Hydrotreating of Free Fatty Acid and Bio-Oil Model Compounds: Effect of Catalyst Support

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Abstract

The effect of catalyst support on catalytic hydrotreating of free fatty acid and guaiacol as model compounds of bio-oil obtained from fast pyrolysis of seed oil cake and lignocellulosic biomass was investigated. Two different supported sulfide catalysts were synthesized and characterized, i.e., molybdenum sulfide on TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} supports. The catalytic performance was studied through catalytic hydrotreating of linoleic acid and guaiacol at 573 K. Hydrotreatment of linoleic acid and guaiacol showed that sulfide catalyst supported on TiO\textsubscript{2} enhanced catalytic activity and hydrodeoxygenation (HDO) pathway while Al\textsubscript{2}O\textsubscript{3} supported catalyst preferred hydrogenation pathway. The increment of free fatty acid in mixed model compounds from 2.5 wt\% to 20 wt\% hindered catalytic hydrotreating reaction and thus reducing catalytic activity enhancement effect of TiO\textsubscript{2} supported catalyst.

Keywords: Bio-oil upgrading ; hydrodeoxygenation ; free fatty acid ; sulfide catalysts ; TiO\textsubscript{2} support

1. Introduction

The development of renewable energy and environmentally friendly alternative fuel is of interest to researchers worldwide. Thailand as an energy imported country, constantly promotes renewable energy

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usage and production plan into the country’s energy policy, typically, renewable energy that can be produced from local biomass resources. Pyrolysis oil from fast pyrolysis of biomass converts lignocellulosic and bio-organic materials into biofuel could be a future of alternative renewable fuels. In general, pyrolysis oil also called bio-oil contains hundreds of organic compounds including hydrocarbons and oxygen containing compounds such as organic acids, aldehydes, ketones and phenolics which cause bio-oil to have low heating value and low stability [1-2]. Thus, pretreatment or upgrading of bio-oil to reduce oxygen containing compounds via catalytic hydrotreatment is a crucial process to improve bio-oil fuels properties and stability.

Catalytic hydrotreating process is a promising path to upgrade bio-oil [3]. In this study, partial hydrotreatment over heterogeneous catalysts is focused for investigation of catalyst support effect on hydrotreatment of bio-oil model compounds. The oxygen and reactive functional groups such as carbonyl group in bio-oil models are partially removed to increase bio-oil stability via hydrodeoxygenation (HDO), hydrogenation (HYD) and decarboxylation/decarboxylation (DCO) processes [4]. Many commercial hydrotreatment catalysts such as CoMoS/Al2O3 or NiMoS/Al2O3 catalysts for hydrodesulfurization (HDS) are suitable for hydrodeoxygenation process as well. Study on molybdenum sulfide catalysts for HDO of bio-oil model using non-traditional support or unsupported MoS2 catalysts had been reported [5-6].

Besides lignocellulosic biomass, bio-oil can also be produced from seed oil cake residue which contains triglycerides and free fatty acids. In this study, guaiacol (2-methoxyphenol) was used as a model compound representing lignin derived bio-oil and linoleic acid as a free fatty acid model. Various amount of linoleic acid from 2.5 wt% to 20 wt% was added to investigate the catalysts performance. The effect of catalyst support on hydrotreatment of bio-oil and free fatty acid model when hydrotreated together was investigated using a non-traditional CoMo sulfide catalyst supported on TiO2 which had known for its great electron transfer property and activity enhancement. The catalytic activity and product selectivity from hydrotreatment over CoMoS/TiO2 and CoMoS/Al2O3 are transcribed from reactant conversion, product selectivity and degree of hydrodeoxygenation (%HDO).

2. Experimental

2.1. Catalyst preparation and characterization

The molybdenum catalysts and supports were prepared via sol-gel method using aluminium isopropoxide (Acros Organics™, 98+%) and titanium (IV) isopropoxide (Acros Organics™, 98+%) precursors for catalyst supported on Al2O3 and TiO2, respectively. After sol-gel, catalyst gel was dried at 318 K for 48 h and calcined in air at 823 K for 4 h. The calcined molybdenum supported catalysts were then sieved in the range of 250-600 μm followed by incipient wetness impregnation of cobalt (II) nitrate aqueous solution to obtain CoMo catalysts. After dried at 318 K for 48 h and calcined at 823 K for 4 h, calcined CoMo catalysts were sulfided with 5%H2S/H2 at 673 K for 4 h just before hydrotreating experiment. All calcined catalysts were characterized for surface area, pore volume and pore diameter according to Brunauer Emmett Teller (BET) technique based on nitrogen adsorption isotherms. Temperature programmed reduction of hydrogen (H2-TPR), temperature programmed desorption of ammonia (NH3-TPD) and Temperature programmed pulse adsorption of nitric oxide (NO-Pulse) for reducibility, acidity and active site evaluation were conducted in BELCAT B equipment.

