



Preparation and Characterization of Co and Co-Mo Loaded on Mesoporous Silica for Hydrocracking of Waste Lubricant

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Abstract : Preparation and characterization of Co and Co-Mo loaded on gelatin template mesoporous silica for the hydrocracking catalysts of waste lubricant have been conducted. Gelatin was extracted from bovine bone at a variation of hydrolysis temperatures of 50 °C, 70 °C and 90 °C. From the FT-IR and SDS-PAGE characterization, we found that the optimum hydrolysis temperature to extract gelatin was obtained at 90 °C. Mesoporous silica (SM) was synthesized by hydrothermal method using gelatin as a template. Cobalt metal was loaded on to the SM by wet impregnation method and denoted as Co/SM. Meanwhile, Co and Mo metals were deposited on to the SM by sequential and co-deposition wet impregnation. The resulting materials were referred as Co-Mo/SM1 and Co-Mo/SM2, respectively. Hydrocracking process of waste lubricant was conducted using a stainless steel reactor of semi-batch system (weight ratio of feed/catalyst = 20:1) at a temperature of 450 °C under hydrogen flow. Liquid product of the process was weighed and analyzed by GC-MS. The SM showed a wormhole-like shaped pores, with the diameter of 4.308 nm. From the hydrocracking test, Co/SM exhibited the highest activity to produce liquid fraction (49.90 wt.%), highest selectivity to produce gasoline fraction (34.13 wt.%) and moderate coke formation (3.20 %).

Key words : gelatin, mesoporous silica, cobalt, molybdenum, hydrocracking, waste lubricant.

Introduction

Owing to the high surface area, combined with the large and uniform pore diameter, mesoporous materials¹⁻¹³ are considered to have potential applications in catalyst supports, separation, selective adsorption and supramolecules-host material.

The synthesis of mesoporous material involves the template agent to form certain pore size. Ionic surfactant, primary amine copolymer group and block copolymer are widely used as the template agents^{8,13}. However, due to the long hydrophobic chain of such agents make them difficult to degrade in a room temperature and prone to pollute the environment. To overcome this problem, replacement using an environmental friendly directing agent i.e neutral or anionic surfactant is necessary.¹⁴⁻¹⁶ Gelatin is an example of neutral surfactant, obtained from the raw animal materials. Gelatin has received widespread interest as an alternative template agent to form mesoporous material,^{9,11,17-19} due to the water soluble characteristic and the presence of amine group (-NH₂). The strong interaction between amine and silanol group (Si-OH) from silicate species through hydrogen bond formation is an important parameter on the synthesis of silica based material.

Hydrocracking is one of the most important processes in the petroleum industry, for converting heavy fractions of crude oils to the smaller ones²⁰⁻²⁴. Similar to crude oils, waste lubricants known to have large

molecules of hydrocarbon that can be broken down into smaller chain of hydrocarbon. This process could provide an idea to obtain economically valuable-fuels from unused material. This process is particularly need catalyst(s) and thermal treatment to ease the cracking process. Transition metals have been reported as promising catalysts²⁰⁻²⁴ in the petroleum refineries. Cobalt based catalyst²⁵⁻²⁷ has been widely applied for CO hydrogenation, formic acid decomposition, alkane hydrogenolysis, dibenzotiofen hydrode sulfurization and steam reforming catalyst. Hydrocracking of waste lubricants has been previously reported by using zeolite based catalyst modified with Ni, Co and Mo²⁰⁻²². However, due to the microporosity of zeolite it can only provide a limited space for large molecule of waste lubricants. Mesoporous materials are considered to be an attractive support material, because it can accommodate large molecules of hydrocarbon^{28,29}. Based on this idea, we attempt to synthesize silica mesoporous material (SM) by using gelatin as a template agent. Cobalt and/or Co-Mo were used as metal catalysts and impregnated to the SM. The catalyst was tested for hydrocracking of waste lubricant at temperature of 450 °C under hydrogen flow.

