Synthesis and Metal Phases Characterization of Mordenite Supported Copper Catalysts

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Abstract. Three catalysts were synthesized by the impregnation method using copper as an active metal and mordenite as a support material. The metal loading was set at 0, 4 and 8 %wt, respectively. The used copper salt solutions were collected as filtrate and analyzed by atomic absorption spectroscopy (AAS) to predict the metal content was successfully loaded onto mordenite. For a further step, catalysts are activated through the calcination and reduction process. The metal content was further confirmed by X-Ray Fluorescence (XRF) and the results were not much different compared to AAS analysis. It was obtained that copper metals were successfully impregnated on the catalyst as 3.74 %wt for Cu/MOR 4 and 5.52 %wt for Cu/MOR 8. Meanwhile, the catalysts were also characterized using X-ray diffraction (XRD) and then followed by match with a mordenite standard diffractogram. Further diffractogram analysis was carried out by the Le Bail method to get semi-quantitative data of metal phases on catalysts. Mordenite phase was consistently obtained as the main content of all catalysts, over 99%. The copper phase at Cu/MOR 4 catalyst was consisted of Cu, Cu(OH)2 and Cu2O. In contrast, Cu/MOR 8 catalysts showed no Cu(OH)2 phase on it, but Cu and Cu2O still found.

1. Introduction
Biomass-based fuels have wide open to be developed as promising alternative fuels due to their renewable nature, sustainability, efficiency, and zero-carbon [1,2]. Unfortunately, their high content of oxygenated compounds was corrosive to the engine. Hydrodeoxygenation (HDO) was one strategy to remove the oxygen from its compound, using hydrogen and catalysts. The catalysts are important, caused their active sites to make the reaction possible. Transition metals have been recognized as good catalysts for HDO reactions [3]. Copper is the interesting one due to its good performance on HDO reaction, the oxygen-free products were quite high and fewer cokes compare to Ni, Co and Mo [4–6].

Modification of transition metal using support material is well known as a good choice to achieve high surface area, thermal stability, and prevent agglomerate formation. Many porous materials have been applied as support material, such as zeolite. Zeolite provides high thermal stability, pore selective, high adsorption capacities, and controllable acidity [6–8]. Mordenite is one kind of zeolite with quite a large pore area by ±7 Å, also has two types of acid site. There are Bronsted and Lewis
acid sites [9–14]. In addition, the high thermal stability of mordenite was presented by its ability to hold its structure up to 800-900 °C [9]. These nature made mordenite a suitable candidate for support material.

The characters and performances of catalysts were very influenced by their synthesis methods, such as support type [3,15] and amount of metal loading [4,5,16–18]. Meanwhile, the metal loading amount affects the metal phase-type, surface area, pores profile, acidity, and catalysts performance.[4,5,16–18]. Therefore, this research aims to synthesize copper-supported mordenite catalysts and investigate the metal contents also their phase-type.

2. Experimental
2.1 Materials
A synthetic zeolite, mordenite (HS-690-Wako) used as support material in this work.. Analytical grade of copper (II) nitrate trihydrate [Cu(NO$_3$)$_2$.3H$_2$O] and ammonia were purchased from Merck.

2.2 Catalysts synthesis
Cu/MOR catalysts were synthesized by the impregnation method. Mordenite (20 g) and copper (II) nitrate were mixed together in the ammonia solution, then refluxed for 16 hours at 30 °C followed by 4 hours at 80 °C. The slurry was filtered, then the filtrate was collected to analyze by AAS. The residue powder was dried under vacuum by rotary evaporator. Finally, the catalysts were activated through calcination in N$_2$ flow at 550 °C for 4 h and then reduced in H$_2$ flow at 400 °C for 4 h by 2 times. Catalysts were labeled as Cu/MOR x, where x is referred to wt% of Cu loaded onto mordenite.

