Research Article

Khoirina Dwi Nugrahaningtyas*, Nining Rahmawati, Fitria Rahmawati, Yuniawan Hidayat

Synthesis And Characterization Of CoMo/Mordenite Catalyst For Hydrotreatment Of Lignin Compound Models

<https://doi.org/10.1515/chem-2019-0120>

received August 30, 2018; accepted May 8, 2019.

Abstract: The synthesis of CoMo/Mordenite (CoMo/MOR) catalysts was conducted using a co-impregnation method at a various Co/Mo ratios. The produced catalysts were then characterized by X-ray diffraction, total acidity analysis, and scanning electron microscopy. The activity of the catalyst in a hydrotreatment reaction was evaluated by applying the catalyst as a reduced-catalyst to the hydrocracking (HC) reaction of anisole molecules. Analysis of the diffraction data using the Le Bail refinement technique showed that the metal phase was successfully impregnated into the MOR. In addition, increasing the metal content resulted in an increase in the acidity of the catalysts and changed the morphology of the catalysts from homogeneous to heterogeneous with larger particle size. According to the data of GCMS, it is known that the catalysts successfully removed methyl group of anisole molecules. Hydrotreatment reaction with the prepared-catalyst produced 4.77% of phenols. It is 122 % higher than the reaction with MOR catalyst.

Keywords: CoMo/MOR catalyst, metal phase, hydrotreatment catalyst.

1 Introduction

Hydrotreatment is a reaction of various hydrogenation processes, such as a reaction to change double/triple bonds into saturated hydrocarbons, a reaction to convert heavy

fraction hydrocarbons into light fraction hydrocarbons, and to remove impurities such as sulfur, nitrogen, oxygen, and metals [1, 2]. A hydrotreatment reaction usually requires a catalyst to reduce the temperature and energy of a reaction. Typical catalysts used are heterogeneous in which a transition metal, for example Co, Mo, Ni, Pt, and Pd, is dispersed on a substrate or supporting agent. Co and Mo are the suitable transition metals for catalysis, for hydrogenation [3] or deoxygenation reactions [4] respectively.

Transition metals can be used as catalysts in both mono-metal and bimetal form. Augustine [5] states that metals in a bimetallic form have better reactivity and selectivity than their monometallic counterparts. In addition, the use of a pure metal as a catalyst has several disadvantages, such as agglomerates easily, undergoes deactivation due to obstruction of the active site, and shorter catalyst life.

The catalytic properties of metals can be developed by the use of supported catalyst. Many porous materials have been widely utilized as catalyst supports such as γ -alumina [6, 7], activated carbon [8], natural zeolites [9–11], ZSM-5 [12–15], and MOR [10, 14, 16, 17]. MOR has quite large pores ($\pm 7\text{\AA}$), high thermal stability and has cavities and channels that make it suitable as an adsorbent, ion-exchange medium and a catalyst [18]. The high thermal stability of MOR is shown by its ability to maintain its structure to a temperature of 800–900°C [18].

Trisunaryanti and coworkers [19] used Co, Ni, and Pd supported on MOR for HC reaction of α -cellulose. It is found that the catalyst can convert α -cellulose to some low mass molecule compound such as ethanoic acid, propanoic acid, ethanol and 2-propanone [19]. Meanwhile, MOR modified with Ni and Co, producing a bimetallic Ni-Co/MOR catalyst, shows a better performance in a cracking process of decalin's ring, than the similar process with a monometallic catalyst of Ni/MOR [20]. A bimetallic NiMo/ Al_2O_3 also shows a better performance in the

*Corresponding author: Khoirina Dwi Nugrahaningtyas, Dept. of Chemistry, Fac. Of Math. and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36A, Surakarta, Indonesia, E-mail: Khoirina@mipa.uns.ac.id

Nining Rahmawati, Fitria Rahmawati, Yuniawan Hidayat, Dept. of Chemistry, Fac. Of Math. and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36A, Surakarta, Indonesia

deoxygenation of vegetable oil, than the monometal Mo/ Al_2O_3 [4].

Some methods to load metals on support materials have been developed, such as deposition [21], impregnation [22] and co precipitation [23]. The impregnation method is a simple one, less time consuming and relatively cheap. The impregnation method can load Pd metal to MOR and produce better catalytic activity and selectivity than the similar Pd/MOR that was prepared by the ion-exchanged method [21].

