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Synthesis and Characterization of Mesoporous Molybdenum Catalysts for Hydrocracking of Atmospheric Residual Oil

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In this study, performances of mesoporous Mo/Al_2O_3 catalysts prepared by sol–gel and post-hydrolysis methods in hydrocracking of atmospheric residual oil were compared. In addition, different methods: (i) the single step and (ii) conventional impregnation method to incorporate active metal over the mesoporous support were also investigated. For single step method, Mo/Al_2O_3 catalysts were synthesized directly by sol–gel and post-hydrolysis method. On the other hand, the impregnation method was a two step procedure which involved the production of alumina via sol–gel or post-hydrolysis method and followed by respective Mo impregnation. In general, mesoporous Mo/Al_2O_3 catalysts prepared by sol–gel method resulted in relatively higher surface area (> 400 m^2/g) and large pore volume (~ 0.8 cm^3/g). Mo/Al_2O_3 catalysts prepared by sol–gel method exhibited higher hydrocracking activity as well. The Mo crystal size was found to relate directly with the hydrocracking result.

Keywords: Hydrocracking, Mesoporous Alumina, Post-Hydrolysis, Sol–Gel, Single Step.

1. INTRODUCTION

Hydrocracking is one of a promising upgrading process to convert high molecular weight hydrocarbons such as residual oil into valuable light molecular weight hydrocarbons (naphtha and diesel). Hydrocracking is normally conducted over a bifunctional catalyst that has a cracking function and hydrogenation–dehydrogenation function.[1] To enhance the performance of catalyst in hydrocracking process and maximize the yields of lighter distillates from upgrading of residual oil, hydrocracking catalysts with mesopores are highly desirable.[2–4] The use of zeolites as hydrocracking catalyst has been reported.[4–6] However, the application of zeolites for hydrocracking of residual oil is limited owing to its small pore size (micropores). Though there were several studies focused on the modified zeolites with pore size within the mesoporous range (2–50 nm), yet the modified zeolites were normally with mesopore size less than 5 nm.[4,6,7]

Among the mesoporous materials, alumina with mesoporous structure has been widely employed in catalysis as a catalyst support for active metals in chemical and petrochemical industries.[8–11] due to its adjustable physical properties, moderate acid capacity,[12] and variable point of zero charge, which makes it easier to load different metals.[13] Extensive research has been devoted on the possibility of tailoring physical properties of alumina for different applications.[9,14–19] Molybdenum supported over alumina is a catalyst widely used in petroleum residue hydrocracking.[20] In order to further improve the molybdenum base catalyst activity, different method to prepare alumina as well as different metal incorporation method on the catalyst support could be tested. There are various preparation procedure for mesoporous alumina. Mesoporous alumina has been synthesized by using different surfactants or template, such as anionic,[16,21] cationic,[22,23] non-ionic[15,24] surfactants that based on sol–gel routes, as well as pre- and post-hydrolysis methods.[14,25,26] In general, active metal on hydrocracking catalyst was incorporated onto the support by conventional impregnation method which is incipient wetness impregnation. Meanwhile, there are variety of alternative methods available for metal incorporation such as precipitation,[27] solvent-assisted spreading,[28] sonochemical vapor deposition[29] and single step sol–gel[30,31] methods which were used for assorted applications.

This study aims to investigate the catalyst preparation method on catalyst properties and its activity in

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hydrocracking reaction. In the present study, mesoporous alumina was synthesized by post-hydrolysis method and compared with that prepared from sol–gel method. These methods were reported to produce alumina with large surface area (~400 m^2/g), mesoporous range pore size[14, 21] and well-organized pore structure.[27] In addition, the resulted mesoporous alumina was incorporated with molybdenum by using single step method which has never been reported. This method is an efficient and simple way for the catalyst synthesis. Activity of prepared Mo/Al_2O_3 catalysts were tested in the hydrocracking of atmospheric residual oil and the performance were evaluated in terms of atmospheric residual oil conversion and product liquid oil fractions.

