyclopentane and methylated MCH. Dehydrogenated product, methyl cyclohex1ene is only found in 12Ni3Mo/H-Beta. The dominance of methylated product can be related to the presence of acid sites from the support[23, 24]. For the case of NiO supported on metal oxides, NiO reducibility with zeolite support is not within favorable range for MCH dehydrogenation, proven by the work of Song’s group in 2019[25]. In the previously mentioned work, it was observed that both Si and Al have poor metal-support interaction with NiO. Poor metal-support interaction causes NiO to have a high reducibility temperature, thus making it have a much slower turn over frequency in term of hydrogen abstraction due to the higher activation energy of NiO reduction[26]. This phenomenon explains the absence of dehydrogenated products in all catalysts except for 12Ni3Mo/H-Beta one. A considerable amount of NiO is required to catalyze the dehydrogenation of MCH. Oppositely when methylation and reforming reaction are being observed, pristine H-Beta has significantly higher conversion which leads to the MCH methylation and reformation. The existence of proton donors within the Beta zeolite framework in the aforementioned catalyst is not hindered by impregnated metal active sites, therefore acid catalyst has full capability of methylating and reforming MCH as cyclic paraffin. Even though methylation agent might come from cracked hydrocarbon, there is another resource that might also bring methylation agent. This aforementioned source is demethoxylated GUA discussed in the next section.

![Figure 3. Product distribution of MCH dehydrogenation reaction (265 °C, 20 bar N2, 4 h reaction time, R/C = 10, MCH/GUA = 10).](image)

3.2.2. Deoxygenation aspect In the case of one-pot reactions conducted in this work, Molybdenum Oxide active site has the role of cleaving oxygen atoms from GUA molecules. In a normal cycle, Molybdenum Trioxide is reduced to Molybdenum Dioxide. Following the formation of Molybdenum Dioxide, oxygen atom from oxygenate substances is then being captured and cleaved leaving Molybdenum Trioxide as an inactive site. Reactivation of Molybdenum Trioxide to
Molybdenum Dioxide is done by hydrogenating it. The aforementioned catalytic cycle is called as reverse Mars Van Krevelen mechanism[27, 28]. In this work instead of supplying pressurized hydrogen for Molybdenum active sites reactivation, abstracted hydrogen from MCH is used instead.

![Figure 4](image)

**Figure 4.** Product distribution of GUA deoxygenation reaction (265 °C, 20 bar N₂, 4 h reaction time, R/C = 10, MCH/GUA = 10)

From figure 4, it can be seen that demethoxylated products are more dominant compared to dehydroxylated ones. This phenomenon happens due to lower energy activation of methoxyl removal compared to hydroxyl[29]. Further discussing observed phenomena in figure 4, it is necessary for the discussion to be divided into impregnated and pristine H-beta catalyst since C-O cleavage undergoes different mechanism compared to reverse Mars van Krevelen[30]. For the metal impregnated ones, an increased amount of Molybdenum increases GUA conversion. Due to Molybdenum capability to abstract and cleave C-O bonds, the previous result is an apparent one due to Molybdenum active sites role for C-O cleavage. For the methylated ones, these products dominate in all catalysts and this phenomenon is mostly related to the existence of Brønsted acid sites on the catalyst surface. As been reported from previous work by Svelle’s group[31], C-O cleavage is possibly initiated by the protonation of aromatic rings of either MCH and GUA molecules to form carbenium ions. Subsequently, in the end, both methylated products and H₂O molecules are produced. Thus, in all zeolite beta-supported catalysts, the methylation reaction rate has the highest reaction rate. Another interesting aspect observed from figure 4 is that pristine H-Beta outperforms in all aspects compared to metal impregnated catalysts. A possible explanation regarding this phenomenon can be related to reducibility aspects of both Ni and Mo metal active sites. Both aforementioned metals have a notably high temperature of reduction[32, 33] compared to reaction temperature at 265°C. Apparently, instead of adding catalyst activities, metal addition is just clogging Brønsted active sites used for C-O cleavage. Thus, complete plausible mechanism of existed reactions within one-pot catalytic conversion of MCH and GUA can be drawn as following:
Figure 5. Complete proposed mechanism of one-pot GUA and MCH conversion.

4. Conclusion
Hydrodeoxygenation of Guaiacol by using hydrogen abstracted has been performed in a one-pot catalytic reaction system. Apparent lower performance of metal impregnated H-Beta can be related to bottleneck effect due to significantly lower rate of reduction of both metal active sites during reaction completion. Surprisingly, pristine H-Beta has better performance due to reactant accessibility to Brønsted active sites. Even though C-O cleavage undergoes different mechanism compared to Mo catalyzed one, during reaction completion time Brønsted acid site has proven its versatility during C-O cleavage. Nevertheless, at some certain amount of Ni active site, dehydrogenation of MCH is proven by product distribution analysis showing Nickel capability to abstract hydrogen from MCH and possibly with some catalyst modification, it can be subsequently used to cleavage C-O bond within oxygenates.

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