The impregnation method is affected by reaction conditions such as temperature, reflux time, pressure and the ratio of metal loaded [24]. While, the determinants factors of the catalysts-supported metals character are metal content [18], crystallinity [25], functional groups [26], acidity [27], surface area, pore size distribution, pore volume, particle size [28], and morphology [29].

In a CoMo/SBA-15 system, it is known that the best performance is obtained at 3% Co content and 8% Mo content [30]. However, another study reported that the best performance was found with 2% and 8% of CoO and MoO_3 impregnation, respectively [31]. The performance was investigated from crystallinity of product and its metal content parameter [31].

This work aims to investigate the effect of Cobalt-Molybdenum composition in MOR to the catalyst character, and to the catalyst activity in an anisole hydrotreatment. Anisole is a typical oxygen-containing hydrocarbon present in lignin or bio-oil. Therefore, this work may contribute to the investigation of catalyst character and its performance in hydrotreatment reaction.

2 Experimental

2.1 Material

This research used a synthetic MOR (HS-690-Wako) as a catalyst support. Analytical grade $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ammonia and anisole were purchased from Merck.

2.2 Catalyst Preparation and Characterization

A series of cobalt molybdate catalysts was prepared by the co-impregnation method. MOR was poured into the solution of cobalt nitrate that was mixed with ammonium molybdate. At first, the Mo, Co, and MOR were mixed in the ammonia solution with deionized-water as a solvent.

The solution was then refluxed at 60°C for 2 hours, followed by drying with a rotary evaporator. The powder was then calcined at 550°C for 3 hours under N_2 gas flow (10 mL min⁻¹) then heated at 400°C for 2 hours under H_2 gas flow, finally being cooled to room temperature under H_2 gas flow. During this process the sample was stored in a desiccator to avoid contact with air.

2.3 Catalyst Characterization

The metal contents of the co-impregnation product were analyzed by X-ray Fluorescence (XRF BRUKER S2 Ranger). Crystallinity and metal phase of the produced catalysts were investigated by X-ray powder diffraction technique (Shimadzu 7000 with Cu-K α radiation $\lambda = 1.5418 \text{ \AA}$ at $3 < 2\theta < 90^\circ$, $\theta/2\theta$ scanning mode, with 0.02° sampling pitch, and $3^\circ/\text{min}$ scan speed). The obtained diffraction patterns were then refined with Le Bail method by RIETICA software, by inputting data of standard diffraction from ICSD file. Strategies for combining X-ray diffraction analysis and fluorescence have been shown to be successful in determining the phase and chemical compositions [32–35]. Meanwhile, the total acidity value is determined by the adsorption method with two types of probe molecules (pyridine and ammonia molecules), followed by evacuation for 30 minutes at 150°C, and recorded by FTIR (Shimadzu IR prestige-21) spectrometer at the wavelength of 4000–500 cm⁻¹. The pyridine and ammonia adsorption methods are based on the combined procedure from Tyagi et al. [36] and Barzetti et al. [37].

The prepared samples were degassed at 180°C for 3 hours and then the N_2 adsorption/desorption isotherm in the sample was measured by Surface Area Analyzer, SAA (Quantacrome ver. 10.1) at low temperatures (77.3 K). The specific surface area, total pore volume, and average pore radius calculated by the BET method (assuming $P/P_0 = 0.98$, and cylindrical shapes of pores). The morphology observed by utilizing SEM (JEOL JSM 6510 LA).

2.4 Catalyst Testing

Anisole and catalyst (in 10:1 weight ratio) were loaded in a mini-batch autoclave reactor (h: 9.5 cm; o.d.: 6.5 cm; i.d.: 5.4 cm) which was then evacuated to remove air. The reaction was carried out under hydrogen gas at a pressure of 1 bar and a temperature of 350°C for one hour. The liquid product was collected and analyzed by Gas Chromatograph Mass Spectrometer (GC-MS) QP 2010 SE. The yield of product was calculated by El-Hakam equations [27].

Figure 1: XRF results analysis of MOR and CoMo/MOR.

3 Results and Discussion

3.1 Catalyst Properties

Elemental analysis of the catalysts was conducted by XRF to MOR before and after modification. The analysis was conducted to prove that Co and Mo are well impregnated into the MOR. The elemental content along with its composition are shown in Figure 1.

