The catalytic activity of CoMo/USY on deoxygenation reaction of anisole in a batch reactor

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Abstract. The catalytic hydrodeoxigenation of the bio oil model compounds (biomass pyrolysis results) typically uses sulphide catalysts. In this study, we studied the activity of non-sulphide catalyst, the effect of temperature and reaction time on anisole deoxygenation. The catalytic activity was performed in a batch reactor, using N₂ gas at 1 bar of pressure. The product was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The result showed that the Co-Mo/USY catalyst perform a highest activity and produce pentamethylbenzene, an oxygen free products, when reaction time is 2 hours. The Co-Mo/USY catalysts has the value of the total yield of the product increased with time increase drastically.

1. Introduction

Bio oil is an alternate energy resource for replacing Crude oils [1]. It is able to minimize air pollution, by mean of replacing the CO₂ emissions released. But the bio oil cannot be directly used as a fuel, because it contains various compounds in the form of alcohols, aldehydes, sulphur, and oxygen. The highest content in the bio oil is oxygenated compounds that will generate undesirable properties, such as high thermal instability, high viscosity, and low heating value [2]. Therefore, to earn quality fuel products, deoxygenation reaction is one alternative to improve the characteristics [3]. The composition of bio oil is very complex, so there is required models compounds such as anisole as reactant, which is capable to representing the actual compounds[4–12].

The deoxygenation process for removing carbonyls group in aromatic compounds need catalyst [11]. According to Mora et al. [13], the catalyst CoMo/Al₂O₃ capable to produce the highest benzene yield from deoxygenation of hydroxyl anisole. Jongerius et al. [14], explained that the catalysts CoMo/Al²O₃ provide a high deoxygenation activity of lignin. Anisole is derivative of lignin, that it has an oxygen atom at methoxy group [15].

However, Al₂O₃ support has a lower catalytic activity than the Ultra Stable Y-Zeolite (USY) on desulphurization reaction of thiophene [16]. This study was investigated the used of the CoMo/USY catalyst for deoxygenation reaction of anisole. The Co metal has a moderate energy for adsorption and desorption mechanism, so it is suitable for the hydrogenation reaction [17]. The Mo metal can activate C-O bonds [18,19], that is making it suitable for deoxygenation reaction [18]. The acid sites of USY serve the active site so that a combination of metal with USY will produce bifunctional catalysts [20–22].

Temperature and time of reaction influent to activate catalyst and to remove the C-O bond. The product of hydroxy anisole using a Pd/Al₂O₃ catalyst increase with reaction temperatures from 200°C until 300°C[23]. But according to Payormhorm et al. [24], at higher temperature (300°C-420°C), the
deoxygenation product is declined. Meanwhile, Lee et al. [25] said that the raising time (30-180 minutes) of hydroxy anisole deoxygenation causes cyclohexane product increased. The catalytic reaction with batch systems [25,26], has a lower cost and simple operation than the flow system. So, this research aimed to test the catalytic activity of CoMo/USY on the anisole deoxygenation in a batch reactor with varied of catalyst types, temperature, and reaction time.

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2. Experimental
The catalyst support used in this study was NH4Y zeolite, that was purchased from Tosoh Inc. (Japan). Catalyst metal precursors for deoxygenation reactions (Co and Mo) were ammonium heptamolybdate and cobalt nitrate hexahydrate purchased from Merck (Germany). Anisole (methoxy benzene) was 99% from sigma Aldrich.

The catalyst that used in this study was prepared by using Rachmadani methods [27]. Deoxygenation reaction was first conducted by oven of catalyst before used for 3 hours at temperature of 110°C. Amount of dry CoMo/USY catalysts (0.5 grams) and 5 mL anisole are added to columns autoclave. The next column autoclave injected into the furnace. Reactor was prepared, as shown as Figure 1. Then the reactor cleaned using N2 gas (all valves opened) for 5 minutes. After 5 minutes, the valve no 2 are closed. The reactor is filled N2 gas until reach 1 bar pressure. Then the first valve was closed or locked, N2 gas removed from the reactor. The reactor heated until 200°C, then left to 60 minutes. After that, the liquid product obtained, analyzed by GC and GC-MS. The same procedure for the reactor temperature 250°C and 300°C, the time on stream for 120 minutes, and the catalyst sample are Co-Mo/USY and Mo-Co/USY.