2. EXPERIMENTAL DETAILS

2.1. Mo/Al_2O_3 Catalyst Preparation

Two methods were employed to prepare alumina: (i) sol–gel and (ii) post-hydrolysis. The sol–gel method used was based on Ref. [21]. For catalyst prepared by single step sol–gel method, aluminum tri-ethylate (Merck, 97%) was first dissolved in ethanol (System, 95 v/v%). Then, a proper aqueous solution of ammonium molybdate (VI) tetrahydrate (Acros) was added into the ethanol mixture solution and stirred. Water was then slowly dropped into the mixture at 70 °C under constant stirring for 30 min. After gel formed, the sample was dried in oven at 120 °C for 24 h. Then, the alumina was calcined in a muffle furnace in air at 500 °C for 3 h. The alumina was prepared by following the molar composition of aluminum tri-ethylate, ethanol and water to a ratio of 1:10:4 respectively.

Preparation of alumina via post-hydrolysis was based on Ref. [14]. For catalyst prepared by single step post-hydrolysis method, stearic acid (Acros, 97%) was used as the anionic surfactant and aluminum sec-butoxide (Acros, 97%) was employed as the aluminum precursor. The mesoporous alumina was prepared by following the molar composition of aluminum sec-butoxide, stearic acid, sodium hydroxide, sec-butanol and water to a ratio of 1:0.20:0.04:5:4 respectively. First, aluminum sec-butoxide and stearic acid were dissolved in sec-butanol separately. In order to enhance the solubility of stearic acid in sec-butanol, small amount of sodium hydroxide was added. Then, two solutions were mixed. The solution with desired amount of ammonium molybdate tetrahydrate was added subsequently. Small amounts of water were slowly dropped into the mixture until white suspension appeared. After that, the resulting suspension was further stirred for 24 h with pH regulated at 7. Subsequently, it was dried at room temperature for 48 h. Finally, the material was calcined in a muffle furnace in air at 450 °C for 3 h.

For impregnation method synthesis, the alumina support was first prepared by conventional sol–gel or post-hydrolysis method as described above without adding the molybdenum precursor. An appropriate amount of ammonium molybdate (VI) tetrahydrate aqueous solution was then mixed with alumina powder and stirred. After that, the Mo impregnated material was dried in an oven at 120 °C for 16 h and followed by calcination in a muffle furnace in air at 500 °C for 3 h.

In order to prepare MoS_2/Al_2O_3 catalyst, *ex-situ* presulfidation was carried out in a batch reactor (Parr 4570). The oxide catalyst was soaked in hexadecane (Sigma, $\geq$ 99%) with 1 wt% of dimethyl disulfide (Aldrich, 99%). The reactor was pressurized with H_2 gas to 400 psig. Sulfidation of catalyst was carried out in a two-stage temperature manner. The reactor temperature was first raised to 250 °C for 2 h, and then further increased to 320 °C for another 3 h. After the presulfiding process, the catalyst was filtered and dried at 120 °C for 16 h under vacuum.[32] Finally, the sulfided catalyst was again loaded into the batch reactor with the atmospheric residual oil to undergo hydrocracking reaction.

Name of prepared material is based on the preparation method. For instance, sample SG-MoMA-1 is mesoporous alumina (MA) prepared by sol–gel method (SG), with molybdenum (Mo) impregnated through single step method (1) or conventional impregnation method (*i*). PH represents catalyst prepared with post-hydrolysis method, while the sulfide catalyst is denoted as *S*.

2.2. Characterization of Catalysts

2.2.1. Nitrogen Adsorption–Desorption Isotherm

Specific surface area of sample was measured by nitrogen adsorption/desorption analysis using Micromeritics ASAP 2020 at 77 K. Prior to analysis, the alumina sample was degassed at 350 °C for 8 h. Barret–Joyner–Hallender (BJH) model on desorption branch was employed to calculate the pore size distributions.

2.2.2. X-Ray Diffraction (XRD)

XRD patterns of catalyst was obtained by using a Philips diffractometer with Cu target Kα-ray. The powder diffraction patterns were recorded in the 2θ range from 20–80°.

2.2.3. Ammonia Temperature-Programmed Desorption (NH_3-TPD)

The acid capacity of catalyst was analyzed by NH_3-TPD conducted using an AutoChem II 2920. The sample was first degassed at 120 °C for 60 min in flowing helium gas to remove water vapour. After pretreatment, the sample was cooled down to ambient temperature under helium gas (20 ml/min). Then, the sample was exposed to 15 % NH_3 in He for adsorption at 100 °C for 60 min to saturate acid sites of the catalyst. Then, the sample was swept with helium at 100 °C for 30 min to remove physisorbed ammonia. After cooling down the sample, furnace temperature was increased from 50 to 500 °C at a ramping rate of 10 °C/min and 20 ml/min of helium total flow rate. The amount of desorbed ammonia from sample was detected by a TCD as desorption peak area. The area under the peak represents quantitative estimation of acid capacity.