Figure 1a. shows the amount of Co and Mo metals on the CoMo/MOR catalysts. The percentage of Co and Mo increase from 2.42% to 8.85% for Co and 0.34% to 1.25% for Mo with increasing precursor addition. However, the presence of Co and Mo metals on MOR cause a decreasing amount of Si and Al (Fig. 1b.).

XRD analysis of the prepared catalysts to understand their crystallinity, crystal structure and the metal phase of the samples. The diffraction patterns are shown in Figure 2.

Based on Figure 2, the diffraction pattern shows characteristic peaks at 2θ ($^{\circ}$) angles of 9.78° ; 13.56° ; 19.70° ; 22.51° ; and 27.78° . This result is consistent with previous research in which some sharp characteristic peaks at 2θ of 9.82° ; 13.56° ; 19.69° ; 22.35° and 27.74° were reported [20, 38]. Figure 2 shows that diffraction pattern of CoMo/MOR is almost similar to the initial MOR. It is probably caused by the highly dispersed support material or the quantity of metal particles added to MOR are very few and still below the limit detection of the XRD instrument [39].

Figure 2 also shows that there is no 2θ shift before and after MOR modification. This indicates that the addition of Co-Mo metals just interfered the MOR's framework [40] rather than damaging or changing the crystallinity which would be signified by a shift in the peak position. For example, the replacement of Al-O bonds with shorter Si-O bonds will cause the shrinkage of the unit cell and a

Figure 2: XRD patterns of MOR and CoMo/MOR.

reduction in crystallinity. As a consequence, the peak in the diffractogram will shift to higher angles[41].

To determine the crystal structure the XRD data was compared with the Inorganic Crystal Structure Database (ICSD) data and then refined using the Le Bail method with RIETICA software. The aim of this refinement is to understand if there are any overlapping reflections of phase that appear on samples[32–35, 42–47]. The first refinement investigated the suitability of the MOR material used with the existing MOR standard based on the residual factor value (R_p and R_{wp}). The residual factor is the limit value of nonconformity in the analysis that is still acceptable. If there is non-conformity between data and the calculation the residual factor value becomes lower. The Le Bail refinement was conducted by inputting standard diffraction ICSD #4393 and found that the MOR was crystallized in orthorhombic structure with space group of $Cmcm$ and cell parameters of $a = 18.007$; $b = 20.269$; $c = 7.465$ Å. The cell volume is 2724.6 Å³ and

Table 1: The refinement result of P-XRD data of CoMo/MOR catalyst.

	MOR (ICSD # 4393)	Co (ICSD # 41507)	Mo (ICSD # 173127)	MoO ₃ (ICSD # 36167)	CoMoO ₄ (ICSD # 281235)
Crystal structure	Orthorhombic	Monoclinic	Cubic	Orthorhombic	Monoclinic
Space Group	C m c m	C 1 2/m 1	I m -3 m	P b n m	P 1 2/c 1
a (Å)	18.118	5,180	3,146	3,954	4,659
b (Å)	20,341	3,015	3,146	13,825	5,686
c (Å)	7,504	3,017	3,146	3,694	4,916
Angle (°)	$\alpha=\beta=\gamma=90$	$\alpha=\gamma=90$ $\beta=125,55$	$\alpha=\beta=\gamma=90$	$\alpha=\beta=\gamma=90$	$\alpha=\gamma=90$ $\beta=90,521$
Cell Volume (Å ³)	2765.715	38.340	31.140	201.930	130.250
Z	48	2	2	4	2

Figure 3: Modeling of MOR framework.

the angle between axes of $\alpha = \beta = \gamma = 90^\circ$. Based on the refinement result the MOR structure framework can be described as shown in Figure 3.

Figure 3 shows that the MOR framework is composed of Si and Al metals, and has two main cavities bounded by oxygen atoms. There is a balancing proton inside the cavities that can undergo a cation exchange with the embedded transition metal. The results of Huertas-Miranda and Martinez-Iñesta [48] study show that the transition metal can occupy the side pockets and the main pore channel depending on temperature, the zeolite's silicon to aluminum ratio (Si/Al) and metal loading.

