Structure and Morphology of The (Ni, Co) Mo/Indonesian Natural Zeolite

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Abstract. The NiMo/Indonesian natural zeolite (NiMo/ZA) and CoMo/ZA catalysts are produced through the impregnation methods. These catalysts were characterized by using X-Ray Fluorescence (XRF), Fourier Transform Infrar-Red (FTIR), X-Ray diffraction (XRD), and Scanning Electron Microscope (SEM). The XRF data show that the CoMo/ZA catalyst has a large amount of metal content more than NiMo/ZA. The FTIR spectra of catalyst show a shift of asymmetric stretching of TO4 group to a larger wavenumbers than the FTIR spectra of ZA. Meanwhile, the metal phase in the CoMo/ZA catalyst is CoO and MoO3, and the metal phase in the NiMo/ZA catalyst is NiO and MoO3.

1. Introduction
Indonesian natural zeolite and clay resources amounted more than 200 million tons [1]. While, natural zeolites that obtained from Java Island, Indonesia, such as West Java (Bayah and Cipatuja), Central Java (Wonosari, Yogyakarta), and east Java (Pacitan) are known to contain modernite [2,3]. It can use as a supporting metal in the preparation of heterogeneous catalysts [1–3].

Preparation processes such as modification and activation of the catalyst support may enhance its catalytic capacity. Many researchers have been modified of natural zeolites with several metals namely Ni, Ni-Mo, Co, Co-Mo [4–9], Pd, Cu, and Cr [3], respectively. Furthermore, Nickel, cobalt, and molybdenum are transition metals that frequently used as a metal catalyst, because they have high activity and selectivity.

The preparation of natural zeolite catalyst can be carried out by the impregnation method [3,4,9–11]. Nugrahaningtyas et al. [10] had modified natural zeolites with NiMo bimetallic catalysts using the impregnation method. The result showed an increase in acidity. Meanwhile, Sriningsih and coworkers [4] had compared the activity of the Mo/activated-natural zeolite (Mo/Z), NiMo/Z, Co/Z, and CoMo/Z catalysts. They obtained that the highest catalytic activity is CoMo/Z catalyst.
Modification of natural zeolite as a support for the catalyst, without initial treatment, has not been done. So, the purpose of this research made a bimetal catalyst with natural zeolite as a catalyst support, without any pre-treatment of natural zeolite. The preparation of the supported catalyst was carried out using the co-impregnation method. Another goal of this work is to determine the character of NiMo/ZA and CoMo/ZA.

2. Experimental

2.1. Raw Material

The natural zeolite, which used in experiments, was supplied from Wonosari, Yogyakarta, Indonesia. As for other chemicals such as Ni(NO$_3$)$_2$.6H$_2$O, Co(NO$_3$)$_2$.6H$_2$O, (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O, and ammonia 25% were purchased from E Merck, while the hydrogen and nitrogen gases were purchased from Samator Gas.

2.2. Catalyst Preparation

The NiMo/ZA and CoMo/ZA catalysts were prepared via the impregnation method. Ten grams of ZA was refluxed with a solution that contained the metal salt of (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O (0.98 gram) and Ni(NO$_3$)$_2$.6H$_2$O (0.78 gram), 15 mL of distilled water, and 6 mL of ammonia. The reflux process was carried out at 60 °C for 2 hours. Then, the sample was evaporated at 80 °C with a pressure of 400 mBar, calcination by using nitrogen gas at a temperature of 550 °C for 3 hours at a flow rate of 15 mL/min, reduction by using hydrogen gas at a temperature of 400 °C for 2 hours at a flow rate of 15 mL/min. This catalyst is named NiMo/ZA. The same procedure was repeated in the preparation of the CoMo/ZA catalyst.

2.3. Catalyst Characterization

X-Ray Fluorescence (XRF) were recorded using BRUKER S2 Ranger for analysis metal composition. Functional groups were observed by using FTIR Shimadzu IR Prestige-21. All infrared spectra were collected data resolution of 4 cm$^{-1}$ in the 4000-400 cm$^{-1}$ range. X-Ray diffraction (XRD) patterns were recorded using Rigaku Miniflex600 for analysis crystallinity of catalysts. The morphology of catalysts was investigated by Scanning Electron Microscope (SEM) using JSM-6510LA. All morphology were collected data magnification in 20.000.

3. Results and Discussion

3.1. X-Ray Fluorescence (XRF)

Table 1 shows that the impregnation process has been successfully carried out. This statement is according to the appearance of metal that embedded in natural zeolites. However, it was found that the metal amount in the natural zeolite differed with the sum of metal added. This possibly because of the uneven metal dispersion, such as accumulation and agglomeration of metals in zeolites.