2.3. Reaction Studies

The mesoporous Mo/Al_2O_3 catalyst activity in hydrocracking reaction was carried out in a high-pressure batch reactor (Parr 4570). The feedstock used in the study was atmospheric residual oil which contained 1.611 of H/C atomic ratio, 10.22 wt% of asphathenes and 81.47 vol% of residue with the boiling point higher than 340 °C.

First, 70 g of atmospheric residual oil was loaded into the reactor with 0.5 wt% of catalysts. The batch reactor was then pressurized with H_2 gas to 500 psig at ambient temperature. This followed by heating up the reactor to 400 °C and maintained for 60 min. There is around 55 min required to reach reaction temperature (400 °C) from room temperature. After the hydrocracking reaction, the reactor was quenched to room temperature by passing cooling water through the cooling coil in the reactor. The reactor was depressurized before unloaded. The liquid product was then recovered. The weight of gas produced after reaction was determined by the yield mass balance before and after a reaction.

The liquid products were analyzed for their boiling point (b.p.) range according to ASTM D86 to determine the yield of the lighter products after hydrocracking reaction. The atmospheric residual oil conversion is defined as ratio of weight percentage of converted liquid fraction with b.p. > 340 °C after hydrocracking reaction to the feed. The liquid oil fraction is defined as volume percentage of a distillate fraction in total volume of converted oil. The liquid product was categorized into naphtha (b.p. < 250 °C), diesel (b.p. 250–340 °C) and residue (b.p. > 340 °C). The experimental errors associated with the atmospheric residual oil conversion was $\pm 0.5\%$, while for products yield and liquid oil fractions data were $\pm 1.5\%$.

3. RESULTS AND DISCUSSION

The main purpose of this work is to compare the hydrocracking activity of Mo/Al_2O_3 catalysts prepared by different methods. The difference in catalyst properties due to different alumina preparation and molybdenum incorporation methods was analyzed for oxide catalyst assuming that the effects are similar in sulfide catalyst.

3.1. Physical Properties of Synthesized Catalysts

Figures 1 and 2 shows the (a) nitrogen adsorption–desorption isotherms and (b) the corresponding BJH pore size distributions, respectively for different oxide catalysts synthesized by sol–gel and post-hydrolysis methods. All these catalysts gave a type IV isotherms, which demonstrates the existence of structural mesoporosity. The adsorption–desorption isotherms of all samples could also be attributed to H_2 hysteresis loops.[33] This suggests that prepared materials exhibited narrow necks with wide bodies of pores made up within alumina,[34] which is common in many inorganic gels. It is clearly seen that all materials prepared in this work had narrow pore size distribution centered at around 5 nm. The average pore size was found reduced following the incorporation of Mo into SG-MA with either single step method or impregnation method (Fig. 1). Meanwhile, by using post-hydrolysis method, similar pore size and pore volume were obtained when the single step method were used to incorporate the molybdenum (PH-MoMA-1). On the other hand, PH-MoMA-*i* catalyst, which prepared through impregnation method, exhibited a relatively small peak of pore size distribution reducing to ∼4 nm, implying that this catalyst possessed relatively smaller pore size with smaller pore volume. This can also be told by the smaller hysteresis loop and much lower adsorbed volume for PH-MoMA-*i* catalyst as shown in Figure 2.

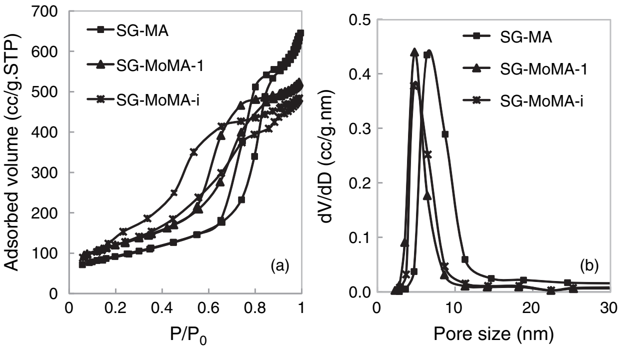

Fig. 1. N_2 adsorption–desorption isotherms and (b) corresponding BJH pore size distributions for mesoporous alumina and MoO_3/Al_2O_3 catalysts prepared with sol–gel method.