The unidentified peaks in the diffraction pattern might be belong to metals, metal oxides, and metal alloys and therefore a more in-depth analysis was carried out by inputting some standard pure metals and metal oxides namely Co (ICSD # 41507), Mo (ICSD # 173127), MoO₃ (ICSD # 36167), and CoMoO₄ (ICSD # 281235) on CoMo / MOR catalysts. The refinement result shows that the residual factor values (Rp and Rwp) decreased after inputting

some standard diffraction above. The result is listed in Table 1. The refinement result proved that Co, Mo, MoO₃, and CoMoO₄ are available or successfully loaded in the modified MOR of CoMo/MOR catalyst.

The FTIR spectrum of the CoMo/MOR catalyst compared to the various MOR spectra is shown in Figure 4. The broadband peak at a wavenumber around 3400 cm⁻¹ is predicted to be a vibrational stretch from isolated groups (Si-O-H) and water molecules that are adsorbed on the surface of catalyst [38, 49]. The presence of water bound to the surface is supported by an absorption band at 1640 cm⁻¹ [38]. Meanwhile, the peak at 1100 – 1050 cm⁻¹ are internal and external symmetric stretching of O-Si/Al-O-. While, the peak at 420-500 cm⁻¹ corresponds to an internal and external asymmetric stretching ($\leftarrow\text{O}(\text{Si}/\text{Al})\rightarrow\leftarrow\text{O}$) of siliceous materials [38]. FTIR analysis of MOR and CoMo/MOR show similar characteristic peaks, however the transmittance shown by the peaks are different. It is probably caused by the different amount of Co and Mo metals in the MOR and the number of acid sites inside the catalyst also may produce a different transmittance value.

Acidity analysis of MOR and CoMo/MOR was conducted using a gravimetric method with ammonia as a probe molecule. The ammonia can also act as Lewis and Bronsted bases, therefore the total acidity of catalyst can be determined. The total acidity of MOR and CoMo/MOR are listed in Table 3.

Table 3 shows that the addition of Co and Mo metals to MOR can increase the acidity. MOR catalyst provides Bronsted acid site due to the presence of hydroxyl functional groups. Meanwhile, Co and Mo act as Lewis acid because both have a half-full d orbital. This causes the acidity of the catalyst to increase after Co and Mo addition. Even though the total acidity increases as the Co content increases, the acidity decreases after 8% of

Table 2: Residual factor value (Rp and Rwp) from the refinement results.

Residual Factor	MOR	Co0Mo/MOR	Co2Mo/MOR	Co4Mo/MOR	Co6Mo/MOR	Co8Mo/MOR
Rp (%)	5.97	2.96	2.25	3.08	1.54	2.03
Rwp (%)	6.62	4.73	4.57	5.77	3.37	2.54

Table 3: Total acidity of MOR and CoMo/MOR catalysts.

Catalyst	Total acidity (mmol/g)
MOR	1.79
Co0Mo/MOR	2.88
Co2Mo/MOR	2.70
Co3Mo/MOR	3.38
Co6Mo/MOR	2.82
Co8Mo/MOR	1.33

Figure 4: FTIR analysis of MOR and CoMo/MOR.

Co metal content. Excessive metal addition can lead to agglomeration that may reduce the total acidity of CoMo/MOR catalysts. However, the acidity of CoMo/MOR catalyst is still higher than the Ni(Co)/MOR catalyst [20]. It means that the CoMo/MOR catalyst is better than Ni(Co)/MOR. The presence of Bronsted and Lewis acid sites of MOR and CoMo/MOR can be analyzed by FT-IR analysis with the spectra as shown in Figures 5 and 6.

Figure 6 shows that all samples have the same type of adsorption isotherm, namely type IV isotherm. All catalyst are included in the category of mesoporous material, confirmed by the presence of a hysteresis loop. Further analysis to the adsorption isotherm may describe the effect of cobalt/molybdenum ratio to the specific surface area, total pore volume and an average pore radius of the CoMo/

MOR catalyst. The adsorption isotherm data is processed using the BET method, and the results are shown in Table 4. Table 4 shows that surface area of MOR decreases due to the addition of Co and Mo. However, the pore radius average and total pore volume of CoMo/MOR increases.

Figure 8 shows that MOR has homogeneous particle size. Co and Mo addition seems to change the morphology of MOR. The Co6Mo/MOR and Co8Mo/MOR are dominated by large size of particles, because of their Co/Mo ratio is great. Particle size analysis from SEM images was conducted with MeasureIt software and the results are shown in Figure 9.

