Potential Activity Evaluation of CoMo/Al_2O_3-TiO_2 Catalysts for Hydrodesulfurization of Coprocessing Bio-oil

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Abstract
This research evaluated a catalyst activity for hydrodesulfurization (HDS) of a petroleum fraction and the mixture of partially hydrodeoxygenated bio-oil (HBO), which was hydrodeoxygenated woody tar (HWT) and the petroleum fraction, which was light gas oil. As results, 340ºC of reaction temperature and 2 hours of reaction period provide positive influence on the catalyst activity. Oxygen and nitrogen compounds in bio-oil exhibit an inhibiting effect on the HDS. Synthesized catalysts supported on titanium-rich and pure titania carriers indicate higher activity than those supported on pure alumina, since TiO_2 acts as an electronic promoter in catalysts. The electronic promotion of Mo by Ti has a limitation, accordingly, 310CoMoAT (1:0.75) catalyst presents the best catalytic behavior. The approach from this research can contribute a direction for further improvement of co-processing bio-oil productions as a sustainable fuel invention.

Keywords: *Coprocessing bio-oil, Hydrodesulfurization, Bio-oil woody tar, Hydrodeoxygination, Mixed oxide catalyst support*

1 Introduction

Increasing Asian population and energy consumption have surged continuously in the world and the increases influence many countries; including Japan and Thailand, to search for alternative sources of renewable energy. Consequently, research on a bio-oil production has gained significance with the prospective to solve the fossil fuel resource running out and also environmental problems, especially to reduce greenhouse gas emissions. Biofuel is one of recent growing interests and it has been strongly recommended as an alternative fuel. Biofuels are impelling food prices and starving underprivileged people. From those effects, researchers pay more attention to a second generation of biofuels which does not impact a food supply. One of biofuel productions is conversion of biomass into bio-oil by fast or slow pyrolysis followed by a suitable bio-oil upgrading process. The bio-oil products resulting from a biomass pyrolysis possess high oxygen contents that include three main families of compounds: (1) small acids, aldehydes and ketones, (2) sugar-derived

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compounds and (3) lignin-derived phenolics [1,2]. Bio-oil typically contains almost 15-40 wt% of oxygen compounds [3].Those oxygen compounds affect bio-oil to have some undesirable properties, such as; high viscosity, non-volatility, poor heating value, corrosiveness, immiscibility with fossil fuels, thermal instability and a tendency to polymerize during storage and transportation [4]. Accordingly, it is necessary to reduce the oxygen content to be lower than 2 wt%, as same as the oxygen content in traditional petroleum [5]. Hydrodeoxygination (HDO) which is a bio-oil upgrading technology is the major reaction for eliminating oxygen. The upgrading technique interest for this project is two-step upgrading bio-oil, since it is an economical technique. Initially, bio-oil is partially hydrodeoxygenated; however, the oxygen content in bio-oil is unsatisfied for an oil refinery process. Secondly, a coprocessing of the HBO and petroleum fraction in a HDS process can be applied for an oil refinery plant. The petroleum fractions are known to contain high amounts of sulfur compounds causing environmental problems during the combustion of petroleum fractions. The elimination of sulfur is, therefore, extremely important. HDO process is also required for the renewable gasoline and diesel productions. The HDO typically takes place during the hydroprocessing of petroleum fractions as well as HDS, the saturation of olefins or aromatics, hydrodenitrogenation (HDN) and hydrodemetallization [6].

This research target was assigned to work on the investigation of the HDS reaction of a petroleum fraction and the mixture of HBO and a petroleum fraction. An inspection of HBO reaction occurring in the duration of HDS was also manipulated. The main objective of this work was to evaluate the catalyst activity for HDS reaction of light gas oil (LGO) which is a diesel fraction on and the mixture of LGO and HWT, collected from middle distillation (HWT-MD). Catalysts used in this project are in the groups of NiMo and CoMo, since conventional NiMo and CoMo on the surface of alumina are typically used for deep HDS [7]. In order to improve a catalyst activity for HDS, the research addressed a synergistic effect of mixed oxide supports on the HDS catalyst activity. The oxide support used in this research is an alumina/titania support, since alumina and titania have attracted curiosity in the vision of a higher HDS activity [8].

2 Experimental Methodology

2.1 *Catalysts*

Eight types of catalysts utilized in the experimental work were a sulfided cobalt-molybdenum and a nickel-molybdenum supported on alumina or/and titania catalysts. Six prepared catalysts were prepared through a sol-gel method. The in-house catalysts diverged ratios of alumina and titania supports to monitor an influence of mixed oxide support on HDS and HDO activities. The other two catalysts (KF 752-1.5E and KF 846-1.3; Nippon Ketjen Co., Ltd.) were commercial catalysts.