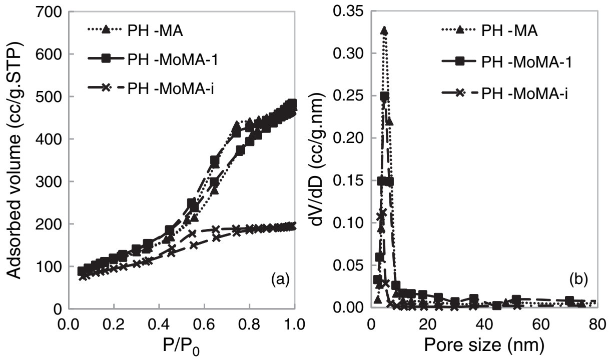

Fig. 2. (a) N_2 adsorption–desorption isotherms and (b) corresponding BJH pore size distributions for mesoporous alumina and MoO_3/Al_2O_3 catalysts prepared with post-hydrolysis method.

Table I. Physical properties of alumina supports and MoO_3/Al_2O_3 catalysts.

Sample ID	Physical properties		
	BET surface area (m^2/g)	BJH pore diameter (nm)	BJH pore volume (cm^3/g)
SG-MA	333	8.2	0.99
SG-MoMA-1	429	5.3	0.83
SG-MoMA-*i*	404	5.7	0.80
PH-MA	418	5.0	0.76
PH-MoMA-1	445	4.8	0.77
PH-MoMA-*i*	327	3.9	0.27

The summary of physical properties of catalysts prepared is given in Table I. All prepared catalysts were in mesoporous range. It is observed that the BET surface areas of SG-MoMA-1 and SG-MoMA-*i* were larger than unloaded alumina (SG-MA). SG-MoMA-1 possesses larger surface area (429 m^2/g) with smaller pore size (5.3 nm) as opposed to SG-MoMA-*i* (404 m^2/g and 5.7 nm). Both SG-MoMA-1 and SG-MoMA-*i* exhibited similar pore volume (~ 0.8 cm^3/g). Meantime, PH-MoMA-1 exhibited larger surface area than PH-MA, however both PH-MoMA-1 and PH-MA had similar pore size (~ 5 nm) and pore volume (~ 0.77 cm^3/g). On the contrary, PH-MoMA-*i* had lower surface area, pore size and pore volume than PH-MA which without molybdenum loading. Comparing the alumina and loaded catalyst prepared by post-hydrolysis method, Mo/Al_2O_3 catalysts prepared by sol–gel method, regardless single step or conventional impregnation method, exhibited rigid structure as both SG-MoMA-1 and SG-MoMA-*i* catalysts had large surface area (> 400 m^2/g) with pore size in the range of 5.3–5.7 nm and 0.80–0.83 cm^3/g of pore volume.

Basically, catalysts prepared via single step method (SG-MoMA-1 and PH-MoMA-1) had larger surface area, pore size and pore volume than the catalysts prepared by using conventional impregnation method (SG-MoMA-*i* and PH-MoMA-*i*). It is likely that such differences in porosity between two Mo/Al_2O_3 catalysts were closely related to the synthesis condition.

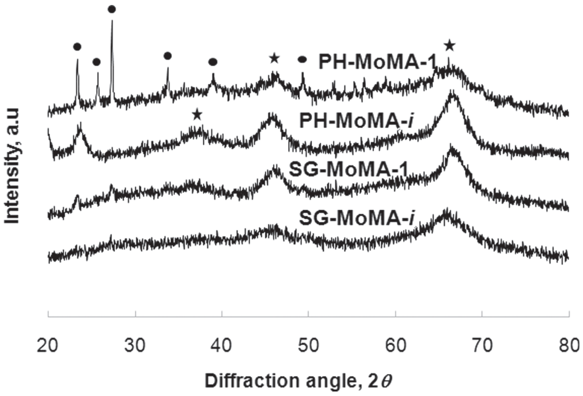

Fig. 3. XRD patterns of MoO_3/Al_2O_3 catalysts (⋆ γ-Al_2O_3; ● MoO_3).