2.3 Catalysts characterization
The filtrates from the used Cu solution were analyzed by atomic absorption spectroscopy (AAS), to predict the Cu content was successfully impregnated onto catalysts. For further confirmation, the catalysts were analyzed by energy dispersive X-ray fluorescence (ED-XRF). Crystal diffraction and metal phases on the catalyst were investigated by powder X-ray diffraction (P-XRD) technique (Cu-Kα radiation λ =1.5418 Å at 3 < 2θ < 90°, 0/20 scanning mode, with 0.02°sampling pitch, and 3°/min scan speed). The catalysts were compared to all possible standards from the inorganic crystal structure database (ICSD) as written in Table 1. Furthermore, X-ray diffraction data was extracted in detail its crystalline structure by the Rietveld method to obtain the metal phase. The refinement was performed using the Le Bail calculation method in the Rietica program, to quantify the crystal phase compositions by fitting experimental XRD data with a calculated diffraction pattern. The refined parameters are the instrument zero, baseline lattice parameters, and the peak shape parameters (u, v, w, and y0 respectively). Each refinement were conducted at 30 cycles. The calculation results was presented as residual percentages (Rp), residual weight percentages (Rwp) and molar phases.

| Standard | ICSD number | Crystal system | Space group | Z | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) |
|----------|-------------|----------------|-------------|---|-------|-------|-------|-------|-------|-------|
| Mordenite | 4393        | Orthorhombic   | C M C M     | 48| 18.007| 20.269| 7.465| 90    | 90    | 90    |
| Mordenite | 9632        | Orthorhombic   | C M C M     | 1 | 18.122| 20.457| 7.515| 90    | 90    | 90    |
| Cu       | 53246       | Cubic          | F M 3- M    | 4 | 3.625 | 3.625 | 3.625| 90    | 90    | 90    |
| Cu(OH)$_2$ | 15455    | Orthorhombic   | C M C M     | 4 | 2.949 | 10.590| 5.256| 90    | 90    | 90    |
| Cu$_2$O  | 53322       | Cubic          | P N 3- M S  | 2 | 4.250 | 4.250 | 4.250| 90    | 90    | 90    |
| CuO      | 61323       | Cubic          | F M 3- M    | 4 | 4.245 | 4.245 | 4.245| 90    | 90    | 90    |
3. Result and Discussion

3.1 Metal content on the catalysts
The copper content on the catalysts were investigated by AAS and XRF method. The AAS analysis performed a very low of limit detection and represented a homogeneous sample. Here, we use AAS to obtain the copper content of the liquid phase of the impregnation process. The results can be used to predict copper content that successfully impregnated on the catalyst. To confirm this result, XRF analysis was also performed in this research. The Cu/MOR 0 catalysts were represented mordenite without metal addition and exhibited no copper content on it as seen in Figure 1. The copper metals were successfully impregnated on Cu/MOR 4 catalysts of 3.74%wt based on based on XRF analysis and 3.90% wt by the AAS analysis, respectively. Although, the copper seems to be difficult to impregnated on the Cu/MOR 8 catalysts. The Cu/MOR 8 exhibited a copper content by 5.52% on it by XRF method, and 6.86% by AAS method. The difference between XRF and AAS method was not significant on Cu/MOR 4, but seems far on Cu/MOR 8 due to the high limit detection of XRF method and also the samples that used were heterogeneous.

![Copper content on Cu/MOR catalysts by AAS and XRF method.](image)

3.2 Metal phases characterizations
Three catalysts were successfully synthesized by impregnating copper onto mordenite. The Cu/MOR 0 catalysts were not modified by Cu and confirmed has no copper by XRF method. The Cu/MOR 4 and Cu/MOR 8 catalysts were performed different colors after modified by Cu impregnation. Before the activation process, both Cu/MOR 4 and Cu/MOR 8 catalysts were blue similar to copper (II) nitrate solutions. However, after the activation process, the color was changed due to the transformation of metal phases. The metal salt precursor was decomposed by high temperature in calcination process, lead to the formation of oxides [19,20]. In a further step, the hydrogen gas flow caused copper oxides to transformed into copper atom or another copper oxide with lower oxidation number [19,21,22]. In this research, the Cu/MOR 4 catalysts were found as green pale and Cu/MOR 8 catalysts were found as reddish-brown. It was indicated that Cu/MOR 4 and Cu/MOR 8 catalysts have different copper phase compositions.
The metal phases were further information produced from X-ray diffraction data of catalysts. Before the calculation started, some suitable standards need to be found. Figure 3 illustrated the X-ray diffraction pattern of the catalysts compared to mordenite standard ICSD numbers 4393 and 9632. Some highest peak of catalysts diffraction pattern found to be similar to the standard. That was indicated that metal impregnation was not ruined the crystal structure of mordenite. However, the X-ray diffraction pattern of copper not observed. This is maybe because the intensity is very low, or the copper metal is well dispersed on the catalyst and does not form a crystal structure.