Figure 9 shows that CoMo/MOR has a more heterogeneous particle size than MOR. The particle size of MOR is between 0.31 – 0.50 μm , meanwhile Co0Mo/MOR, Co2Mo/MOR and Co4Mo/MOR has particle size of 0.91 – 1.20 μm , Co6Mo/MOR is 0.71 – 0.70 μm , and Co8Mo/MOR is between 0.71 – 0.90 μm . The presence of metals, metal oxide and metal alloy seems to increase heterogeneity of the catalyst particle size as well increasing the particle size itself [20].

3.2 Preliminary Study of Catalyst Activities

Based on the characterization of the prepared catalyst, it is found that all catalysts have almost similar properties except for the total acidity value. Therefore, in the pre-study of the HC reaction of anisole, the moderate acidity catalyst, i.e., Co6Mo/MOR was chosen. The main products of the reaction are o-methoxy toluene and phenol. The amount of conversion of anisole to o-methoxy toluene and phenol is calculated based on GC [27]. The yields of product conversion are presented in Figure 10.

The product analysis of the HC reaction of anisole shows that the CoMo/MOR catalyst is not suitable for opening the anisole ring. Weak HC properties of catalysts are possible because of the low strength of Lewis acid [20]. The percentage conversion of anisole HC reaction with Co6Mo/MOR catalyst is 3.55% o-methoxy toluene and 4.77% phenols. Meanwhile, when MOR was used as catalyst the percentage conversion is 0.02% o-methoxy toluene, and 0.39% phenols. It shows a better activity of CoMo/MOR than MOR. If the product redress is assumed

Figure 5: FTIR spectra of ammonia adsorption, (A) & (C) after evacuated at room temperature; (B) & (D) at 150°C.

Figure 6: FTIR spectra after pyridine adsorption, (A) & (C) after evacuated at room temperature; (B) & (D) at 150°C.

Figure 7: Profile of the adsorption isotherm of MOR and CoMo/MOR catalysts.

to be the same as the catalyst activity, then the CoMo / MOR catalyst activity is better than Ni (Co)/MOR catalyst activity [20].

4 Conclusion

The results show that MOR was successfully modified with Co and Mo metals which is shown by the increase of the Co and Mo metal content in the CoMo / MOR catalyst. The addition of metals does not change the functional group, however it decreases the crystallinity and surface area of MOR. Meanwhile, the total acidity of the catalyst tended to increase along with the increase in the metal content. The Co and Mo addition also change the morphology to become more heterogeneous with larger particle size. The anisole HDO reaction with Co6Mo/MOR has higher

Figure 8: Morphology of MOR and CoMo/MOR catalysts.

Table 4: The parameters of porous structure of MOR and CoMo/MOR catalysts.

Catalyst	Specific surface area (m ² /g)	Total pore volume (cc/g)	Average pore size (Å)
MOR	381	0.156	18.938
Co0Mo/MOR	311	0.151	19.023
Co2Mo/MOR	306	0.182	19.043
Co3Mo/MOR	277	0.180	18.992
Co6Mo/MOR	279	0.184	18.960
Co8Mo/MOR	332	0.188	19.004

Figure 9: Particle size distribution of MOR and CoMo/MOR catalysts.

Figure 10: Product yields.

product yield than the reaction with MOR as catalyst. It indicates a better catalytic activity of Co₆Mo/MOR than MOR. Based on the product yield of the anisole HC reaction, it is also known that Co₆Mo/MOR catalyst has better catalytic activity than MOR.

Acknowledgement: This research is part of Penelitian Dasar perguruan Tinggi (PDUPT) with contract number of 474/UN.27.21/PP/2018. Authors acknowledge the Ministry of Research, Technology and Higher Education, Republic of Indonesia, for funding this grant.