The catalysts prepared by conventional impregnation method showed lower physical properties than those prepared by single step method because of pore blocking by metal after impregnation. Asforementioned, the Mo loading employed in this study was 18 wt%, a relatively large amount of molybdenum. When molybdenum is impregnated on alumina, pore plugging by metal is unavoidable, particularly for support with larger pore size. In addition, the pore walls of alumina might be partly destroyed owing to the aluminum dissolution in Mo solution during the impregnation step.[30] Besides, the increase of pH of impregnation solution was reported to reduce the dispersion of Mo species on alumina surface[30] as the natural pH of impregnation solution is close to point of zero charge of alumina (pH 6–8). As a result, the adsorption was not very strong causing only part of Mo species in the solution be adsorbed during the impregnation onto the support surface.[28]

3.2. X-Ray Diffraction Pattern

XRD patterns of oxide catalysts are shown in Figure 3. γ-alumina and molybdite (MoO_3) phases were observed in XRD patterns. In this study, two obvious diffraction peaks that appeared at 2θ of 46° and 67° for all catalysts are assigned to γ-Al_2O_3.[14, 21, 27] Another diffraction peak at 2θ of 37° that oserved for both PH-MoMA-*i* and SG-MoMA-1 catalysts is also by γ-Al_2O_3.[15, 27] Several prominent diffraction peaks for MoO_3 at 2θ of 25.5°, 33°, 39° and 49.2°[27, 35] were appeared in PH-MoMA-1 catalyst. From XRD patterns, molybdite phase in sol–gel prepared catalysts were more amorphous than that from post-hydrolysis method. PH-MoMA-1 catalyst especially showed sharp and intense peaks for MoO_3 phase. This indicates that a high crystallinity of MoO_3 was found in PH-MoMA-1 catalyst. The dispersion of MoO_3 on PH-MoMA-1 catalyst surface was poor. The crystal sizes of MoO_3 were estimated by using Scherrer Eq. (1):

$$D_c = K\lambda/(\beta\cos\theta) \tag{1}$$

where D_c is the average crystal size, K is the Scherrer constant (0.89), λ is the X-ray wavelength (0.154 nm), β is full width at half-maximum (in radian) and θ is the diffraction angle. The catalysts prepared via single step method, which were SG-MoMA-1 (12.33 nm) and PH-MoMA-1 (36.84 nm) exhibited larger MoO_3 crystal sizes compared to SG-MoMA-*i* (1.87 nm) and PH-MoMA-*i* (5.03 nm) which prepared by conventional impregnation method.

3.3. Acid Capacity of Prepared Mo/Al_2O_3 Catalysts

NH_3-TPD measurements were carried out to examine the acid capacity of mesoporous molybdenum catalysts prepared by different methods. Figure 4 shows the NH_3-TPD

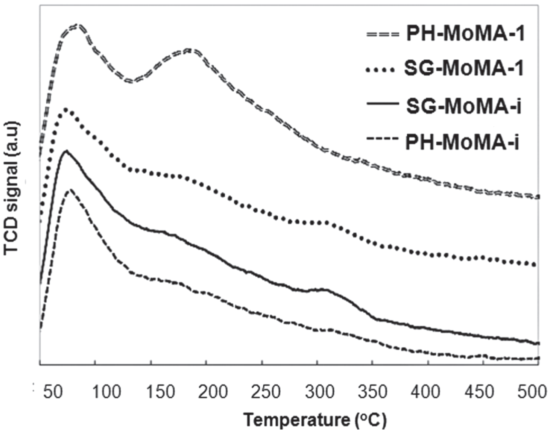

Fig. 4. NH_3-TPD profile for MoO_3/Al_2O_3 catalysts.

profile of MoO_3/Al_2O_3 catalysts and there are three different desorption peaks presented. The desorption peaks before 100 °C was attributed to the physically adsorbed ammonia.[36] Generally, the acid sites were attributed to the weak, moderate and strong acid sites corresponding to the NH_3 desorption within 150–250, 250–400 and 400–500 °C, respectively.[37] Amongst the MoO_3/Al_2O_3 catalysts synthesized, PH-MoMA-1 catalyst displayed significant desorption peaks for weak acid sites, as shown in Figure 4.