Experimental

Materials

The materials used in this research bovine's bone bought in Condong Catur Sleman Yogyakarta market, acetic acid (Merck), sodium hydroxide (Merck), chloride acid (Merck), sodium silicate (Merck), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6(\text{Mo})_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ metal precursor salt (Merck), , distilled water and Sodium Dodecyl Sulphate Polyacrylamide Gel Electrophoresis (SDS-PAGE) test device.

Instrumentation

The instrumentation used in this research were fourier transform infrared spectrophotometer (FT-IR, Shimadzu Prestige 21), gas Chromatography-Mass Spectrophotometry (GC-MS, Shimadzu QP 2010 S), Gas Sorption Analyzer (GSA, Quantachrome Novawin2 vers. 11.0), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX, Jeol JSM-6510), Transmission Electron Microscope (TEM, Jeol JEM-1400), hydrocracking reactor (Physics workshop, FMIPA UGM).

Procedure

Gelatin Extraction from Bovine's Bone and the Hydrolysis

Collected bovine's bone was cut soaked in 4 %v acetic acid solution (ratio of bone/solution is 1:2 for 9 days), 0,1 M NaOH solution (ratio 1:6 for 24 hours) and 1 M HCl solution (ratio 1:3 for 1 hour), respectively to remove oil and blood from the bone (degrease). After each treatment, the bone was washed till pH = 5,0. The pre-treated bones were then hydrolyzed at different temperatures (50 °C, 70 °C dan 90 °C) by boiling the bones in distilled water for 5h in a weight ratio of bone/water (1:4) and followed with filtration. The filtrate then dried with maximum temperature 50 °C to retrieve the gelatin.

Mesoporous Silica Synthesis

Gelatin of 1 g diluted in 25 g distilled water at temperature of 40 °C (solution I). Sodium silicate of 10 g was added in 25 g distilled water and heated at temperature of 40 °C (solution II). Solution II was added with H_2SO_4 0,100 M drop by drop till pH = 5,0 (mixture I). Solution I was added on mixture I drop by drop (mixture II). The mixture II then stirred with constant speed of 1 hour until gel phase formed. The gel was moved in the autoclave and heated of 24 hours at temperature of 100 °C. The solids were separated from the filtrate. The solids the collected and washed until pH = 5,0, followed with drying at a temperature of 80 °C. The dried solids then calcined at temperature of 550 °C and 5 hours with a heating rate of 5 °C/minutes.

Co and CoMo Impregnation on the Mesoporous Silica

Co/SM Catalyst Sample Preparation

Catalyst was prepared by loading 1% wt of metal onto support material (SM). $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as metal precursor salt. Salt was dissolved in distilled water at a weight ratio of 1:3. Impregnation was done by soaking SM into the solution, and heated at a temperature of 90 °C for 5 hours. The mixture then

evaporated and dried at temperature of 120 °C.

Co-Mo/SM1 Catalyst Preparation

The Mo metal was impregnated first on to the SM sample (0.5 % wt), followed with Co metal loading at the same weight ratio. Impregnation procedure was done similar to Co/SM preparation, with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was used as Mo precursor salt.

CoMo/SM2 Catalyst Preparation

The step of Mo metal impregnation was the same of the Co/SM 1 %wt but both of the metals, Mo and Co were impregnated at the same time (0,5 % wt.)

After Impregnation Treatment

After impregnation process, the as prepared catalyst was activated by oxidation and reduction treatment under O_2 and H_2 atmosphere, respectively. The treatment was conducted at a heating temperature of 400 °C for 1.5 h under 20 mL/min flow of determined gas.