The refinement and calculation result of Cu/MOR 0 catalysts was presented in Figure 4 and Table 2. The black line with + symbol indicated the experimental data, the red line referred to the refined standard data, the blue bars referred to expected peak points, and the green line has represented the difference between the experimental data and the calculations. As seen in Figure 4, the +++ line was almost fit to the red line, and the green line also almost flat indicating a high similarity of Cu/MOR 0 catalysts data with the mordenite standard ICSD numbers 4393 and 9632. For detail, Table 2 was presented the calculation values of Cu/MOR 0 catalysts compared to mordenite standards. According to the calculation, the Cu/MOR 0 catalysts were consisted by 97.91% of mordenite ICSD no. 4393 and 2.09% of mordenite ICSD no. 9632. Both Rp and Rwp values were below 10%, which indicated to high similarity of experimental data and standard. The crystal system of Cu/MOR 0 catalysts was orthorhombic with space group of CMMC, and the cell volume also lattice parameters were not significant to the standard data.
Figure 4. Refinement and calculation result of Cu/MOR 0 catalysts with mordenite standard ICSD number 4393 and 9632. +++: experimental data, ---: calculation results, ----: peak points, and ----: difference between experimental data and the calculation results.

Table 2. Cell parameter results of Cu/MOR 0 catalysts by using Le Bail method compared to standards.

| Catalyst     | Mordenite 4393 | Mordenite 9632 | Cu/MOR 0 |
|--------------|----------------|----------------|----------|
| Molar percentages (%) |                 |                |          |
| Mordenite 4393 | 97.91          |            |          |
| Mordenite 9632 | 2.09           |            |          |
| Rp           | 6.054          |            |          |
| Rwp          | 7.982          |            |          |
| Crystal system | orthorhombic   | orthorhombic | orthorhombic |
| Space groups  | C M C M        | C M C M      | C M C M   |
| Cell volume   | 2724.6         | 2785.97      | 2788.04  |
| a             | 18.007         | 18.1220      | 18.1249  |
| b             | 20.269         | 20.457       | 20.4632  |
| c             | 7.465          | 7.515        | 7.5171   |
| α (°)        | 90             | 90           | 90       |
| β (°)        | 90             | 90           | 90       |
| γ (°)        | 90             | 90           | 90       |

The refinement and calculation result of Cu/MOR 4 was presented in Figure 5 and Table 3. Based on metal content results, Cu/MOR 4 catalysts were successfully impregnated by copper. Therefore, further standards were tested such as Cu ICSD number 53246, Cu(OH)$_2$ ICSD 15455, Cu$_2$O ICSD number 53322 and CuO ICSD number 61323 to investigate the metal phase-type and also their composition. According to Figure 5, the Cu/MOR 4 catalysts were matched to the combination of the five standards. The diffraction pattern of mordenite was seen as a dominant composition for Cu/MOR 4 catalysts, which also similar to Figure 3. In addition, the refinement result of Cu/MOR 4 catalysts has confirmed the presences of copper. The green line was obtained as more flat when Cu ICSD number 53246, Cu(OH)$_2$ ICSD number 15455, and Cu$_2$O ICSD number 53322 were added into the
calculation. The Rp and Rwp also decreased by the copper standard addition. However, the detailed calculation was presented in Table 3.

**Figure 5.** Refinement and calculation result of Cu/MOR 4 catalysts with mordenite standard ICSD no. 4393, mordenite no. 9632, Cu no. 53246, Cu(OH)$_2$ no. 15455 and Cu$_2$O no. 53322. +++: experimental data, -----: calculation results, ------: peak points, and ----: difference between experimental data and the calculation results.