2.2 *Reactants*

Reactants used for the HDS process comprised two types of oil. The first oil was LGO which represents a petroleum fraction and the second one was LGO-HWT-MD (Hydrodeoxygenated woody tar-middle distillation) used for observing coprocessing bio-oil. The HWT-MD manufacture could be divided into two main parts. First, woody tar crude oil was partially hydrodeoxygenated in a slurry reactor at 400ºC and under 7.07 MPa of hydrogen pressure. The partially HWT was collected and then the product was distillated. Distillate products were light gas, middle distillate (HWT-MD, at 220-225ºC) and a residual. LGO-HWT-MD was created from the mixture of 80 wt% of LGO and 20 wt% of HWT-MD.

2.3 *Sulfidation process*

To activate all catalysts into a sulfide form, the catalysts were mixed with LGO and Dimethyl disulfide (DMDS) in a quartz tube covered by a small quartz capillary tube. The quartz tube was inserted into metal 80 mL-reactors at room temperature and then hydrogen gas was initially pressurized into the reactors at 3 MPa. Following, reactors were inserted into a tube furnace and swing mixer which was rose temperature up to 350ºC. The temperature of the system was ramping from room temperature to 350ºC in approximately an hour and remaining constant at 350ºC for 3 hours. Subsequent to sulfidation, reactors were removed from the furnace and cooled down until reactors' temperature reached room temperature. Gas over LGO in the reactors was collected into a sample bag and then the gas volume check was carried out. The sulfided catalysts were repeatedly washed with hexane and dried under nitrogen atmosphere via vacuum filtration process. Please note that the sulfided catalysts must be used rapidly after drying to prevent an oxidation reaction between the catalysts and oxygen in the air. This oxidation could affect on a catalyst activity. Finally, the catalyst products were kept in sample bottles and weighed to check an absolute amount of catalysts.

2.4 *Hydrodesulfurization process*

LGO and LGO-HWT-MD were carried out in batch reactors. Sulfided catalysts with 0.2000 g. were introduced into 50 ml-microautoclave reactors and the reactors were filled with 5.00 g of a reactant. The components inside the reactor were purged by 1.5 MPa of hydrogen gas, subsequently the reactors were pressurized up to an initial pressure under 5 MPa. Please note that the hydrogen gas quantity before the reaction must be recorded to observe the hydrogen consumption during HDS reactions. Two sets of reactions were undergone in the same period using the swing tube furnace controlled by an electronic temperature controller. HDS reactions were operated under 320ºC and 340ºC and allowed to proceed for 1 and 2 hours. Afterwards, reactors were removed from the furnace and cooled down to room temperature. Gas in the reactors was collected for a volume measurement and further analyses. Liquid products in the reactors were purged by 3 MPa of nitrogen gas pressure. The nitrogen gas had been mixing for 15 minutes in swing mixer to ensure that hydrogen sulfide gas or undesirable gases would be purge from the liquid products. Catalysts in liquid products needed time to precipitate at least 20 minutes. Lastly, liquid products were removed from reactors, separated from catalysts and filtered via a vacuum filtration technique.

2.5 *Quality and quantity analyses*

All filtered oil products were analysed by a gas chromatography technique using a mass spectrometry detector (GC-MS; Hewlett Packard HP 6890), a flame ionization detector (GC-FID; Agilent 6890N) and a sulfur chemiluminescence detector (GC-SCD; Agilent 04AA9185) to evaluate catalyst activities. The three detectors were applied for different propositions. GC-MS was used to identify chemical compounds in products, whereas GC-FID was used to determine hydrocarbon compounds in products. In the case of the GC-SCD, the detector utilized for defining amounts of sulfur compounds remaining in products. Furthermore, a nitrogen-sulfur analyser was also applied to analyse the quantity of nitrogen contents in products and to compute %HDN.

3 Results and Discussion

3.1 *Catalyst sulfidation*

Catalysts for hydrotreatment processes in refineries to eliminate heteroelements and polyaromatics from petroleum feedstocks are primarily prepared in the form of highly dispersed molybdenum oxide and promoters. For example, the conventional catalysts for HDS of diesel fractions are the Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3. Since the catalysts are regularly prepared in an inactive form, they are subsequently exposed to a sulfiding atmosphere to be converted into the active form. The catalysts can be activated in the first step by a sulfiding agent either directly inside hydrotreating reactors or preimpregnation with polysulfides followed by a subsequent reactivation of the catalyst inside reactors. Hydrogen sulfide (H_2S) has usually been used for catalysts sulfidation, H_2S is, however, limited to laboratory scale applications. For that reason, some researchers turned to use organosulfide agents, such as dimethyldisulfide (DMDS: CH_3-S-S-CH_3) for the sulfidation of HDS or HDO catalysts. The use of DMDS can increase HDS performance, particularly CoMo/Al_2O_3 [9]. This research also chose DMDS as a sulfiding reagent for the catalyst sulfidations. After the sulfidation, catalysts were transformed to the sulfided form: Co-Mo-S or Ni-Mo-S. They will have a strong interaction with support if they have low degree of sulfidation. In the case of fully sulfidation, they will be held on the support surface by van der Waals forces. During the sulfidation hydrogen molecules interact with bridge sulfur of the Mo catalyst promoted by Co or Ni and then the heterolytic dissociation of the H_2 occurs. In the heterolytic dissociation process a -SH group and hydride hydrogen bond with the atom of Co or Ni.