Activity and Selectivity Test

The activity tests were conducted for SM, Co/SM, Co-Mo/SM1 and Co-Mo/SM2. For standard, thermal hydrocracking was also done without any catalyst. Hydrocracking of waste lubricant was conducted with a feed/catalyst weight ratio of 20:1 in a semi batch type of stainless steel reactor. The reactor then placed in tube furnace and kept at 450 °C in a hydrogen flow of 10 mL/minutes. Analyzed samples was the oil product as the main product target. The selectivity was determined by comparing the broad area of $\text{C}_5\text{-C}_{12}$ compounds (gasoline fraction), $\text{C}_{12}\text{-C}_{20}$ (diesel fraction) and $>\text{C}_{20}$ for heavy oil fraction. The sum of the broad area then compared with the total broad area.

Characterization

The quantitative and qualitative character of the gelatin was characterized by FT-IR spectrophotometer and SDS-PAGE. The mesoporous silica (SM) and metal loaded catalysts was characterized by gravimetric method, FT-IR spectrophotometer, GSA, SEM-EDX and TEM. The hydrocracking products were characterized by GC-MS. Meanwhile, H_2S gas was trapped in I_2 solution then calculated based on iodimetry titration.

Result and Discussion

Temperature Hydrolysis Optimization and Gelatin Characterization

In this research, the hydrolysis temperature optimization was conducted at 50 °C, 70 °C dan 90 °C for 5 hours. Fig. 1 showed characteristic peaks of standard gelatin such as amide A ($3600\text{-}3300\text{ cm}^{-1}$)-stretching vibration absorption of N-H groups paired with stretching O-H groups, amide B ($3000\text{-}2300\text{ cm}^{-1}$)-stretching vibration absorption of asymmetric CH_2 groups and stretching of symmetric CH_2 groups, amide I ($1658\text{-}1635\text{ cm}^{-1}$)-stretching vibration of C=O groups which merged with stretching vibration CN groups, deformation of CCN dan bending-in vibration N-H groups, amide II ($1540\text{-}1330\text{ cm}^{-1}$)-bending vibration absorption of CH_2 groups and flicking of CH_2 from proline amino acid and amide III ($1240\text{-}500\text{ cm}^{-1}$) showed bending vibration absorption of N-H groups, stretching of C-O groups and stretching of the framework^{11,12}. Despite, gelatin derived from different hydrolysis temperatures has similar FT-IR spectra, a slight shift can be seen in the range of amide 1. Gelatin hydrolyzed at 90 °C show amide 1 peak shift to 1627 cm^{-1} (standard- 1635 cm^{-1}). This suggests that hydrolysis at 90 °C result in random coil gelatin.