From TPD analysis, the total acid capacities of Mo/Al_2O_3 catalysts were also calculated. The acid capacity of catalyst increased in the order: PH-MoMA-*i* (0.017 mmol/g) < SG-MoMA-*i* (0.019 mmol/g) < SG-MoMA-1 (0.020 mmol/g) < PH-MoMA-1 (0.022 mmol/g). As expected, catalyst with alumina as support was catalyst with weak acid capacity if no special treatment was caried out. Besides that, the acid capacity of catalysts prepared by conventional impregnation method were lower as compared to catalysts synthesized via single step method. One of the reasons could be those catalysts prepared via single step method, especially PH-MoMA-1 catalyst possessed high surface area, which had more concentration of active sites on surface. In Figure 4, PH-MoMA-1 showed the largest desorption peak for weak acidity as compared to PH-MoMA-*i*. In addition to that, there might be due to the chemical reaction between molybdenum species and stearic acid during preparation of alumina in post-hydrolysis through single step procedure and resulted in more acid sites to appear on PH-MoMA-1 surface.

3.4. Hydrocracking of Atmospheric Residual Oil Over Mo/Al_2O_3 Catalyst

Table II reports the results of hydrocracking of the atmospheric residual oil. Thermal hydrocracking in the absence of catalyst at 400 °C achieved only 14.08 wt% of conversion, with 7.53 vol% of naphtha and 35.12 vol% of diesel in the liquid product. The presence of mesoporous oxide or sulfided Mo/Al_2O_3 catalyst was found to increase the conversion. For hydrocracking reaction with mesoporous MoO_3/Al_2O_3, the highest conversion (44.66 wt%) was achieved by using catalyst prepared via single step sol–gel method (SG-MoMA-1), while the lowest conversions (40.25 wt%) was obtained in the reaction using PH-MoMA-1 which prepared via single step post-hydrolysis method. For hydrocracking reaction with mesoporous MoS_2/Al_2O_3, higher conversion was observed as expected. The trend results for conversion was found to be similar to which that using MoO_3/Al_2O_3. SG-MoMAS-1 gave the highest conversion (51.39 wt%) while PH-MoMAS-1 gave the lowest conversion, 47.02 wt%. Meanwhile, SG-MoMAS-*i* and PH-MoMAS-*i* catalysts obtained 49.41 wt% and 49.56 wt% of conversion, respectively. For oxide catalyst, the highest liquid product (97.94 wt%) with the least gas product (2.06 wt%) was obtained by using SG-MoMA-*i* catalyst, whilst SG-MoMAS-*i* and PH-MoMAS-*i* catalysts gave high liquid product yield (92.54 wt% and 92.27 wt%, respectively) as compared to the rest of sulfided catalysts did in the present study.

Hydrocracking of atmospheric residual oil over mesoporous MoO_3/Al_2O_3 catalysts produced naphtha (b.p. < 250 °C), diesel (b.p. 250–340 °C) and atmospheric

Table II. Residual oil hydrocracking over MoO_3/Al_2O_3 and MoS_2/Al_2O_3 catalysts.

Catalyst	Conversion, (wt%)	Liquid product yield (wt%)	Gas product yield (wt%)	Coke (wt%)	Diesel (vol%)	Naphtha (vol%)
Thermal hydrocracking						
None	14.08	98.44	1.56	–	35.12	7.53
MoO_3/Al_2O_3						
SG-MoMA-1	44.66	97.14	2.86	–	42.46	7.82
SG-MoMA-*i*	41.00	97.94	2.06	–	33.78	13.51
PH-MoMA-1	40.25	96.67	3.33	–	42.51	7.19
PH-MoMA-*i*	41.22	97.20	2.80	–	38.89	11.11
MoS_2/Al_2O_3						
SG-MoMAS-1	51.39	90.16	8.87	0.97	38.47	19.23
SG-MoMAS-*i*	49.41	92.54	6.75	0.71	34.55	18.29
PH-MoMAS-1	47.02	90.48	8.81	0.71	38.22	18.53
PH-MoMAS-*i*	49.56	92.27	6.92	0.81	35.22	18.65