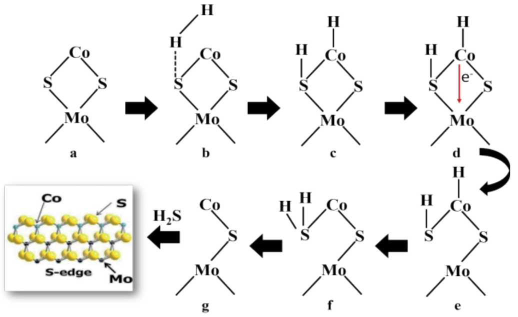

Figure 1: Mechanism of H_2 interaction during sulfidation process [10].

Kogan proposed that the hydride hydrogen begins a relocation of an electron from the atom of Co or Ni to Mo atom and then Mo accepts the electron [10]. This action causes Mo-S bonds declining and rupturing. Hydride hydrogen concurrently becomes positive and departs from Co atom for bonding sulfur atom. Mo-S bond weakens and breaks and then the formation of H_2S takes place. This process becomes a cycle until the sulfidation is complete (Figure 1).

3.2 *Hydrodesulfurization*

Hydrotreating processes of a diesel fraction are extensively practiced in an petroleum industry and one of the major interests in hydroprocessing is the removal of sulfur atoms via HDS. Examples of S-compounds found in diesel fraction are thiols (mercaptans), sulfides and disulfides, thiophenes, benzothiophenes and dibenzothiophenes. During the sulfidized catalyst is under hydrogen atmosphere in the period of HDS, a sulfur atom in the sulfidized catalyst surface reacts with hydrogen atoms; and then H_2S is produced. Afterward, an anion vacancy site, which is an active site for HDS, is created. The sulfur elimination in a sulfur compound begins with nucleophilic attack by basic sulfur on the vacancy site. The C-S bond of the S-compound is cleaved and then a sulfur atom is remained at that vacancy. In terms of heterocyclic compounds, a rearomatization process will take place after the nucleophilic attack (Figure 2).

3.3 *Hydrodeoxygenation*

One of the possible operating options for the production of advanced biofuels is the coprocessing

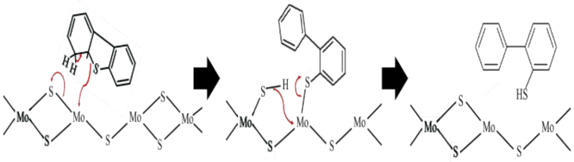

Figure 2: The HDS of dibenzothiophene on MoS_2-based catalyst [9].

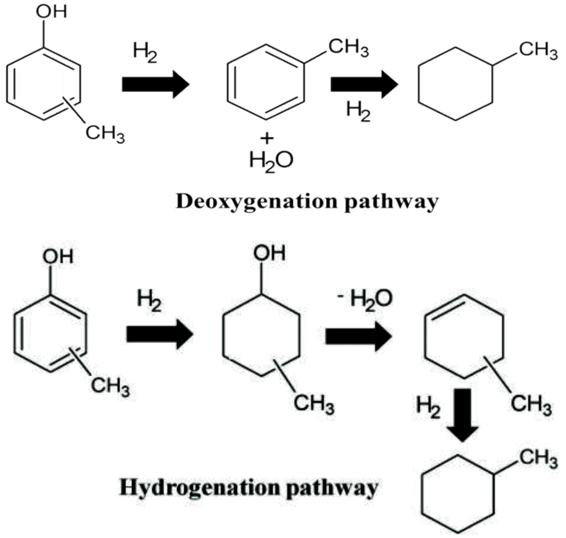

Figure 3: Schematic of cresol HDO mechanism via a DDO and HYD pathways [12,13].

of partially HBO in standard refineries, however; the properties of the HBO have not been appropriate for the coprocessing yet. Previous research suggested that the HBO should be sent to the distillation tower where the fractions could be diluted in different refinery cuts before sending to advance processing [11].

Since cresol is one of the main oxygen compounds in HWT, the quantity of cresol was determined for the investigation of the HDO performance. The cresol can also convert from guaiacol throughout the HDO hydrotreating process. Cresol included in HWT-MD has three isomers: meta-cresol, para-cresol and ortho-cresol. Many research papers reported that the isomers established the following order of HDO reactivity: meta > para > ortho [4]. The HDO of cresols is known to proceed by two pathways: a hydrogenation (HYD) and a direct deoxygenation (DDO) as exhibited in Figure 3. In the case of meta-cresol, it can transform to phenol during HDO process.