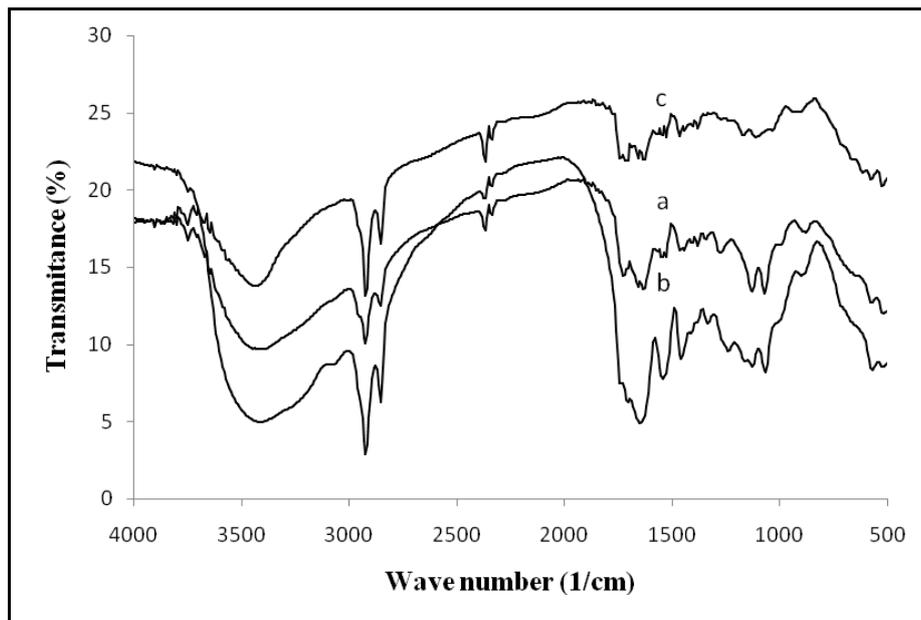


Fig. 1. FT-IR spectra of gelatin at temperature of (a) 50°C (b) 70°C dan (c) 90°C

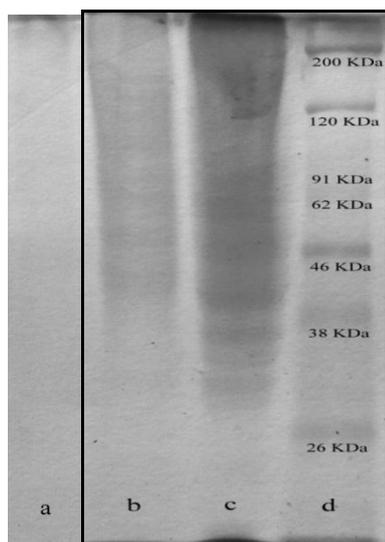


Fig. 2. SDS-PAGE performance of gelatin at temperature of (a) 50°C (b) 70°C dan (c) 90°C (d) marker

The molecular weight distribution was analyzed by SDS-PAGE method showed in Fig. 2. Gelatin has several different morphologies, like α -chain and β -chain of peptide. α -chain has molecular weight in the range of 120-160 kDa, while β -chain is about 200 kDa¹⁷⁻¹⁹ and gelatin that contain high α -chain showed a better functional characteristic. From our result, it can be seen that gelatin obtained at 90°C has the largest distribution of molecular weight, with thicker marker can be seen in the 120-160 kDa range. This may suggest that gelatin extracted at temperature of 90°C has the highest content of α chain peptide with a yield of 8.50 wt.%, indicating that hydrolysis temperature at 90°C is the optimum condition to extract gelatin.

Characterization of Mesoporous Silica (SM) by FTIR

Fig. 3 showed the FT-IR spectrogram of SM sample before and after calcination process. It can be seen that peaks correlated to gelatin (wave number of 3410, 2924, 2854 and 1543 cm^{-1}) were absent after calcination at 550°C. This suggests that gelatin was completely removed after heating treatment (Fig. 3).