References

- [1] Robinson P., Practical advances in petroleum processing, 2006.
- [2] Topsøe H., Clausen B.S., Massoth F.E., Hydrotreating catalysis. In: Anderson J.R., Boudart M. (Eds.), Catalysis, Vol 11, 1996.
- [3] Wang W., Yang Y., Luo H., Liu W., Characterization and hydrodeoxygenation properties of Co promoted Ni-Mo-B amorphous catalysts: Influence of Co content, React. Kinet. Mech. Catal., 2010, 101,105–115, DOI: 10.1007/s11144-010-0201-3.
- [4] Kubička D., Kaluža L., Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts, Appl. Catal. A Gen., 2010, 372,199–208, DOI: 10.1016/j.apcata.2009.10.034.
- [5] Augustine R.L., Heterogeneous catalysis for the synthetic chemist, Marcel Dekker Inc., 1996.
- [6] Trueba M., Trasatti S.P., γ-alumina as a support for catalysts: A review of fundamental aspects, Eur. J. Inorg. Chem., 2005, 3393–3403, DOI: 10.1002/ejic.200500348.
- [7] Paranjpe K.Y., Alpha, beta and gamma alumina as a catalyst -A Review, Pharma Innovation, 2017, 6, 11, 236-238.
- [8] Fukuyama H., Terai S., Uchida M., Cano J.L., Ancheyta J., Active carbon catalyst for heavy oil upgrading, Catal. Today, 2004, 98,207–215, DOI: 10.1016/j.cattod.2004.07.054.
- [9] Nugrahaningtyas K.D., Cahyono E., Widjonarko D.M., The Parafin Cracking Reaction With NiMo/Active Natural Zeolite Catalyst: The Effect Temperature On The Catalytic Activity, ALCHEMY J. Penelit. Kim., 2016, 11, 111–126.
- [10] Sesario R., Dwi K., Rahmawati F., Herald E., Rachmadani, Characterization of metal particles on supporting materials mordenite, ultra stable γ zeolita, and natural zeolit, Proceeding of 4th International Conference on Research, Implementation, and Education of Mathematics and Sciences, (14 – 16 May 2017, Yogyakarta, Indonesia), AIP Conference Proceeding, 2017, 1868-1874, DOI: 10.1063/1.4995088.
- [11] Nugrahaningtyas K.D., Widjonarko D.M., Trisunaryanti W., Triyono, Preparation and characterization of NiMo/active natural zeolite catalysts, In: Kai L (ed) Chemical, Biological and Environmental Engineering - Proceedings of The International Conference On CBEE 2009 (9 - 11 October 2009, Singapore), World Scientific Publishing Company, 2009, 171–174.
- [12] Dědeček J., Kaucký D., Wichterlová B., Co²⁺ ion siting in pentasil-containing zeolites, part 3.: Co²⁺ ion sites and their occupation in ZSM-5: a VIS diffuse reflectance spectroscopy study, Micropor. Mesopor. Mat., 2000, 35, 483–494, DOI: 10.1016/S1387-1811(99)00244-9.