![Figure 1. The batch reactor for anisole deoxygenation [26].](image)

The conversion of anisole (total yield) and the selectivity of component i are calculated based on the following equation [25]:

\[
\text{Conversion} \% = \frac{(\text{Weight of reactant})_{\text{initial}} - (\text{Weight of reactant})_{\text{final}}}{(\text{Weight of reactant})_{\text{initial}}} \times 100 \tag{1}
\]

\[
\text{Selectivity of component } i \% = \frac{\text{Weight of product } i}{\text{Weight of total products}} \times 100 \tag{2}
\]
3. Result and Discussion

The catalytic activity tests of CoMo/USY, Co-Mo/USY, and Mo-Co/USY on deoxygenation reaction of anisole at temperature from 200°C until 300°C. The total yield is the yield of products containing oxygen and without oxygen. Correlation between the types of catalysts and total yield anisole at various temperatures with a reaction time of 1 hour is presented in Figure 2.

Based on the graph in Figure 2, the highest total yield is provided by CoMo/USY catalyst at 300°C is 24.64%. It was estimated that the total acidity of CoMo/USY catalyst highest compared with other catalysts, is 11.206 mmol/g (showed in Table 2). This will indicate the strength of the Brönsted and Lewis acid sites is high, so that the catalytic activity is maximal [25].

The product yield increases with rising reaction temperature (from 200 to 300 °C) for all types of catalysts. This is according with research that conducted by Hong et al. [23]. Hong research [15] found that rising reaction temperatures from 200 to 300 °C resulted in increased deoxygenation products of hydroxyanisole.

![Figure 2. The correlation of catalyst type and total yield on various temperatures at 1 hour reaction time.](image)

For each type of catalyst, the increased temperatures will generally rise deoxygenation activity, which is characterized by high conversion of anisole. In addition, at higher temperatures, the reactants are more actively moving, so the probability of collisions between the reactants and the catalyst becomes larger. The greater of collision probability, the more rapid the reaction and the more and more the product is formed. This phenomenon applies equally to anisole deoxygenation reactions using CoMo / USY, Co-Mo / USY, Mo-Co / USY or USY catalysts. Based on the data of variation temperature at 1 hour reaction time (Figure 2), it was found that the best reaction temperature was 300 °C.

Meanwhile, the Co-Mo / USY catalyst has the highest surface area, total acidity of the medium, and many particle types, as shown in Table 1. Therefore, the highest total yield of the anisole deoxygenation reaction is obtained in reaction with Co-Mo / USY catalyst. This is consistent with research Osakoo et al. [28], that a sequentiale impregnation catalyst that has a higher surface area (473 m²/g) were able to produce more product than co-impregnation catalyst (397 m²/g). The higher surface area indicates that the distribution of active sites on the catalyst is more evenly distributed and becomes homogeneous[28]. The availability of an evenly active site allows more opportunities to interact between reactants and
catalysts. The interaction causes the reactants to become active, so that the reaction is more effective and the more products are formed. It makes the role of Co-Mo / USY as a catalyst getting better [29], product yields are increasing, and stable over a long reaction period.

Table 1. The total acidity and surface area specific of catalyst [27].

| Type of Catalyst | Total Acidity (mmol/g) | Surface Area Specific (m²/g) |
|------------------|------------------------|-----------------------------|
| Mo-Co/USY        | 8.304                  | 437.782                     |
| Co-Mo/USY        | 10.849                 | 557.172                     |
| CoMo/USY         | 11.206                 | 497.004                     |

Table 2 shows the deoxygenation reaction anisole using USY, CoMo/USY, Co-Mo/USY, Mo-Co/USY catalyst compared with HY zeolite. HY zeolite uses H₂ gas in the catalytic reaction [30]. Based on the analysis of table 2, it was found that all of the catalysts have almost the same ability in terms selectivity of deoxygenation and hydrogenation.

Table 2. Total Product Selectivity of anisole deoxygenation at temperature 300°C and 1 hours.

| Product          | HY zeolite* | USY | CoMo/USY | Co-Mo/USY | Mo-Co/USY |
|------------------|-------------|-----|----------|-----------|-----------|
| Phenol           | 0.60        | 0.56| 0.48     | 0.71      | 0.17      |
| 2-methylanisole  | 0.13        | –   | –        | –         | 0.25      |
| 4-methylanisole  | 0.15        | 0.40| 0.17     | 0.28      | 0.54      |
| 2-methylphenol   | 0.11        | –   | 0.19     | –         | –         |
| 2,3-dimethylanisole | –       | 0.03| 0.02     | –         | –         |
| 2,6-dimethylphenol | 0.01   | –   | –        | –         | –         |
| 4-methylphenol   | 0.04        | –   | –        | –         | –         |

*Runnebaum, et al. (2011) [30]

Co and Mo metal content for each type of catalyst has the same amount, so the reaction occurs in the impregnation catalyst and co-impregnation produce almost the same product. The results showed that the reaction product that always formed was phenol and 4-methylanisole. In addition, also obtained that all products produced still contain oxygen. This is possible because the supply of hydrogen is only anchored from a USY carrier, resulting in a hydrogen source deficiency reaction. The lack of hydrogen source causes the hydrogenation reaction not to occur maximally. Although hydrogen is slightly, there is still a methyl transfer reaction at the Brønsted acid site of USY.