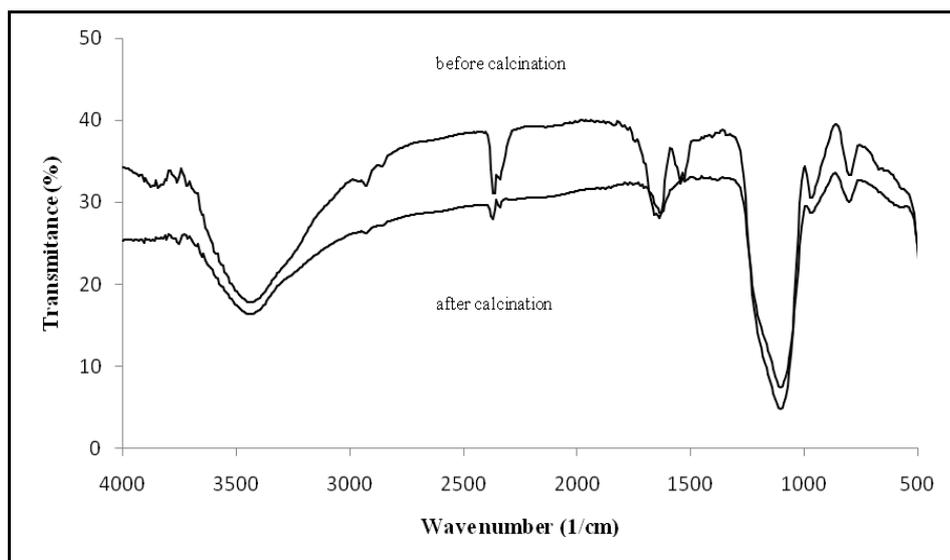


Fig. 3. FT-IR spectra of SM samples before and after calcination process

Metal content and acidity of Silica Based Catalyst

Table 1 showed the metal content of three different samples, Co/SM, Co-Mo/SM1 and Co-Mo/SM2. Despite the same weight ratio of metal was loaded into support material (SM), the actual metal loading was different.

Table 1 Metal content of catalyst

Catalyst	Co (%)	Mo (%)	Total metal (%)
Co/SM	0.86	-	0.86
Co-Mo/SM1	0.12	0.72	0.84
Co-Mo/SM2	0.06	0.58	0.64

Acidity of each catalysts was investigated by ammoniasorption and the results for each catalyst were 12.99, 15.35, 13.21 and 13.12 mmol/g for SM, Co/SM, CoMo/SM1 and CoMo/SM2, respectively. It can be seen that Co/SM catalyst sample has higher acidity than other catalysts. This can be explained by the fact that the as-prepared Co/SM containing largest metal loading than other catalysts (Table 1). Metal impregnation on to the SM increased the acidity of the catalyst system because of the presence of vacant orbitals on transition metals (Co and Mo) that act as Lewis acid site (paired electron acceptor).

Surface and Morphology Characterization of the Mesoporous Silica Based Catalyst

Surface area analysis was conducted by nitrogen adsorption-desorption and the results are listed in Table 2. Surface area was calculated using BET equation. It can be seen after metal loading, the surface area of the SM increased. This is reasonable as the metal residue on support material surface will increase the contact area. The pore diameters are calculated by BJH model of the desorption part. The pore distribution curves for each samples are showed at Fig.4. All catalyst samples have type IV adsorption pattern and H2 type hysteresis loops suggesting its mesoporous characteristic⁵. Meanwhile, the H2 type hysteresis indicated that the materials have a bottle-neck pore structure⁶.

Table 2.Porosity of silica materials

Catalysts	A (m ² /g) ^a	D (nm) ^b	V (cc/g) ^c
SM	550.077	4.308	1.097
Co/SM	593.501	4.918	1.117
CoMo/SM1	579.938	4.339	1.095
CoMo/SM2	576.853	4.362	1.135

Notes: ^aSurface area calculated by BET; ^bPore diameter calculated by BJH desorption; ^cPore volume determined by nitrogen adsorption at relative pressure 0,97-0,98