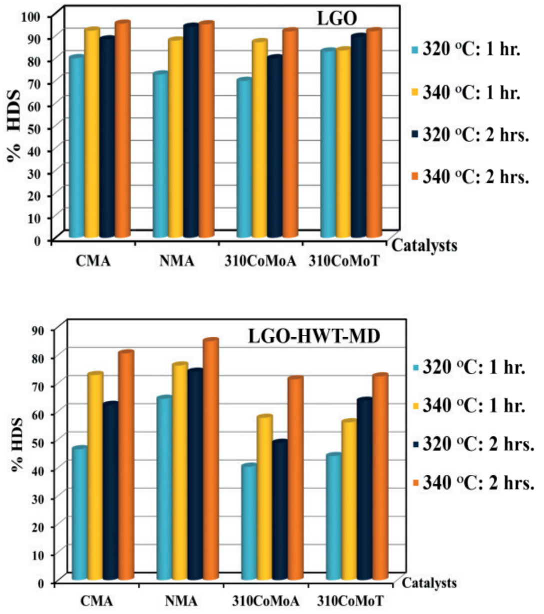

Figure 4: Relation between %HDS and reaction temperature of LGO and LGO-HWT-MD.

3.4 *Effects of reaction temperature and time on catalyst screening*

In this research, 320ºC and 340ºC of reaction temperatures were controlled to study the effect of reaction temperature on %HDS, %HDO and %HDN for catalyst screening. (Figure 4 and Figure 5)

The 320ºC of temperature was initially used for the HDS process with the period of 1 and 2 hours. Please note that reaction temperature at 320ºC was selected from earlier work of JICA's project demonstrated the effects of temperature on the HDO and HDS performances of bio-oil models. The %HDS values for HBO vary from 84% to 35% depending on catalyst types. To ensure that 320ºC was suitable for the hydrotreating processes of the coprocessing bio-oil, %HDO was also investigated. The HDO reaction was observed, because it may cause HDS restraining or competitive to presence of HDS. Low %HDO results of LGO-HWT-MD (Figure 5) indicated that 320ºC was not proper for the most of catalysts, especially the prepared catalysts. These results agree with the information from literature which stated that the HDS reaction of LGO is characteristically performed at 330-390ºC of reaction temperature and 3.0-5.0 MPa of total pressure, while HDO of bio-oil is typically operated under 330-350ºC [14]. Hence, temperature for HDS process was increased to 340ºC to enhance the performance of HDO. As anticipated, higher operating temperature enhances %HDS as well as a reactivity of HDS (Figure 4).

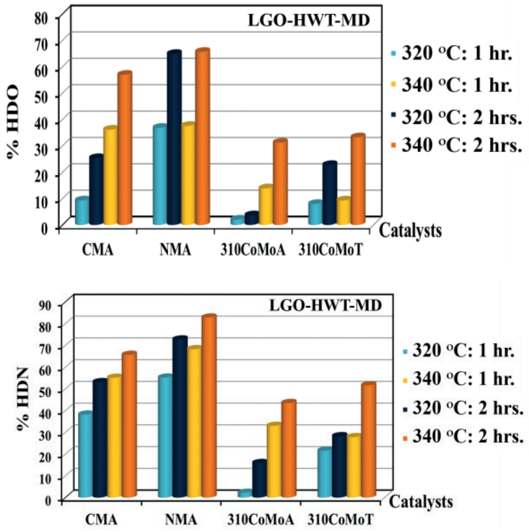

Figure 5: Relation between %HDO or %HDN and reaction temperature of LGO-HWT-MD.

Increasing reaction temperature to 340ºC may drive Mo-S bonds and C-S bonds in S-compounds rupturing, forming new bonds and creating new carbon compounds (Figure 2). Results of kinetics correspond to the tendency for %HDS (Figure 6).

$$-\frac{dS}{dt} = kS^{n} \qquad (1)$$

The deviations from regression approach (according to equation (1) and (2)) were attributed to rate constant determination that conveyed the HDS performance.

The abbreviation S means sulfur content which can be separated into S_p (sulfur content of product) and S_f (sulfur content of feed), where *n* represents apparent reaction order. The symbol *k* means rate constant and *t* is reaction time. The 2.25 of reaction order kinetics was used in the calculation of the rate constants and plots from this reaction order revealed a good deviation, especially for LGO-HWT-MD.

$$k = \frac{\left(\frac{1}{S_p{}^{(n-1)}} - \frac{1}{S_f{}^{(n-1)}}\right)}{\frac{(n-1)}{t}} \qquad (2)$$

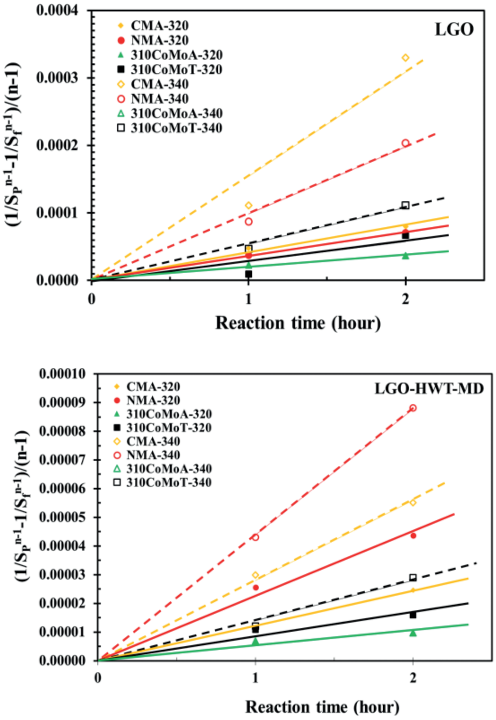

Figure 6: Relative reactivity of HDS reactions calculated from 2.25 of a reaction order.