- [13] Zhao X., Wei L., Cheng S., Huang Y., Yu Y., Julson J., Catalytic cracking of camelina oil for hydrocarbon biofuel over ZSM-5-Zn catalyst, *Fuel Process Technol.*, 2015, 139, 117–126, DOI: 10.1016/j.fuproc.2015.07.033.
- [14] Kaucký D., Vondrová A., Dědeček J., Wichterlová B., Activity of Co ion sites in ZSM-5, ferrierite, and mordenite in selective catalytic reduction of NO with methane, *J. Catal.*, 2000, 194, 318–329, DOI: 10.1006/jcat.2000.2925.
- [15] Mlekodaj K., Sadowska K., Datka J., Góra-Marek K., Makowski W., Porosity and accessibility of acid sites in desilicated ZSM-5 zeolites studied using adsorption of probe molecules, *Micropor. Mesopor. Mat.*, 2014, 183, 54–61, DOI: 10.1016/j.micromeso.2013.08.051.
- [16] Oprea C., Popescu V., Birghila S., New studies about the modified mordenites, *Rom. Rep. Phys.*, 2008, 53, 231–239.
- [17] Mohamed M.M., Nohman A.K.H., Zaki M.I., Development of catalytic properties of mordenite zeolite via chemical modification, *Curr. Top. Catal.*, 2005, 4, 80–99, DOI: 10.1002/chin.200638241.
- [18] Trisunaryanti W., Triyono T., Denti F.A., Preparation of Ni-Mo/Mordenite catalysts under the variation of Mo/Ni ratio and their characterizations for stearic acid conversion, *Indones. J. Chem.*, 2003, 3, 80–90.
- [19] Trisunaryanti W., Triyono, Armunanto R., Hastuti L.P., Ristiana D.D., Ginting R.V., hydrocracking of α -cellulose using Co, Ni, and Pd supported on mordenite catalysts, *Indones. J. Chem.*, 2018, 18, 166, DOI: 10.22146/ijc.26491.
- [20] Chawla M., Rafiq S., Jamil .F, Usman M.R., Khurram S., Ghauri M., Muhammad N., Al-muhtaseb A.H., Aslam M., Hydrocarbons fuel upgradation in the presence of modified bi-functional catalyst, *J. Clean. Prod.*, 2018, 198, 683–692, DOI: 10.1016/j.jclepro.2018.06.286.
- [21] Cañizares P., De Lucas A., Dorado F., Durán A., Asencio I., Characterization of Ni and Pd supported on H-mordenite catalysts: Influence of the metal loading method, *Appl. Catal. A.*, 1998, 169, 137–150, DOI: 10.1016/S0926-860X(98)00008-8.
- [22] Shimizu T., Hiroshima K., Honma T., Mochizuki T., Yamada M., Highly active hydrotreatment catalysts prepared with chelating agents, *Catal. Today*, 1998, 45:271–276 . doi: 10.1016/S0920-5861(98)00227-2.
- [23] Jung Y.S., Yoon W.L., Seo Y.S., Rhee Y.W., The effect of precipitants on Ni-Al₂O₃ catalysts prepared by a co-precipitation method for internal reforming in molten carbonate fuel cells, *Catal. Commun.*, 2012, 26, 103–111, DOI: 10.1016/j.catcom.2012.04.029.
- [24] Hegedus L.L., *Catalyst design: progress and perspectives*, Wiley, New York, 1987.
- [25] Al-Zeghayer Y.S., Sunderland P., Al-Masry W., Al-Mubaddel F., Ibrahim A.A., Bhartiya B.K., Jibril B.Y., Activity of CoMo/gamma-Al₂O₃ as a catalyst in hydrodesulfurization: Effects of Co/Mo ratio and drying condition, *Appl. Catal. A.*, 2005, 282, 163–171, DOI: 10.1016/j.apcata.2004.12.021.
- [26] Okamoto Y., Ishihara S.Y., Kawano M., Satoh M., Kubota T., Preparation of Co-Mo/Al₂O₃ model sulfide catalysts for hydrodesulfurization and their application to the study of the effects of catalyst preparation, *J. Catal.*, 2003, 217, 12–22, DOI: 10.1016/S0021-9517(03)00029-0.
- [27] El-Hakam S.A., Samra S.E., El-Dafrawy S.M., Ibrahim A.A., Salama R.S., Surface acidity and catalytic activity of sulfated titania supported on mesoporous MCM-41, *Int. J. Modern Chem.*, 2013, 5, 55–70.
- [28] Leofanti G., Padovan M., Tozzola G., Venturelli B., Surface area and pore texture of catalysts, *Catal Today*, 1998, 41, 207–219, DOI: 10.1016/S0920-5861(98)00050-9.
- [29] Ching Tian T., Effects of catalyst morphology on hydrotreating reactions, *J. Eng. Sci. Technol.*, 2008, 3, 117–123.
- [30] Dhar G.M., Kumaran G.M., Kumar M., Rawat K. S., Sharma L.D., Raju B.D., Rao K.S. R., Physico-chemical characterization and catalysis on SBA-15 supported molybdenum hydrotreating catalysts, *Catal. Today*, 2005, 99, 309–314, DOI: 10.1016/j.cattod.2004.10.005.
- [31] Nugrahaningtyas K.D., Hidayat Y., Saputri T.D., Effect of concentration metal precursor Co and Mo on character of CoMo/USY catalyst, *Alchimy J. Penelit. Kim.*, 2014, 10, 40–48, DOI: 10.20961/alchimy.v10i1.9.
- [32] Lutterotti L., Dell'Amore F., Angelucci D.E., Carrer F., Gialanella S., Combined X-ray diffraction and fluorescence analysis in the cultural heritage field, *Microchem. J.*, 2016, 126, 423–430, DOI: 10.1016/j.microc.2015.12.031.
- [33] Bortolotti M., Lutterotti L., Pepponi G., Combining XRD and XRF analysis in one Rietveld-like fitting, *Powder Diffr.*, 2017, 32, S225–S230, DOI: 10.1017/S0885715617000276
- [34] Serafini A., Lutterotti L., Gross S., Gialanella S., Characterization of nanograined powder samples using the Rietveld method applied to electron diffraction ring patterns, *Powder Diffr.*, 2017, 32:S63–S68, DOI: 10.1017/S0885715617000343.
- [35] Secchi M., Zanatta M., Borovin E., Bortolotti M., Kumar A., Giarola M., et al., Mineralogical investigations using XRD, XRF, and Raman spectroscopy in a combined approach, *J. Raman Spectrosc.*, 2018, 49, 1023–1030, DOI: 10.1002/jrs.5386.
- [36] Tyagi B., Chudasama C.D., Jasra R.V., Characterization of surface acidity of an acid montmorillonite activated with hydrothermal, ultrasonic and microwave techniques, *Appl. Clay Sci.*, 2006, 31, 16–28, DOI: 10.1016/j.clay.2005.07.001.
- [37] Barzetti T., Selli E., Moscotti D., Forni L., Pyridine and ammonia as probes for FTIR analysis of solid acid catalysts, *J. Chem. Soc. Faraday Trans.*, 1996, 92, 1401–1407, DOI: 10.1039/ft996201401.
- [38] Narayanan S., Vijaya J.J., Sivasanker S., Alam M., Tamizhdurai P., Kennedy L.J., Characterization and catalytic reactivity of mordenite - Investigation of selective oxidation of benzyl alcohol, *Polyhedron*, 2015, 89, 289–296, DOI: 10.1016/j.poly.2014.12.038.
- [39] Cohen J.B., X-ray diffraction studies of catalysts, *Ultramicroscopy*, 1990, 34, 41–46, DOI: 10.1016/0304-3991(90)90055-Q.
- [40] Anderson J., Garcia M., *Supported metals in catalysis*, Imperial College Press, Singapore, 2005.
- [41] Zhu X., Lobban L.L., Mallinson R.G., Resasco D.E., Tailoring the mesopore structure of HZSM-5 to control product distribution in the conversion of propanal, *J. Catal.*, 2010, 271, 88–98, DOI: 10.1016/j.jcat.2010.02.004.
- [42] Le Bail A., New Developments in microstructure Rietveld refinement analysis, *Adv. X-Ray Anal.*, 2000, 42, 191–203.
- [43] Le Bail A., Whole powder pattern decomposition methods and applications: A retrospection, *Powder Diffr.*, 2005, 20, 316–326, DOI: 10.1154/1.2135315.