2.2. Catalytic hydrotreatment of free fatty acid and bio-oil model compounds

The hydrotreating reaction of guaiacol and linoleic acid was carried out in a 25 ml microreactor (Parr model 4590). Each batch was filled with 20 g of feedstock, which is a mixture of guaiacol, linoleic acid
and dodecane as solvent with 0.4 g of sulfide catalyst. The reactor system was closed and to avoid any air contamination, N\textsubscript{2} gas was flowed through the reactor with feedstock for 10 min. Then system was flushed with H\textsubscript{2} gas three times before H\textsubscript{2} was filled to reach an initial hydrogen pressure of 4 MPa. Hydrotreating temperature was set at 573 K for 1 h reaction time. Investigation of catalytic hydrotreatment performance was performed using two supported catalysts, cobalt molybdenum sulfide on TiO\textsubscript{2} (CMT) and cobalt molybdenum sulfide on Al\textsubscript{2}O\textsubscript{3} (CMA). A set of feedstock with a fixed 5 wt% guaiacol and various linoleic acid loading at 2.5, 5, 10 and 20 wt% were hydrotreated. After the reactor was cooled down to room temperature, the liquid product was collected and analyzed by GC-MS and GC-FID equipped with a non-polar dimethylsiloxane capillary column (DB-1, 60m × 250μm × 0.1μm and HP-1, 60m × 250μm × 0.25μm, respectively). The conversion of guaiacol and linoleic acid reactants were calculated from the ratio of relative amount of reactants in liquid product over initial amount of reactants. The hydrodeoxygenation degree (%HDO) was calculated from the ratio of relative amount of oxygenates in liquid product over total products.

3. Results and Discussion

3.1. Catalyst preparation and characterization

Two calcined catalysts, cobalt molybdenum on TiO\textsubscript{2} designated as CMT and cobalt molybdenum on Al\textsubscript{2}O\textsubscript{3} named CMA were characterized by BET technique to determine surface area. The results of surface area, pore volume and pore diameter from BET analysis are shown in Table 1. CMA has more surface area at 219.45 m\textsuperscript{2}/g compared to CMT which has lower surface area at 91.07 m\textsuperscript{2}/g. Furthermore, CMA exhibits larger pore volume but with smaller average pore diameter of 3.86 nm. Al\textsubscript{2}O\textsubscript{3} support is an amorphous gamma-phase and known for its high surface area and stability. On the other hand, TiO\textsubscript{2} support prepared by sol-gel method is mainly an anatase phase and has semi-crystalline property which resulted in less surface area compared to amorphous gamma-Al\textsubscript{2}O\textsubscript{3}.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Average pore diameter (nm)</th>
<th>NO absorbed (μmol/g)</th>
<th>NH\textsubscript{3} adsorbed (surface acidity) (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMA</td>
<td>219.45</td>
<td>0.21</td>
<td>3.86</td>
<td>8.04</td>
<td>1.04</td>
</tr>
<tr>
<td>CMT</td>
<td>91.07</td>
<td>0.18</td>
<td>7.89</td>
<td>3.07</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The result from H\textsubscript{2}-TPR analysis was used to evaluate catalyst reducibility. As depicted in Fig. 1(a), CMT shows three peak zones with a low temperature peak identified as a reduction peak of Mo\textsuperscript{6+} to Mo\textsuperscript{4+}. Therefore, CMT catalyst is easier to reduce than CMA indicated by lower initial reduction temperature of Mo\textsuperscript{6+} around 523 K compared to CMA at 603 K. CMT also exhibits larger H\textsubscript{2} consumption as shown in Fig 1 (a). The low temperature reduction peak under sulfidation could be assigned to the reduction of surface MoO\textsubscript{3} to MoS\textsubscript{2} active sites where the coordinative unsaturated sites (CUS) are created.
The plot of NH$_3$ desorption profile is shown in Fig. 1(b) and the NH$_3$ adsorption result of both catalysts is listed in Table 1. CMA catalyst displays two desorption peaks around 443 K and 873 K referred to weak and strong acid sites, respectively. Surface acidity as represented by NH$_3$ adsorbed amount of CMA is approximately three times as much as CMT, indicating Al$_2$O$_3$ is more acidic than TiO$_2$ and this result is still in agreement to the acidic nature of Al$_2$O$_3$ and TiO$_2$ supports.

