Preparation, Characterization, and Catalytic Activity of MoCo/USY Catalyst on Hydrodeoxygenation Reaction of Anisole

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Abstract. This research aims to prepare, characterize, and study the catalytic activity of Molybdenum (Mo) and Cobalt (Co) metal with supporting material Ultra Stable Y-Zeolite (USY), to produce catalysts with activity in hydrotreatment reaction and in order to eliminate impurities compounds that containing unwanted groups heteroatoms. The bimetallic catalysts MoCo/USY were prepared by wet impregnation method with weight variation of Co metal 0%, 2%, 4%, 6%, 8%, and Mo metal 8% (w/w), respectively. Activation method of the catalyst included calcination, oxidation, reduction and the crystallinity was characterized using X-ray diffraction (XRD), the acidity of the catalyst was analyzed using Fourier Transform Infrared Spectroscopy (FT-IR) and gravimetry method, minerals present in the catalyst was analyzed using X-Ray Fluorescence (XRF), and surface of the catalyst was analyzed using Surface Area Analyzer (SAA). Catalytic activity test (benzene yield product) of MoCo/USY on hydrodeoxygenation reaction of anisole aimed to determine the effect of Mo-Co/USY for catalytic activity in the reaction hydrodeoxygenation (HDO) anisole. Based on characterization and test of catalytic activity, it is known that catalytic of MoCo/USY 2% (catalyst B) shows best activities with acidity of 10.209 mmol/g, specific area of catalyst of 426.295 m²/g, pore average of 14.135 Å, total pore volume 0.318 cc/g, and total yield of HDO products 6.06%.

1. Introduction
The conventional petroleum component comprises of 50-98% hydrocarbon compounds and non-hydrocarbon compounds with 83 – 87% carbon content, 11 – 14% of hydrogen, 3% of sulfur, 2% oxygen, and 1% of nitrogen [1]. Hydrotreating is a cracking process by the addition of hydrogen gas to saturate the hydrocarbons and eliminate sulfur, oxygen, nitrogen and metal impurities. One of the hydrotreating processes is hydrodeoxygenation (HDO). Hydrodeoxygenation (HDO) aims to remove the oxygen contaminant compounds that attached to hydrocarbon compounds. HDO can be done in two ways, which include the conventional thermal cracking and the catalysis systems. The catalysis systems, will conduct great results due to lower temperature and pressure usages [2]. These properties
are formed by a supported material and addition of metal in a solid carrier such as silica-alumina, alumina and zeolite [3].

One type of the supported material that can be used for the process is the Ultra Stable Y-zeolite (USY). There was recent studies about Kazuhisa, et al. studied Si/Al2O3 catalysts with several variations of supporting materials, such as Al2O3 gamma, mordenite, USY and ZSM-5 [4]. The supporting material USY is a type of zeolite-Y can be synthesized so that it has a higher pore structure and crystallinity. Types of metals commonly used in the petroleum industry include Ni, Co, Mo, Pt and Pd with carrier USY or other synthetic zeolites.

Mo metal has a vital role for deoxygenation reaction [5]. Mo metal will bind the hydroxyl group of phenol to the hydrogenolysis process. The hydrogenolysis process occurs the H2O released and formed the benzene products. Metal Co plays a role for the hydrogenation reaction, the content of Co metal on Mo-Co/USY catalyst were variated because the higher Co content the greater the ability to break the hydrogen bond [6].

Methods for the incorporation of metals onto the supporting material include ion exchange methods [7], impregnation methods [8] and precipitation methods [9]. Each of these methods will give the results of different catalyst characters. The parameter condition of catalyst preparation is influenced by temperature, time of reflux, pressure as well as ratio of the added metal. Due to these factors will affect the character of the catalyst, such as the crystallinity properties, the amount of metal that was carried [10], specified surface area [11], particle size [12], pore size distribution, volume pore, mechanical strength, and the acidity properties [13].

Based on the results of these studies, the catalytic activity of MoCo/USY was tested on anisole for hydrodeoxygenation reaction. The main reason anisole as a feed compound based on the simplicity of the molecular structure that already represent the compound of the petroleum constituent component, since it bond with the oxygen atom of methoxy representing the main reaction and the benzene ring which may be represented for the hydrogenation reaction. HDO anisole products are cyclohexane, cyclohexene, benzene, toluene, and phenol [6].