- [44] Schönenberger J., Momose T., Wagner B., Leong W.H., Tarnawski V.R., Canadian field soils I. Mineral composition by XRD/XRF measurements, *Int. J. Thermophys.*, 2012, 33, 342–362, DOI: 10.1007/s10765-011-1142-4.
- [45] Tamer M., Quantitative phase analysis based on rietveld structure refinement for carbonate rocks, *J. Mod. Phys.*, 2013, 04, 1149–1157, DOI: 10.4236/jmp.2013.48154.
- [46] Sanches E.A., Carolino A.D.S., Santos A.L.D., Fernandes E.G.R., Trichês D.M., Mascarenhas Y.P., The use of Le bail method to analyze the semicrystalline pattern of a nanocomposite based on polyaniline emeraldine-salt form and α -Al₂O₃, *Adv. Mater. Sci. Eng.*, 2015, 2015, 1-8, DOI: 10.1155/2015/375312.
- [47] Toraya H., A new method for quantitative phase analysis using X-ray powder diffraction: Direct derivation of weight fractions from observed integrated intensities and chemical compositions of individual phases, *J. Appl. Cryst.*, 2016, 49, 1508–1516, DOI: 10.1107/S1600576716010451.
- [48] Huertas-Miranda J.A., Martinez-Iñesta M., Monte Carlo studies of the effect of temperature, Si/Al, and metal loading on the templated synthesis of Pt nanowires in MOR-type zeolites, *J. Nanosci. Nanotechnol.*, 2010, 2, 633–636.
- [49] Korkuna O., Leboda R., Skubiszewska-Zięba J., Vrublevs'ka, T., Gun'ko V.M., Ryzkowski J., Structural and physicochemical properties of natural zeolites: Clinoptilolite and mordenite, *Micropor. Mesopor. Mat.*, 2006, 87, 243–254, DOI: 10.1016/j.micromeso.2005.08.002.