Meanwhile, there is a difference between Si/Al mole ratios in each catalyst. The Si/Al mole ratio decreased after metal loading, wherein the Si/Al mole ratio of the ZA material is 5.7, while the Si/Al mole ratio of NiMo/ZA and CoMo/ZA are 4 and 3.3, respectively. This confirmed that the amount of Al atoms decreased after the addition of NiMo and CoMo. These probably caused by an Al replacement on the zeolite framework.
### Table 1. Chemical composition of natural zeolite, NiMo/ZA and CoMo/ZA

| Metal element | Concentration (% w) | ZA   | NiMo/ZA | CoMo/ZA |
|---------------|---------------------|------|---------|---------|
| O             |                     | 47.56| 42.84   | 41.71   |
| Si            |                     | 31.48| 22.69   | 22.33   |
| Al            |                     | 5.34 | 4.49    | 4.32    |
| Co            | -                   | -    | -       | 3.06    |
| Ni            | -                   | -    | 3.41    | -       |
| Mo            | -                   | -    | 4.26    | 5.92    |
| Si/Al mole ratio |               | 5.7  | 4       | 3.3     |

3.2. *Fourier Transform Infra-Red (FTIR)*

The spectra of natural zeolites before and after metal loading shows different patterns (Fig.1). The bands typical for natural zeolite structures are present at wave numbers of 794.67 cm\(^{-1}\) due to the vibration of the Si-O bending of the zeolite framework. The Si-O/Al-O vibration occurs at the wave number of 462.96 cm\(^{-1}\) for natural zeolite, 463.90 cm\(^{-1}\) for NiMo/ZA catalyst and 461.97 cm\(^{-1}\) for CoMo/ZA catalyst, respectively.

![Figure 1. Spectra FTIR of (a) ZA (b) NiMo/ZA (c) CoMo/ZA](image)

The band of 4000-3000 cm\(^{-1}\) shows the vibration of O-H hydroxyl stretching on the zeolite structure[12,13]. In addition, the OH bending of water molecules in the natural zeolite, NiMo/ZA, and CoMo/ZA catalyst is shown at the band of 1645.36 cm\(^{-1}\), 1636.67 cm\(^{-1}\), and 1628.95 cm\(^{-1}\), respectively[14]. The shift occurs at the peak of 1100-1000 cm\(^{-1}\) due to asymmetric stretching vibrations of group TO\(_4\) to larger numbers[15]. In the
infrared spectra of the natural zeolite, the \( \text{TO}_4 \) asymmetric stretch vibration is shown in the 1045.46 cm\(^{-1}\), whereas the NiMo/ZA catalyst has a shift of wave numbers at 1092.72 cm\(^{-1}\) and the shift at 1089.83 cm\(^{-1}\) occurs in CoMo/ZA catalysts.

3.3. X-Ray diffraction (XRD)

Figure 2 shows that the natural zeolite from Wonosari, Yogyakarta mainly consisted of modernite crystals [3]. The crystallinity of natural zeolites is poor, because there are still contained impurities in the natural zeolites, and the presence of tetrahedral framework of zeolite is still irregular. The diffractogram intensity of NiMo/ZA and CoMo/ZA catalysts are lower than natural zeolite (ZA). It indicated that the metals loading causes reduced crystallinity of NiMo/ZA and CoMo/ZA. Modification of natural zeolites with transition metals causes reduced crystallinity as indicated by a decrease in the intensity of some characteristic peaks[16].

![Diffractogram of (a) ZA (b) NiMo/ZA (c) CoMo/ZA](image)

Furthermore, the appearance of new peaks in the diffractogram of NiMo/ZA and CoMo/ZA indicates that the metal impregnation process succeeded. The results of further analysis using Le Bail methods show that metal phases scattered in the natural zeolite are NiO, CoO and MoO\(_3\), respectively.

3.4. Scanning Electron Microscope (SEM)

Natural zeolite before modified with metals has an irregular morphological shape (Fig. 3). The changes of natural zeolite morphology due to metal oxide exposure to the natural zeolite. In figure 3b, showed that NiO metal oxides are scattered on the surface of natural zeolite which is identified by white spherical. Meanwhile, in figure 3c showed that CoO metal oxides with rhombic shape and MoO\(_3\) with hexagonal shape scattered on the surface of the natural zeolite.

Various surface morphologies indicated that the metals dispersion are not the same on each catalyst. Figure 3b and 3c showed that the surface characteristics of the natural zeolite completely disappeared. This is indicated that metals embedded and scattered on the surface of the natural zeolite.
4. Conclusion
NiMo and CoMo metals can be added on the natural zeolite by the co-impregnation method and followed by calcination and reduction. The small amounts of transition metals loading into natural zeolites did not affect the zeolite crystallinity but significantly affected the morphology of the catalyst. Ni, Co, and Mo metals are as metal oxides NiO, CoO, and MoO3.

Acknowledgement
The authors are grateful to Ministry of Research, Technology and Higher Education of the Republic of Indonesia for support of this research under Penelitian Dasar Unggulan Perguruan Tinggi (PDUPT) Research Grant (Contract No.: 474/UN27.21/PP/2018).

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