2. Experimental
MoCo/USY was prepared by using wet impregnated method. First, 10 g of H-USY were soaked in aquabides with addition of solution ammonium heptamolybdate tetrahydrate [(NH4)6Mo7O24·4H2O] and solution Cobalt (II) nitrate hexahydrate [Co(NO3)2·6H2O] with weight variation of Co metal 0%, 2%, 4%, 6%, 8%, and Mo metal 8% (w/w), which signed later as sample of A, B, C, D, and E, respectively. The solution was mixed in total volume of 50 mL aquabides. The solution was refluxed at 60 °C for 2 hours, the solution is filtered and the filtrate was obtained. Filtrate were dried using rotary evaporator at pressure of 200 mBar, with constant temperature of 48 °C until turned to dried powder. Dried powder samples were thermally calcined, oxidated and reduced. The following procedure for catalytic activity amount of 0.5 g sample was set into the reactor column. The hydrogen gas flow rate was adjusted to 5 mL/min for 1 H and the feed through the reactor containing with the catalyst. Same step procedure was repeated for thermal reaction (without samples), USY, and PtAl2O3 as commercial catalyst. Several characterization was determined by Fourier Transform-Infra Red (FT-IR) type shimadzu 8201 PC, X-Ray Diffraction (XRD) Phillips type X’Pert, Surface Area Analyzer (SAA) NOVA 1200e.

2.1. Catalytic activity product analysis.
Gas Chromatography – Mass Spectroscopy (GC-MS) type 2010 SE data were analyzed based on the amount of peak band on chromatogram showing the number of compounds contained in the sample. From the GC data, the product distribution was obtained and total product conversion. HDO product conversion, product intermediate conversion and product selectivity were calculated with the following formula percentage of total product shown in equation (1):

\[
\text{Percentage of total product} = \left( \frac{\text{Product Area}}{\text{Initial Volume}} \right) \times \frac{\text{Product Volume}}{\text{Initial Volume}}
\]  

(1)
The activity (yield) of HDO product was the amount of conversion from anisole to benzene and toluene products. Yield of benzene product and total yield of HDO were shown in equation (2) and (3):

\[
\text{Yield of benzene product} = \% \text{Area of Benzene Product} \times \frac{\text{Product Volume}}{\text{Initial Volume}}
\]

\[
\text{Total yield of HDO} = \text{yield of benzene product} + \text{yield of toluene product}
\]

The calculation of the yield of toluene product is the same as the calculation of the yield of the benzene product.

3. Result and Discussion

3.1. Functional Groups

The FT-IR analysis of the MoCo / USY samples was conducted qualitatively to determine the type of functional groups present in the MoCo/USY samples (Figure 1). Based on Figure 1, The FT-IR results show no significant differences in functional groups for each samples. The variation of the addition of Co metal on the catalyst shows no any change in the resulting FT-IR spectra. The absorptions in the spectra was matched with previous results of Bhatia [14], such as the absorption at wavenumber region of the 3450 – 3400 cm\(^{-1}\) signified the presence of hydroxyl –OH stretch, adsorption at wavenumber region of 1650 – 1600 cm\(^{-1}\) indicated the presence of a bending Si – OH vibration. The presence of functional group adsorption bands of a wavenumber of around 3400 cm\(^{-1}\) in H-USY was estimated as a Brønsted acid site of H-USY. That is in accordance with Weitkamp [15]. The FT-IR spectra results analysis shows the O-H stretch appeared in the 3450-3400 cm\(^{-1}\) wavenumber. In addition, in the wavenumber area of 1650 – 1600 cm\(^{-1}\) indicated the existence of –OH bending accordance with Korkuna [16]. Then the spectra occur in the wavenumber region of the 1100 – 1050 cm\(^{-1}\) was detected as a bond of Si – O – Si stretching. Therefore further analysis of other catalytic characters such as acid site values was required.

Based on Figure 2, it can be seen that the FTIR spectra show the relationship between the adsorbed ammonia in the solid surface and the bonding vibrations spectra. The change in vibrational wavenumber can be used to differentiate Brønsted or Lewis acidic sites. The spectra after ammonia adsorption showed the effect of acidity on Brønsted and Lewis acid characters in the samples. The initial absorption of the image spectra remains, such as absorption in the 3450-3400 cm\(^{-1}\) wavenumber region indicating the –OH stretch, then the 1650– 1600 cm\(^{-1}\) denoted as a bending -OH vibration. After the adsorption of ammonia, the estimated absorption area of Brønsted acid site increased in the
The wavenumber area of 3593.54-3229.94 cm\(^{-1}\) showing the absorption -O-H stretch and attached to the uptake of -N-H amine. This phenomenon occurs in every sample produced. Variations in the addition of Co and Mo metal do not indicate the presence of new functional groups, but produce different absorption rates. The FT-IR spectra analysis in Figure 2 shows that the absorption present in the wavenumber region of 1100-1050 cm\(^{-1}\) is the Si – O – Si stretching bond [15]. In the new absorption the amine -N-H stretching function group was found in the wavenumber region of 3229.94 cm\(^{-1}\) and in the wavenumber region 1402.31 cm\(^{-1}\).