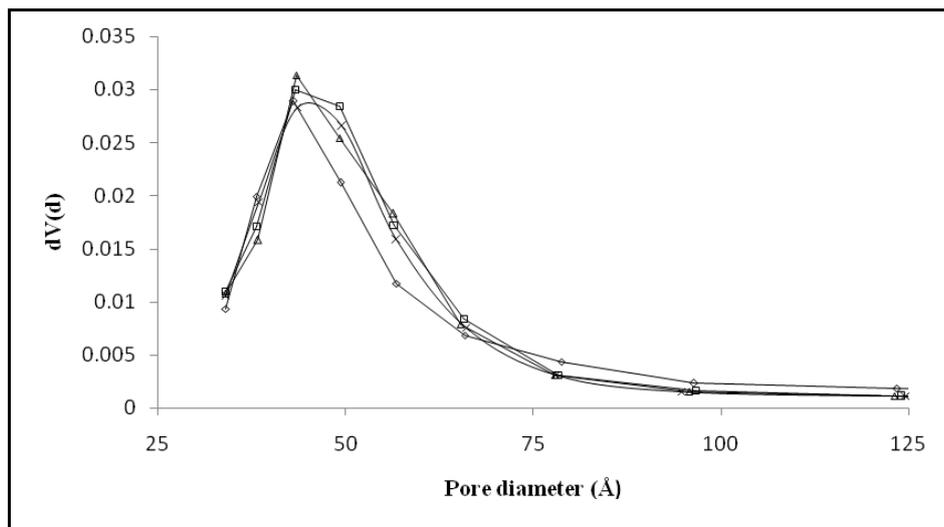


Fig. 4 Pore distribution of each catalyst samples SM (—◇—) Co/SM (—■—) CoMo/SM1 (—△—) CoMo/SM2 (—×—)

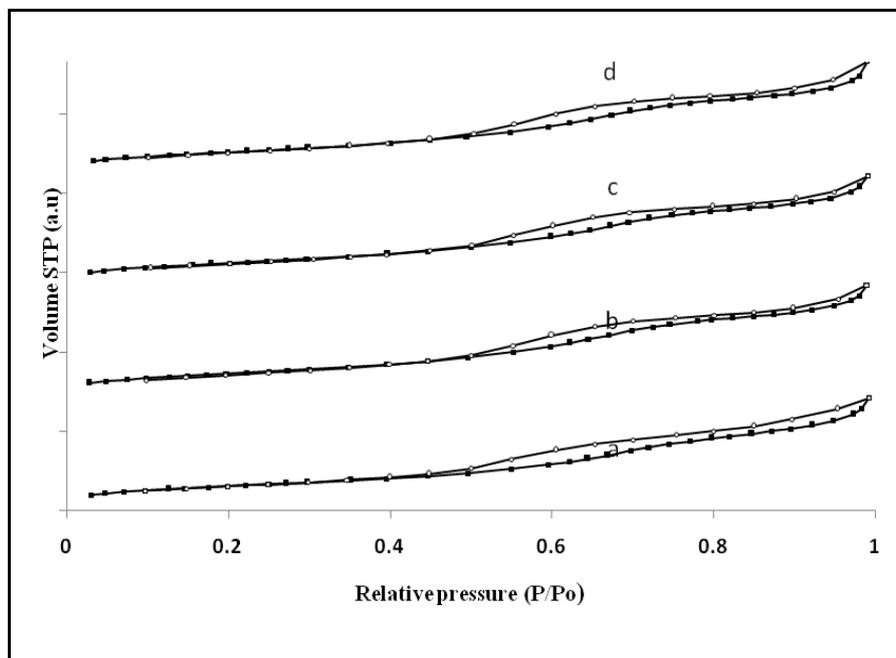


Fig. 5. Nitrogen isotherm adsorption-desorption (a) SM (b) Co/SM (c) CoMo/SM1 (d) CoMo/SM2