residue (b.p. >340 °C). The diesel yield produced by SG-MoMA-1 (42.46 wt%) and PH-MoMA-1 (42.51 wt%) catalysts were higher than that by SG-MoMA-*i* and PH-MoMA-*i*, which are 33.78 vol% and 38.89 vol%, respectively. Similarly, both MoS_2/Al_2O_3 catalysts prepared via conventional impregnation method (SG-MoMAS-*i*and PH-MoMAS-*i*) gave 34.55 vol% and 35.22 vol% of diesel, which were lower than that produced by reactions with SG-MoMAS-1 (38.47 vol%) and PH-MoMAS-1 (38.22 vol%). Correspondingly, the catalysts prepared with conventional impregnation method (SG-MoMA-*i* and PH-MoMA-*i*) showed higher naphtha yield (13.51 vol% and 11.11 vol%, respectively). On the contrary, both SG-MoMA-1 and PH-MoMA-1 catalysts produced 7.19–7.82 vol% yield of naphtha. After sulfidation, naphtha yield increased generally in all the catalyst used. SG-MoMAS-1 produced the highest yield of naphtha, which is 19.23 vol%, while the rest of sulfided catalysts gave 18.29–18.65 vol% of naphtha (Table II). Obviously, MoS_2/Al_2O_3 catalysts produced more naphtha. It also gave higher gas product with lower liquid product yield as compared to MoO_3/Al_2O_3 catalyst did. This indicated that MoS_2/Al_2O_3 catalyst was good in promoting secondary cracking into lighter distillates.

Negligible amount of coke was formed during reactions with MoO_3/Al_2O_3 catalyst. This could be due to the slight acid capacity of alumina employed and its moderate C—C bonds splitting capacity[38] at the reaction temperature. High acid capacity of catalyst tend to cause coking.[7] However, small amount of coke (0.7–1.0 wt%) was generated in hydrocracking reactions with MoS_2/Al_2O_3 catalysts.

These results showed that mesoporous Mo/Al_2O_3 catalysts prepared through conventional sol–gel method, especially catalyst prepared with single step method, offered a better performance for hydrocracking, in terms of conversion. The catalysts prepared through single step sol–gel method (SG-MoMA-1 and SG-MoMAS-1) gave the highest conversion in the present study. This could be explained by SG-MoMA-1 possessed larger surface area (429 m^2/g) that had more concentration of acid sites (0.02 mmol/g) and efficient dispersion of active metals in the pores.[39] Besides that, high surface area with larger pore volume of mesoporous catalyst assisted in reducing the mass transfer resistance of heavy hydrocarbons in the hydrocracking reaction,[9] therefore the accessibility of larger molecules in atmospheric residual oil to acid sites of catalyst is increased and enhance the cracking activity. On the contrary, both PH-MoMA-1 and PH-MoMAS-1 catalysts showed relatively poor conversion. This could be owing to the presence of stearic acid as hinder during preparation of catalyst in post-hydrolysis method.[31] Aluminum source was hydrolyzed in the presence of solution consisting of molybdenum species and stearic acid during preparation of alumina in post-hydrolysis through single step procedure. This phenomenon might limit the contact between Mo species with alumina owing to the presence of stearic acid. Mo species could not uniformly disperse on alumina surface. Hence, poor metal dispersion or higher crystallinity was obtained in the post-hydrolysis prepared catalysts.

The surface acidity was reported as one of the properties of catalysts responsible for hydrocracking processes.[7] In general, conversion is increased with the increasing of catalyst acid capacity. However the catalyst synthesized via single step post-hydrolysis method (PH-MoMA-1) gave the lowest hydrocracking conversion in the present study, although it had the highest total acid capacity (0.022 mmol/g). Aside from conversion, PH-MoMA-1 catalyst produced the least of liquid product. This observation suggests that high acid capcity are not required in producing liquid product. It rather caused excess cracking leading to more gaseous products. It is in agreement with the trend result of liquid and gas product yields produced by using sulfided catalyst.

Interestingly, the MoO_3 crystal sizes on alumina surface was found to gave significant impact on hyrocracking reaction products. As shown in Figure 5, there is an optimum crystal size of MoO_3 for conversion. The liquid product and naphtha yields were observed to decrease with increasing MoO_3 crystal size of catalysts. On the contrary, gas product and diesel yields were found to increase with increasing MoO_3 crystal size of catalysts (Figs. 6 and 7). A high crystallinity of MoO_3 was found in PH-MoMA-1 catalyst (Fig. 3). PH-MoMA-1 showed 37 nm of large MoO_3 crystal size, which is triple size of that SG-MoMA-1 possessed (∼12 nm). This could be resulted from poor dispersion of Mo on alumina surface prepared via single step post-hydrolysis method. Both SG-MoMA-*i* and PH-MoMA-*i* prepared via impregnation method exhibited small MoO_3 crystal size (<6 nm). High naphtha