![Figure 2. FT-IR spectra of MoCo/USY: sample A (A), sample B (B), sample C (C), sample D(D), and sample E (E) after ammonia adsorption.](image)

3.2. The Powder X-Ray Diffraction and Structural analysis

XRD analysis was performed to determine the type of particle that was carried on the catalysts which can be used to support the previous catalyst characterization. XRD analysis is qualitatively performed on the angle range (2\(\theta\)) = 5-90°. Based on the characterization, it appears that USY and catalyst of the research results was almost the same diffraction pattern. This almost identical pattern shows that metal impregnation does not alter the cell parameters on each catalyst significantly. When changing the cell parameters, it will affect the peak position in the diffractogram, for example the replacement of the Al-O bond with the shorter bond Si-O causes the cell unit to contract. This would caused the decreased d value and shifts the diffraction peak toward the higher 2\(\theta\) [7]. Further analysis to find out the compatibility of XRD diffraction data with crystal structure that was generated based on comparison with Inorganic Crystal Structure Database (ICSD) data, and then performed refinement by using Le Bail method with RIETICA software. The refinement of all catalysts carried out by entering the standards were USY according to ICSD #31542 [17] data with cubic crystal structure and space group (F d group -3 m z), CoO (ICSD #9865) [18], MoO\(_3\) (ICSD #36167) [19], CoMoO\(_4\) (ICSD #281235) [20], Co (ICSD #41507) [21]. The overall results of refinement with USY standards are presented are presented in Figure 3.
Figure 3. Refinement results of CoMo/USY (sample C) diffractogram with 5 standards phases i.e. Y zeolite (ICSD #31542), CoO (ICSD #9865), MoO$_3$ (ICSD #36167), CoMoO$_4$ (ICSD #281235), and Co (ICSD #41507) + : experimental data ----- : calculation results, ---- : difference between experimental data and the calculation results.

The residual factor is the acceptable limit of the analyzed phase. The more phases that can be analyzed, the residual factor value will be smaller. The unanalyzed peaks are estimated to be the peaks of the metal compounds that emerge on the catalyst. Therefore, further analysis is required by comparing ICSD data from other standards phases are presented in Figure 3. Based on the results of refinement in Figure 3, it is known that the residual factor values (Rp and Rwp) was decreased from the value of one USY standard (the values of Rp and Rwp from 8.86 and 8.61 to 4.48 and 5.77, respectively). Indicates a detected peak of CoO (ICSD # 9865), MoO$_3$ (ICSD # 36167), CoMoO$_4$ (ICSD # 281235), Co (ICSD # 41507) and in accordance with RIETICA calculations.

3.3. Specific surface area, Total pore volume and Average pore size

Further analysis was an analysis with SAA to determine the effect of the ratio of Co and Mo metals on the specific surface area of the catalyst, pore radius average and total pore volume. It shown Catalyst B was relatively highest in specific surface area than the other samples. It is predicted that Co and Mo metals exhibit relatively unequal dispersion on the surface of the catalyst so that it has a specific surface area smaller than the samples of A, C, D, and E. The surface area of A, B, C, D, and E catalysts were 399.745 m$^2$/g, 426.295 m$^2$/g, 418.965 m$^2$/g, 406.028 m$^2$/g, and 416.852 m$^2$/g, respectively. The catalyst undergoing a specific surface area increase is assumed that the Co and Mo metals carrying the dispersion are uniformly distributed, so that in the end the catalyst-specific surface area is the total surface area between USY and the Co Mo metal). However, catalytic activity needs to be tested to prove the nature of all the characterization that has been done.