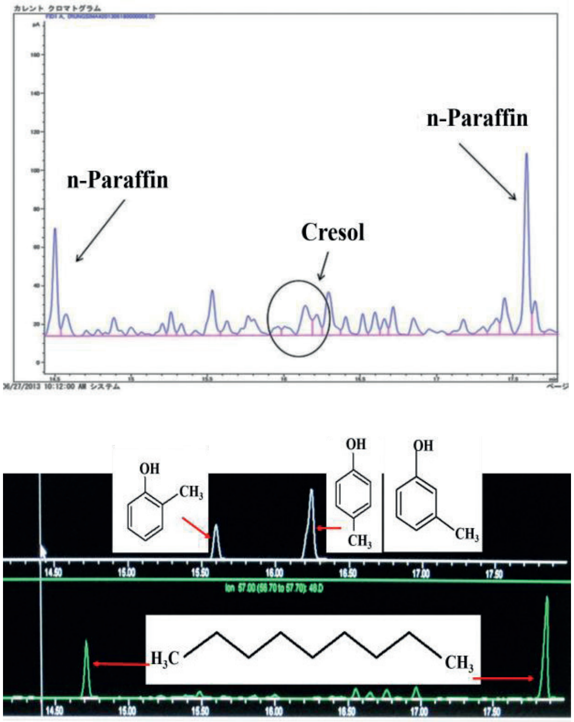

Figure 7: Spectra of cresol and n-paraffins created from GC-FID and GC-MS.

The quantity of dibenzothiophene (DBT), 4-methyldibenzothiophene (4MDBT) and 4,6-dimethyldibenzothiophene (46DMDBT) were also observed through GC-SCD spectra. The spectra indicated that the amount of those sulfur compounds in all samples decreased with the increase in reaction temperature and time. At 340ºC of reaction temperature, %HDO of all reactions significantly increased and %HDO of some reactions increased higher than two times compared to the reaction running at 320ºC (Figure 5). An interesting point was found from GC-FID and GC-MS. The spectra of cresols from Figure 7 show that the quantity of o-cresol is lower than the quantities of p-and m-cresol. The result concurs with information mentioned in 3.3. The low o-cresol quantity appears to be associated with an entropic or steric effect [13].

HBO also contains N-compounds, for instance, quinoline, tetrahydroquinoline, indole and indoline and it is important to deduct them to be lower than 1%. HDN reaction occurring in the period of HDS process was also observed. The reaction temperature positively affects on HDN reaction. %HDN increases in a range of 5-28% depending on catalyst kinds as well as the temperature effects on HDN and HDO reactions (Figure 5).

3.5 *Effects of HDO and HDN reactions on HDS reaction*

%HDS values demonstrated that LGO, which was diesel fraction, gave a greater %HDS (85-93%) than the one of LGO-HWT-MD (65-84%). In actuality, HDO and HDN reactions are suppressed in the presence of a sulphur having functionality, either in the same or in a separate molecule with the oxygen and nitrogen functionalities [15]. It implies that HDO and HDN reactions account as competitive for HDS, since oxygen and nitrogen compounds necessitate similar anion vacancy site to sulfur. The purpose of eliminating oxygen and nitrogen atoms from the reactants is, therefore, required. Oxygen and nitrogen compounds would inhibit the HDS of sulfur compounds owing to competitive adsorption between the oxygen and sulfur included in the compounds [16].

According to previous work under JICA's research, it is also possible that nitrogen compounds such as quinoline may poison the active site for HDS of S-compounds in bio-oil. The inhibiting effects were found to increase in residual S-compounds in the order as DBT (2.71−3.69 times) > 4MDBT (1.96−1.28 times) > 46 DMDBT (1.16 times) for HDS of LGO-HWT-MD. The inhibition was similar in the transformation of DBT and 4MDBT for all catalyst types. In the case of 46 DMDBT, the inhibition was found in HDS reaction using NMA catalyst, however; the inhibiting effect on 46 DMDBT was lower than the effects on DBT and 4MDBT. It is interesting that the 46 DMDBT was increasingly dehydrosulfurized if HDS of LGO-HWT-MD using CoMo catalysts. It is imperative to do further research achieve more understanding about these data.

3.6 *Effects of catalyst types on HDS, HDO and HDN reactions*

Molybdenum supported on alumina promoted by nickel or cobalt comprises the important catalysts for petroleum hydrotreating process. Thus, commercial catalysts (CMA and NMA) and the synthesized catalysts were ivestigated for a comparison. The commercial catalysts provided higher activity in LGO and LGO-HWT-MD reactions those can be seen the evidences in Figure 4.