The refinement and calculation result of Cu/MOR 8 was presented in Figure 6 and Table 3. According to Figure 6, the Cu/MOR 4 catalysts were only fit to the combination of the four standards. The diffraction pattern of mordenite was seen as a dominant composition for Cu/MOR 8 catalysts, which also similar to the Figure 3. The refinement result of Cu/MOR 8 catalysts has confirmed the presences of copper, but in different phases compared to Cu/MOR 4 catalysts. The green line was obtained as more flat, also both Rp and Rwp were decreased when Cu ICSD number 53246 and Cu$_2$O ICSD number 53322 were added into the calculation. In contrast, Cu(OH)$_2$ number 15455 was not suitable to the Cu/MOR 8 catalysts, due to rising values of Rp and Rwp.

**Figure 6.** Refinement and calculation result of Cu/MOR 8 catalysts with mordenite standard ICSD no. 4393, mordenite no. 9632, Cu no. 53246 and Cu$_2$O ICSD no. 53322. +++: experimental data, -----: calculation results, ------: peak points, and ----: difference between experimental data and the calculation results.
Clear calculation results of catalysts metal phase compositions were presented in Table 3. Both Rp and Rwp values were below 10%, so the calculations data were acceptable. The mordenite standard ICSD number 4393 was shown as a dominant component of all catalysts, over 97%. It obviously explained that copper impregnation was not influenced the crystal structure of mordenite, which is good for catalysts performance due to the pore structure and high surface area of mordenite were not ruined.

The metal phases on Cu/MOR 4 and Cu/MOR 8 catalysts were different. The Cu/MOR 4 catalysts were contained by some Cu(OH)₂, due to the imperfect reduction process. On other hand, Cu/MOR 8 catalysts weren’t contained by Cu(OH)₂. It may explain the different colors between Cu/MOR 4 and Cu/MOR 8 catalysts. In normal conditions, Cu/MOR 4 catalysts should be easier to reduce compared to Cu/MOR 8 catalysts due to the lower weight percent of metal addition. However, the current data was not enough to understand this phenomenon.

Overall, the low molar percentages of Cu, Cu(OH)₂, and Cu₂O indicated that copper metals were only impregnated below 1% on the catalysts or copper metals were well dispersed on the catalysts. Based on the metal content results, the copper metals were achieved more than 3% both on Cu/MOR 4 and Cu/MOR 8 catalysts. Therefore, the possible explanation is copper metals were well dispersed on the surface of catalysts and only formed a very small amount of crystal. The high dispersion of copper also good for catalyst’s performances, cause lead to the high surface area of active metal sites on the catalysts. Although, the explanation of metal dispersion needs to confirmed by other characterization technique.

Table 3. Calculation results of Cu/MOR 0, Cu/MOR 4 and Cu/MOR 8 catalysts by using Le Bail method compared to standards.

| Catalyst          | Cu/MOR 0 | Cu/MOR 4 | Cu/MOR 8 |
|-------------------|----------|----------|----------|
| Molar percentage (%) |          |          |          |
| Mordenite 4393   | 97.91    | 97.20    | 97.66    |
| Mordenite 9632   | 2.09     | 2.07     | 2.08     |
| Cu                | 0.14     | 0.14     |          |
| Cu(OH)₂           | 0.48     |          |          |
| Cu₂O              | 0.11     | 0.11     |          |
| Rp                | 6.054    | 5.838    | 5.349    |
| Rwp               | 7.982    | 7.749    | 6.972    |

4. Conclusions
Three catalysts were successfully synthesized by the impregnation method. The Cu/MOR 0 catalysts were obtained with no copper content, while Cu/MOR 4 catalysts were consisted by 3.74% and Cu/MOR 8 catalysts were consisted by 5.52% of copper. According to the metal content results, Cu/MOR 4 catalysts were more efficient in carrying copper. The metal phases of catalysts were achieved from the calculation of X-ray diffraction data compared to several standards data using the Le Bail method. Mordenite standard ICSD number 4393 was found as dominant composition of all catalysts over 97%, which indicated that the crystal structure of mordenite wasn’t ruined by copper impregnation. The Cu/MOR 4 and Cu/MOR 8 catalysts showed different metal phase-type. The Cu/MOR 4 catalysts were consisted by Cu(OH)₂, while Cu/MOR 8 catalysts were not. Overall, the molar percentages of Cu, Cu(OH)₂, and Cu₂O were obtained below 1% on Cu/MOR 4 and Cu/MOR 8 catalysts, which indicated that copper metals were well dispersed on the catalysts.

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