NO chemisorption experiment used to evaluate sulfide active site of molybdenum sulfide catalysts is calculated and reported in Table 1. This result indicated that CMA catalyst contains more MoS$_2$ active sites according to higher NO adsorbed on CMA at 8.04 µmol/g compared to CMT at 3.07 µmol/g.

3.2. Catalytic hydrotreatment of free fatty acid and bio-oil model compounds

The conversion of guaiacol over CMA and CMT catalysts displayed reaches 100 %, whereas linoleic displays 100% conversion with 2.5 wt% linoleic acid and then decreases with increasing linoleic acid as shown in Fig. 2(a). This indicates the deactivation caused from the steric hindrance effect of linoleic acid on MoS$_2$ active site. The high HDO activity of 2.5 wt% linoleic acid shows in Fig. 2(b), while HDO activity of guaiacol is lower. However, HDO of both linoleic acid and guaiacol decreases with increasing linoleic acid because MoS$_2$ active site was suppressed. %HDO of guaiacol over CMA is less affected by increment of linoleic acid comparing to CMT due to larger surface area of CMA.
The liquid product from hydrotreatment of 5 wt% guaiacol and 2.5 wt% linoleic acid over CMT and CMA at 100% conversion was analyzed. It has been proposed that guaiacol reacts through direct deoxygenation (DDO) or hydrogenation (HYD) pathways [7]. DDO pathway yields aromatic products such as benzene through direct C-O bond breaking. On the other hand, HYD pathway yields mainly cyclohexane and cyclohexene products. The product selectivity displayed in Fig. 3(a) and Fig. 3(b).

For HDO of guaiacol, CMT catalyst yields more aromatic products than CMA indicated that CMT has high selectivity toward direct deoxygenation (DDO) pathway. This is due to the effect of TiO$_2$ support which acts as an electronic promoter to enhance generation CUS active sites for hydrodeoxygenation pathway [8]. CMA catalyst yields not only naphthenes or phenol but also methyl substituted products such as methylcyclohexane and cresol via methylation process catalyzed by acidity on CMA surface.

Hydrotreatment products of linoleic acid include C-17 hydrocarbons and C-18 hydrocarbons as major products. C-17 hydrocarbons were obtained via de carbonylation/decarboxylation processes with CO or CO$_2$ was removed. On the contrary, HYD process yields C-18 hydrocarbons through removal of H$_2$O via CUS active sites. As shown in Fig. 3(b), CMT catalyst yields C-18 hydrocarbons more than C-17 hydrocarbons referred that CMT has preferred toward HYD and HDO [9]. CMA catalyst yields remained saturated acid (i.e., stearic acid) and esters indicating that CMA preferred toward HYD and esterification.

Moreover, increment of linoleic acid to 5 wt% limits direct deoxygenation (DDO) of guaiacol to aromatics over CMT as a resulted of limited access to sulfide active sites on CMT. However, HYD and methylation of guaiacol over CMA continues and produces naphthenes, methyl-substitutes and cresol as displayed in Fig. 3(c). For linoleic acid, HYD over CMA still actives but HDO over CMT is suppressed. Fig. 3(d) showed esters products from hydrotreatment over CMT. This could be resulting from thermal or acid catalyzed reactions and confirmed that CUS active site is deactivated.
4. Conclusion

The CMT exhibited higher catalytic activity than CMA for hydrotreatment of both free fatty acid and guaiacol bio-oil model compounds. The catalytic activity was enhanced through an electronic effect of TiO₂ support resulted in high selectivity towards DDO of guaiacol and HYD/HDO of linoleic acid. CMA catalyst has high surface area with acidity surface leading to hydrogenation and methylation pathways of guaiacol. In addition, decarbonylation/decarboxylation was preferred pathways for hydrotreatment of linoleic acid over CMA. Moreover, the increase in linoleic acid hindered hydrotreatment process in both CMT and CMA catalysts. CMT with low surface area was affected greatly by linoleic acid causing blockage and suppression of CUS active sites. At 5, 10 and 20 wt% linoleic acid, esterification reaction was dominated. Decrease in %HDO was due to the inhibition of sulfide active sites by reactants resulting in decrement of oxygen removal ability from transportation limitation.

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