3.4. Catalytic Activity

3.4.1. Product Distribution.

Based on the overall data, an activity test was required on the Catalyst sample to prove its catalytic properties. This test reaction needs to be compared with thermal test treatments, Commercial Catalyst (PtAl$_2$O$_3$) and USY. The HDO anisole reaction using sample B was carried out using a flow model reactor. The products were analyzed using GC-MS from the liquid fraction. It was found that from thermal obtained four products, USY five products, whereas with catalyst B made seven products, and PtAl$_2$O$_3$ made 10 products. In general, it shown that sample B catalyst has better selectivity than PtAl$_2$O$_3$ catalyst.
3.4.2. Catalytic Activity of HDO
HDO product activity is the amount of anisole conversion into benzene and toluene products. The value of anisole conversion to benzene and toluene is calculated based on GC-MS data. The catalytic activity of HDO refers to the yield of HDO products. The relationship of products yields and different treatment types will be presented in Figure 4.

![Figure 4. Yields of HDO product of various treatment types.](image)

Based on the Figure 4, the reaction of HDO anisole using catalyst B was obtained benzene of 5.33%, which was higher than by thermal (without catalyst) or USY. In a sequence of benzene yields i.e Catalyst B > PtAl₂O₃ > thermal > USY. On the other hand, catalyst B obtained toluene products of 0.73%. This phenomenon of hydrodeoxygenation conversion from anisole to benzene and toluene mostly influenced by the presence of Co and Mo metals that incorporated onto supporting material surface (USY). This is due to the Lewis acid sites of Co metal and Brønsted acid sites from USY. In this HDO reaction, the first reaction mechanism is the simultaneous reaction of demethylation and methyl transfer [6]. Demethylation occurs in Co metal of catalyst B. The Co metal is an active site where H₂ gas adsorption. Metal Co will break the H₂ bond, followed by the formation of bonds between hydrogen atoms with methyl form methane. Meanwhile, the hydrogen atoms from the Brønsted acid site of USY will bind to the oxygen atoms of the anisole that have lost the methyl group. At this stage occurs the formation of phenol compounds. Mo metal will bind the oxygen from the phenol hydroxyl group so that when there is a hydrogen supply, there will be a hydrogenolysis reaction. From the process of hydrogenolysis can occur the release of H₂O and form benzen products.

4. Conclusion
In this study, the acidity of the catalyst will decrease with increasing Co to Mo metal ratio. In the XRF analysis result, Co metal content recorded increased with the addition of metal ratio. The porosity analysis showed that the optimum specific surface area was 426,295 m² / g, the optimum pore size was 14,135 Å and the optimum pore volume of 0.318 cc / g was obtained for catalyst B. Furthermore, the MoCo / USY catalyst (Catalyst B) can be used as HDO catalyst anisole with 6.06% HDO product.
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Reference

[1] Ratna 2010 Oil Petroleum Fraction (Depok: UI)
[2] Gates B C 1992 Catalytic Chemistry (New York: John Wiley and Son. Inc.)
[3] Sofia A K 2014 Applied Cat. A: General 470 261
[4] Kazuhisa, Inaba M 2007 J. of the Japan Petroleum Inst. 51 234
[5] Kubicka D 2010 Applied Cat. A: General 372 199
[6] Viljava T R 2001 Cat. Today 60 11
[7] Hamdan H 1992 Introduction to zeolites: synthesis, characterization and modification (Kuala lumpur: UTM)
[8] Augustine R L 1996 Heterogenous Catalysis for the synthetic chemist (New York: Marcel Deklar Inc.)
[9] Hegedus L L 1987 Catalyst Design progress and perspective (New York: John Willey and Sons)
[10] Zeghayer Y 2005 J. of Applied Catalysis 282 163
[11] Okamoto Y 2003 J. of the Japan Petroleum Institute 46 343
[12] Rodica Z, Cristina R 2001 Int. Chem. Eng. Conf. 1 399
[13] Maria U 2012 Reactor 14 151
[14] Bhatia V L, Arias J F, Encheandia 2011 Conf. Series: Material science and eng. 17 1
[15] Weitkamp J 1999 Catalysis fundamentals and applications (Berlin: Springer)
[16] Korkuna O 2006 Mic. and Mesoporous Materials 87 163
[17] Gallezot, Beaumont P, Barthomeuf R 1974 J. of Physical Chemistry 78 1447
[18] Sasaki S, Fujino, Takeuchi K 1979 Proceed. of the Japan ac. 55 43
[19] Braeckken H 2002 Golden book of phase transitition (Poland: Wroclaw)
[20] Livage, Hynaux C, Marrot A 2002 J. of Materials Chemistry 12 1370
[21] Haglund, Fernandez J, Grimvall F 1993 Phys. Review 48 11673