According to Ruiz et al. [31], the catalyst activity for 2-hydroxy anisole becomes more optimal in the event of a relatively long interaction between the reactants with the catalyst. They found that the longer reaction time (0-4.15 hours) of deoxygenation of 2-hydroxy anisole, the more liquid product of phenol and cyclohexene was formed. Therefore, in this study deoxygenation reaction applied with various types of catalyst at reaction temperature of 300 °C for 2 hours. Correlation types of catalysts with a total yield of the product at 300°C for 1 and 2 hours is presented in Figure 3.
After 2 hours reaction time, CoMo / USY catalyst becomes unstable and total product yield decreases. This is possible because of the relatively smaller surface area of CoMo / USY and the highest acidity compared to other catalysts, causing the CoMo / USY catalyst become rapidly faster deactivated. The catalyst deactivation can be characterized by a decreased conversion reaction, although the deoxygenation of anisole has only been running for 1 hour. These results are consistent with Runnebaum, et al. [32]. According to Hellinger, et al. [33], deactivation of the catalyst occurs rapidly at elevated temperatures (250 - 380 ° C). However, the total yield is not proportional to the anisole conversion value. Whereas, the catalyst is said to be good when it produced more free oxygen products.

Table 3. Total product selectivity of Anisole at temperature 300°C and 2 hours.

| Product              | Product selectivity (%) |
|----------------------|-------------------------|
|                      | CoMo/USY | Co-Mo/USY | Mo-Co/USY |
| Phenol               | 31        | 20        | 18        |
| 4-methylphenol       | 2         | 3         | 1         |
| 2-methylphenol       | -         | 18        | 12        |
| 2-methylanisole      | 4.4       | 35        | 40        |
| 4-methylanisole      | 1.8       | 19        | 23        |
| 2,3-dimethylanisole  | -         | 6         | 3         |
| 1,2,3,4,5-pentamethyl benzene | -       | 1         | -         |

Product selectivity at 2 hours reaction time are presented in Table 3. Catalysts Co-Mo/USY produce one compound deoxygenation oxygen-free products i.e. 1,2,3,4,5-pentamethyl benzene. Large surface area capable to make the catalyst remains stable in absorb reactants, although the reaction time become
longer. This is in accordance with Messou et al. [34], that a sequential impregnation of catalyst is able to produce oxygen-free (C6) compared co-impregnation catalyst in the transformation of sorbitol. Meanwhile the anisole deoxygenation used CoMo/USY and Mo-Co/USY catalyst are not produce oxygen-free products. The main reaction all of catalysts are transferring of a methyl group.

The Oxygen-free product of anisol deoxygenation only owned by Co-Mo/USY catalyst that produce 1,2,3,4,5-pentamethyl benzene. The yield product of anisole deoxygenation is 17%. Although the few supply of hydrogen from the carrier USY, but the catalyst Co-Mo/USY capable of breaking the hydrogen to react with anisole compound, thus forming an oxygen-free product. The formation of 1,2,3,4,5-pentamethylbenzene with demethylation and methyl transfer reaction.

Based on these results and in agreement with previous studies [30,35], that phenol is the product intermediate. The yield of the product intermediate is presented in Figure 4. The intermediate product yield is shown in Figure 4. The CoMo / USY catalyst has the best phenol yield, ie 11.774% at 1 hour reaction time. Meanwhile, at 2 hours reaction time, the best result is owned by Co-Mo / USY catalyst which is 5.718%. The result of the greatest 4-methylanisol product obtained by Mo-Co / USY catalyst was 6.2474% at reaction time 1 hour and for reaction time 2 hours, the biggest result was owned by Co-Mo / USY catalyst which was 5.387%.

![Figure 4](image)

**Figure 4.** The yield of the product intermediate phenol (black) and 4-methylanisole (white) at (A) 1 hours and (B) 2 hours.

### 4. Conclusion

The product yield rises with increasing reaction temperature (200 ° -300 ° C). Meanwhile, the Co-Mo / USY catalyst has the best activity, that it is shown from the increase of the yield value (14.21% to 28.92% from reaction time 1 h to 2 h) and obtained oxygen-free products (1,2,3,4,5-pentamethyl benzene). The highest yield towards phenol products when 1 hours is CoMo/USY catalyst (11.774%) and at 2 hours is Co-Mo/USY catalyst (5.718%). While the highest yield to 4-methylanisole product when 1 hour is the catalyst Mo-Co/USY (6.274%) and time of 2 hours is the catalyst Co-Mo/USY (5.387%).
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