In terms of kinetics results, the rate constant values (k) of HDS using CMA (k = 2.0×10^{-4} ppm$^{-0.25}$.hr) illustrated that CMA was the best catalyst for HDS of LGO, while k values of HDS using NMA (k = 4.0×10^{-5} ppm$^{-0.25}$.hr) was more suitable for LGO-HWT-MD. The k value of HDS using the prepared catalyst (310CoMoA) for LGO was 2.0×10^{-5} ppm$^{-0.25}$.hr and the value for LGO-HWT-MD was 5.0×10^{-6} ppm$^{-0.25}$.hr. It implies that 310CoMoA gives lower performance than the two commercial catalysts. (Figure 8).

In this work, the data cannot explain whether which reaction pathway that CoMo and NiMo catalysts will promote. The catalysts ordinarily performed the HDS reaction of DBT, 4MDBT and 46DMDBT through two pathways; HYD and direct desulfurization (DDS) for diesel fuel. As a state of art, the successive DDS pathway is more enunciated for the CoMo catalysts, but not for NiMo catalysts [17]. The HYD route is more important in the HDS of DBT and 46DMDBT over NiMo [18]. The synthesized 310CoMoA catalyst has lower activity than the both commercial catalysts in the both cases. In terms of HDO of LGO-HWT-MD, %HDO implies that commercial NMA establish more activity for HDO of cresols than the others do. As the results (Figure 5), %HDO values are pretty low for HDO of cresols that may be because of the effect of alumina support. Bui stated that the use of alumina support for CoMoS causes methyl-substitution reactions after C (sp^3)–O cleavage. The methyl-substituted reaction would create cresols, so higher amount of cresol than expected was detected [19]. HDN of LGO-HWT-MD gives the similar tendency of catalyst activities as HDO.

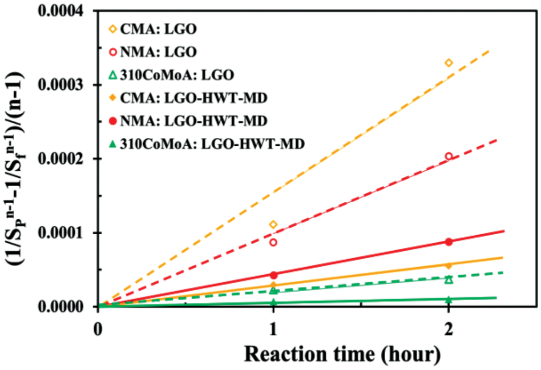

Figure 8: Relative reactivity of HDS reactions using different catalysts (at 340ºC) and they calculated from 2.25 of a reaction order.

3.7 *Effects of mixed oxide support on HDS reactions*

It is well known that a catalyst support also affects on HDS, therefore; one of enhancements of catalyst activities is a catalyst support modification. Mixed oxide supports have received high attention in current research. Molybdenum sulfide supported titania has attracted contemplation for HDS reaction. There was publication maintained that Mo catalysts supported on titania are four times more active for thiophene of the HDS than those supported on alumina [20]. Conversely, using single titania support would face some impediments, because the titania support presents low specific surface area (titania ~50 m^2/g and alumina ~ 200 m^2/g) and poor thermal stability of the anatase phase at high temperatures [20]. The results from Figure 9 and Figure 10 substantiate that the incorporation of TiO_2 into Al_2O_3 had a positive

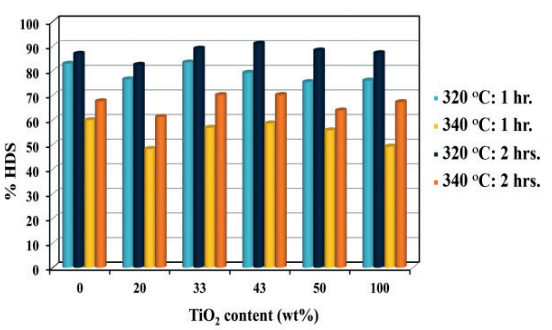

Figure 9: Relation between %HDS and TiO_2 in the mixed oxide support.

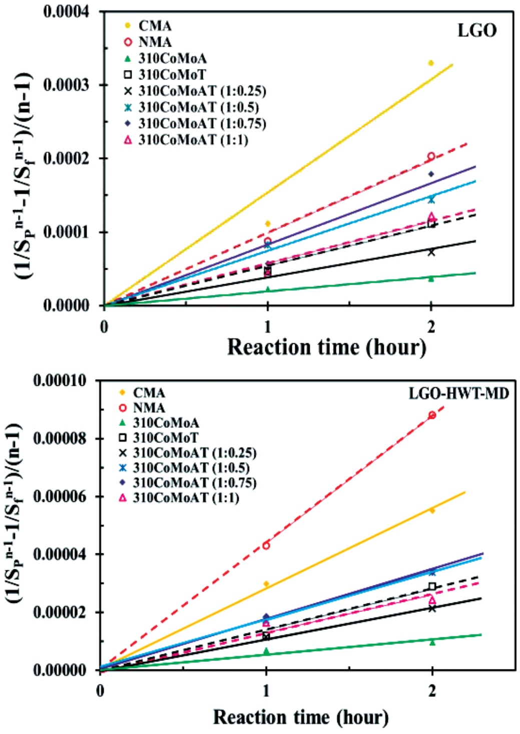

Figure 10: Relative reactivity of HDS of LGO and LGO-HWT-MD (reaction temperature = 340ºC).

influence on activity of CoMo catalysts for HDS of LGO and LGO-HWT-MD.