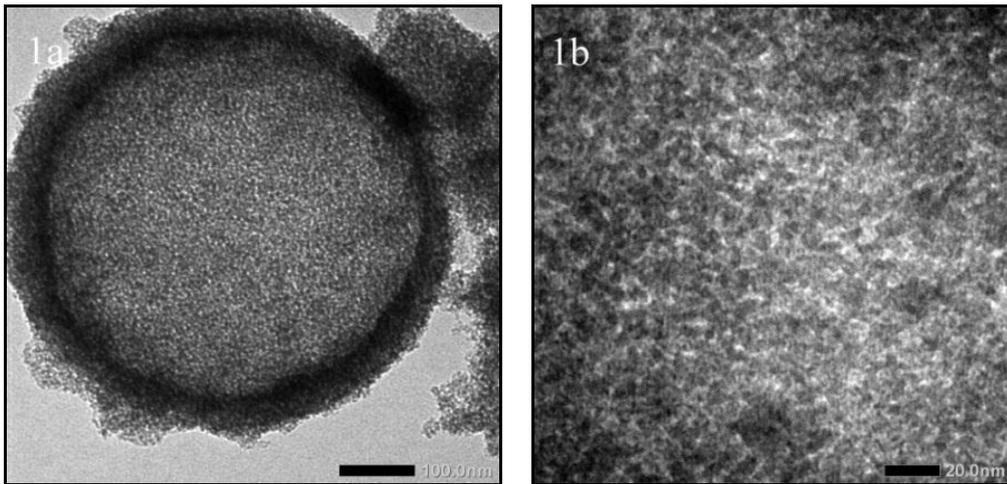


Fig.6. TEM image of mesoporous silica

The morphology of the samples were characterized by TEM and SEM analysis Fig. 6a-b showed that formed mesoporous silica has wormhole-like structure. This is in agreement with the previous report⁵.

Activity and selectivity tests

Table 3. Hydrocracking product distribution

Catalyst	Hydrocracking product distribution (wt.%)					
	Residue	Sulphur	Liquid	Gas	Coke	Total
Without catalyst	49.62	0.11	6.63	43.64	0	50.38
SM	1.22	0.10	21.07	77.45	0.16	98.78
Co/SM	1.58	0.10	49.90	45.22	3.20	98.42
CoMo/SM1	2.74	0.12	14.93	76.05	6.16	97.26
CoMo/SM2	2.90	0.10	44.61	52.35	0.04	97.10

Table 3 listed the hydrocracking product distribution derived from each catalyst sample. Table 3 showed that Co/SM catalyst has the largest ratio of liquid product as the main target product from hydrocracking of waste lubricants with a moderate coke formation. The coke was formed on the surface of catalyst after hydrocracking reaction at high temperature. The presence of coke could deactivate the catalyst²¹ due to the pore blocking. This may explain the reason that Co-Mo/SM1 has lower ratio of liquid product than that of Co-Mo/SM2, where a larger volume of coke formed on the surface of Co-Mo/SM1.

Table 4. Liquid product distribution

Catalyst	Liquid product distribution (%wt)			
	gasoline	diesel	Heavy oil	other
Without catalyst	4.43	1.37	0.25	0.58
SM	11.68	9.28	0.11	0
Co/SM	34.13	15.04	0.28	0.45
Co-Mo/SM1	11.76	2.80	0.23	0.14
Co-Mo/SM2	24.16	17.99	1.85	0.61

GC-MS analysis of the liquid products was shown in Table 4. It can be seen that Co/SM catalyst sample has the highest selectivity to produce gasoline fraction. This could be related to the largest surface area and highest acidity character of the sample. Such characteristics may provide more active space to cut the long hydrocarbon chain. Meanwhile, with similar acidity and surface area, Co-Mo/SM2 showed better selectivity to

gasoline than that of the Co-Mo/SM1. This could be explained by the fact that Co-Mo/SM1 has more coke formation on the surface than the counterpart catalyst. However, the origin of such characteristic is not well understood.

Conclusion

1. Gelatin hydrolyzed at temperature of 90 °C was the highest quantitatively and qualitatively among the gelatin hydrolyzed at temperature of 50 °C and 70 °C.
2. Gelatin can play the role as a template in mesoporous silica (SM) synthesis with pore diameter of 4,308 nm and wormhole-like/bottle-neck pore type.
3. Metal content, acidity, surface area and pore diameter of catalyst followed this order: SM<CoMo/SM2<CoMo/SM1<Co/SM catalyst.
4. The catalytic activity to produce liquid fraction increased as the following: without catalyst (6.63 wt.%) <CoMo/SM1(14.93 wt.%) <SM (21.07 wt.%) <CoMo/SM2 (44.61 wt.%) <Co/SM(49.90 wt.%)catalyst.
5. The highest selectivity to produce gasoline fraction was reached by Co/SM catalyst (34.13 wt.%) and the highest diesel fraction was produced by CoMo/SM2 catalyst (17.99 wt.%).

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