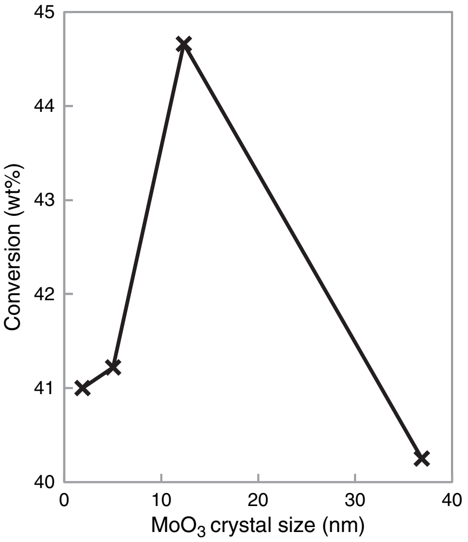

Fig. 5. Effect of MoO_3 crystal sizes on conversion.

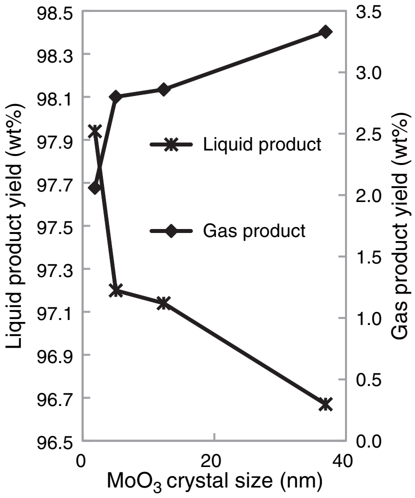

Fig. 6. Effect of MoO_3 crystal sizes on liquid and gas products.

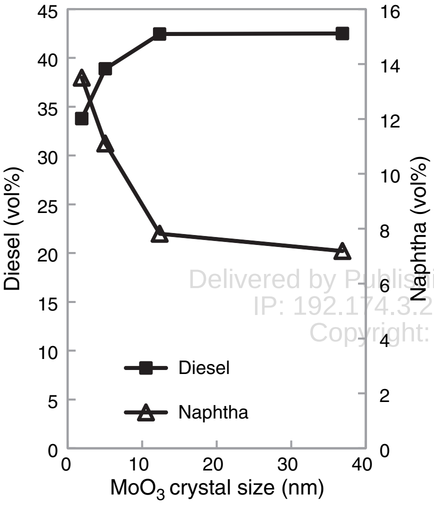

Fig. 7. Effect of MoO_3 crystal sizes on diesel and naphtha yields.

yield attained by using these catalysts (SG-MoMA-*i*and PH-MoMA-*i*) could be directly related to the dispersion of Mo species on alumina surface.

Noted that metal behaves as the active site for hydrogen evolution during hydrocracking reaction. Metal generates reactive hydrogen species from hydrogen in gas phase for hydrogenation reaction.[40] If Mo disperse on alumina surface finely, it make dissociate hydrogen easier to be transferred from metal on mesopore surface to acid sites.[41] The cracked products in primary cracking reactions (diesel) were adsorbed and further cracked on the acidic support sites to generate lighter secondary cracking product (naphtha). Hence, lower naphtha yield was obtained for reactions by using catalyst with large MoO_3 crystal sizes.

4. CONCLUSION

Hydrocracking activity of mesoporous Mo/Al_2O_3 catalysts prepared by conventional sol–gel or post-hydrolysis method as well as molybdenum loading through single step or conventional impregnation method were investigated. Catalysts prepared by sol–gel method exhibited preferable physical properties (> 400 m^2/g large surface area, ~ 5 nm narrow pore size and ~ 0.8 cm^3/g of pore volume) in regardless conventional impregnation or single step method employed. Similar result trend was obtained in residual oil hydrocracking over MoO_3/Al_2O_3 and MoS_2/Al_2O_3 catalysts. We observed that a much more stable catalytic performance was attained with catalysts prepared by conventional sol–gel method. Catalysts with small MoO_3 crystal size would promote higher liquid product yield and lighter secondary cracked product yield. Both MoO_3/Al_2O_3 and MoS_2/Al_2O_3 catalysts prepared via single step sol–gel method showed highest atmospheric conversion in the hydrocracking reaction due to its large porosity and moderate acid capacity that can crack more residual oil into lighter oil. Meanwhile, catalysts which attained lower conversion but with higher naphtha yield could be considered a better hydrogenation catalyst that slightly depressed the radical reactions and resulted a lower gas yield and coke yield.

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