It was found that catalyst supported on alumina - titania with 43 wt% (TiO_2/ (Al_2O_3+TiO_2)) or 1:0.75 by weight (Al_2O_3:TiO_2) showed the highest HDS activity compared to catalysts supported on alumina -titania of other compositions. The relative reactivity plots also supported the %HDS values (Figure 10). The highest reaction rate constant appeared in reactions using catalyst supported on alumina - titania with 1:0.75 by weight of Al_2O_3:TiO_2. These results are quite different from previous research. Maity studied on characterization of HDS catalysts supported on Al_2O_3-TiO_2 for Maya heavy crude. They observed that intrinsic HDS activity was highest with TiO_2:Al_2O_3 ratio of 1:1. That catalyst support showed 5 times higher than Al_2O_3 support and 2 times higher than TiO_2 supported catalysts [21].

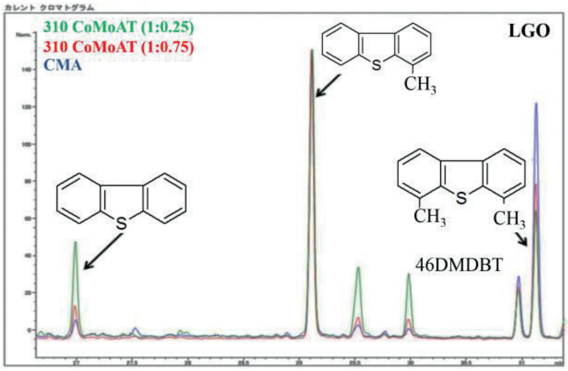

Figure 11: GC-SCD spectra for HDS reactions using CMA and catalysts containing TiO_2.

Olguin found that if TiO_2/(Al_2O_3+TiO_2) lower than 0.9, the supports appeared to have surface properties close to those of pure Al_2O_3 [8]. The difference of results may be due to rationale of feeds and catalysts preparation. The methodology of catalyst support preparation affected to catalytic activities [22]. Leliveld gave an explanation about catalyst support preparation whether during the preparation $CoMoO_4$ can be formed on titania the promotion of Mo with Co. The $CoMoO_4$ will provide less active sulfidation. Furthermore, it is not only the total amount of Ti in the support that is relevant, but also the structures of the TiO_2 species on the surface. Spectra from GC-FID illustrated that CMA can convert DBT better than the others do, but a synthesized catalysts has better selectivity for HDS of 46DMDBT in LGO than the commercial CMA catalyst has (Figure 11). However, synthesized 310CoMoT catalyst accepts more retardant effect for HDS of DBT, 4MDBT and 46DMDBT than the other catalysts do. That implies the isolated TiO_2 does not increase significantly the HDS activity of those three S-compounds. To accomplish better activity, the presence of reducible surface TiO_2-like structures is essential [23]. TiO_2 acts as an electronic promoter in catalysts for HDS.

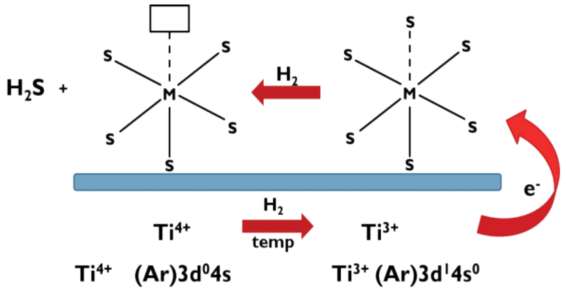

Figure 12: Scheme of the promotional effect of Ti over Mo-HDS catalysts [23].

In TiO_2, Ti^{3+} species perform as electron donors which can be effortlessly transferred. The Ti^{3+} can transfer through the conduction band of support to Mo 3d conduction band and this electron relocation gives an advantage for the promotion of molybdenum sulfidized catalysts (MoS_2) used for the HDS reaction (Figure 12). As another fact, TiO_2 has the character of semiconductor that can support charge transport in sulfidized catalysts in contrast to the insulating character presented by Al_2O_3.

At titania contents higher than 43 wt%, the percentage of HDS decreased approximately 3-6% for both cases. It has a limitation of TiO_2 loading, since electronic promotion of Mo by Ti also has a boundary. The excessive weakening of Mo-S bonds could cause an unsuitable interaction between a sulfur compounds and an active site [23]. In the case of mixed oxides with low TiO_2 content, titanium ions are bonded mainly via Ti-O-Al bridges instead of Ti-O-Ti bridges, therefore; the transfer of electrons does not happen as easy as for Ti-O-Ti bonds [24]. Sulfidation on mixed oxide supports (Al_2O_3-TiO_2) is more efficient over composite supports than over pure Al_2O_3 or TiO_2 [24]. Ramı ´rez also claimed that catalysts containing TiO_2 is suitable for deep HDS, since there is the formation of a greater number of coordinatively unsaturated sites in the MoS_2 active phase. The formation favors HDS via a 46DMDBT pathway. Results from GC-FID consent with this claim as 310CoMoAT with 20 and 43 wt% could reduce 46DMDBT more than CMA in the LGO reaction.

The observation of HDN percentage gave the same tendency as the HDS percentage inclination (Figure 13). The maximum activity was observed in the reaction using the catalyst consisting of 43 wt% of TiO_2 and the lowest activity went to catalysts containing 20 wt% of TiO_2.

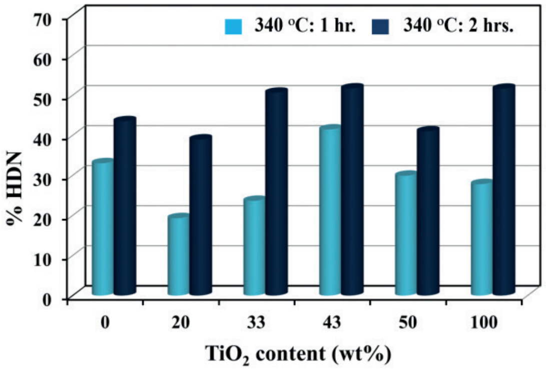

Figure 13: Effect of TiO_2 loading in the mixed oxide support on %HDN of LGO-HWT-MD reaction.

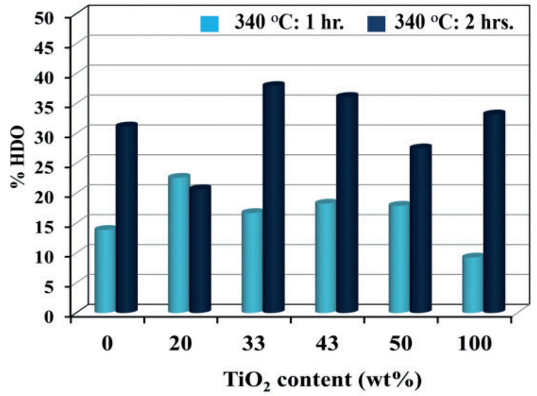

Figure 14: Effect of TiO_2 loading in the mixed oxide support on %HDO of LGO-HWT-MD reaction.

There is a little bit different in terms of HDO reaction. The 310CoMoAT containing 33 wt% of TiO_2 gave highest activity for HDO of cresols in LGO-HWT-MD, however; the hydrotreating activity of synthesized catalysts were still low compared to commercial NMA and CMA catalysts (Figure 14). These results agree with the state in publication of Bui. HDO reactions principally occurred with lower rate for titania supported CoMoS system [3].

4 Conclusions

The result data of this study presented in this paper for synthesized HDS catalysts, many characteristics can be highlighted as following details. Even though reaction temperature at 320ºC can be used for HDO of bio-oil models, according to previous work of JICA's project, it is not appropriate for HDO of cresols in the real coprocessing bio-oil as LGO-HWT-MD. Therefore, reactions were operated under 340ºC. The 340ºC of reaction temperature and 2 hours of reaction period provided a positive effect on the catalyst activity. Actually, at least three reaction temperatures and periods should be investigated in order to determine the rate constant statistically. This work was preliminary work for catalyst screening via batch reactors to observe an initial catalyst activity for further catalyst development. The current work of the project are addressing on the investigations of optimum condition of a bio-oil HDS reaction and catalyst performances; selectivity, activity, kinetics and degradation, in a continuous reactor.

Throughout HDS reactions HDO and HDN reactions were observed, O- and N-compounds reveal inhibiting effect on the HDS reaction for LGO-HWT-MD. In terms of catalyst support effects, Ni is a better promoter for Mo-A based catalyst for hydrotreating reactions. The synthesized catalysts supported on titanium-rich and pure titania carriers exhibit higher activity for HDS, HDO and HDN reactions than those supported on pure alumina, since TiO_2 is an electronic promoter in HDS catalysts. The electronic promotion of Mo by Ti has a limitation, consequently the 310CoMoAT catalyst with 1: 0.75 of alumina: titania ratio presents the best catalytic behaviour on the activity of HDS, HDO and HDN among other synthesized catalysts. The 310CoMoAT (1:0.25) shows the worst performance, because at low TiO_2 content, the mixed oxide catalysts have more character of insulator for sulfinding catalysts. Sulfidation on mixed oxide supports (Al_2O_3-TiO_2) is more efficient over composite supports than over pure Al_2O_3 or TiO_2.

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