Effect of Zeolite-Y Modification on Crude-Oil Direct Hydrocracking

Lianhui Ding,* Husin Sitepu,* Saad A. Al-Bogami, Duhaiman Yami, Mazin Tamimi, Kareemuddin Shaik, and Essam Sayed

1. INTRODUCTION

Hydrocracking is the most versatile and efficient process to convert heavy oils to clean fuel and petrochemical feedstock. The typical feedstocks to the units are vacuum gas oils (VGO, boiling range 350–550 °C) or VGO blended with light cycle oil or coker gas oil. Due to the much higher impurities (e.g., sulfur, nitrogen, metals, and asphaltenes) in crude oils than in the VGO fraction, crude oils are not directly charged to the units. They are fractionated to reject the 550 °C + residue fraction to remove the majority of the impurities.

Hydrocracking catalysts are bifunctional: cracking function contributed by acidic sites such as amorphous oxides (silica-alumina) and/or zeolites, and hydrogenation function by metals such as Co−Mo, Ni−Mo, or Ni−W. Before 1960, the amorphous silica-alumina catalysts were widely used. After that, via intense research and studies, the zeolites (mainly zeolite-Y and zeolite-β) were found to have much higher acidity and higher thermal/hydrothermal stability, and showed significant improvements in activity, ammonia tolerance, and higher gasoline selectivity. Until now, zeolite-Y has been widely used as a cracking component for commercialized catalysts.1,2

Two main factors that significantly affect the target product rates and product quality are catalyst acidity and pore structures.3−5 Ideally, the catalysts should have a well-developed secondary pore structure (mesopores) and appropriate acidity distribution. Therefore, zeolite-Y modification to create mesoporosity and adjust the acidity and its distribution was extensively studied. Ferraz et al.3 studied three NiMo catalysts with various acidity supports (alumina, amorphous silica-alumina, and zeolite-Y) regarding the hydrogenation and hydrocracking activities of tetralin conversion. The results showed that support acidity enhanced the ring opening of tetralin and thus increased the yields of aromatic compounds. Meanwhile, the catalyst with high acidity also presented high activities for both ring opening/cracking and hydrogenation reactions.

Sato and his co-workers8 investigated two kinds of NiMo/HY catalysts, with and without mesopores. For both catalysts, most of the NiMo sulfides were dispersed inside the micropores. The remaining NiMo sulfides (relatively large 3−10 nm particles) were located on the mesopore surface for the catalyst with mesopores. For the catalyst without mesopores, large particles were located on the external surface of the zeolite particles. Both catalysts showed similar catalytic performance in the tetralin, due to no diffusion problem for the reaction. However, in the atmospheric residue, the catalyst with mesopores was superior to that without mesopores. These results revealed the importance of mesopores in the hydrocracking of heavy oils.

To improve the middle distillate selectivity of the VGO catalyst, Chang et al.10 modified USY zeolites with multi-hydroxyl carboxylic acid and phosphate. The treatment resulted in mesopore creation, appropriate acid distribution,
and good crystallinity. The testing results showed that the 140–370 °C middle distillate yield was 66.04%, and middle distillate selectivity could reach up to 80.43% using Daqing as feedstock. Compared with the commercial catalyst, the yield and selectivity were increased by 5.62 and 4.05%, respectively.

The studies on VGO over micro–mesoporous zeolite-based catalysts indicated that the increase of recrystallization degree resulted in the increase of mesopore to micropore ratio of zeolite-Y as well as the decrease of strong Brønsted acid sites in faujasite cages and the increase of Brønsted acid sites in...
mesopores. NiMo-based catalysts were compared between parent and recrystallized micro–mesoporous zeolites. The highest conversion of 75.5% and middle distillates yield of 53.0 wt % were achieved for the catalyst with micro–mesoporous material, mainly due to the improved accessibility of active sites and easier transport of bulky molecules in mesopores than in micropores. Meanwhile, the performance enhancement was also contributed by the optimized zeolitic acidity distribution.

Almost all previous studies based on zeolite-Y catalysts used either model compounds, or VGO, or lighter oils as feedstocks. Fewer studies were reported on crude oil. Due to the greater number of large molecules present in the heavier fraction of the crude oil (>540 °C), the diffusion of these molecules into and out of the active sites located inside the zeolites becomes critical in determining the catalyst activity, selectivity, and stability. This article studies the effect of zeolite acidity and mesoporosity on crude-oil direct hydrocracking.

2. RESULTS AND DISCUSSION

2.1. Textural Properties of the Zeolites and the Catalysts. The textural properties of the five zeolites and the catalyst samples were characterized by 

| zeolite sample | Z-1 | Z-2 | Z-3 | Z-4 | Z-5 |
|---------------|-----|-----|-----|-----|-----|
| total surface area (m²/g) | 590 | 542 | 404 | 422 | 447 |
| micropore | 520 | 392 | 223 | 250 | 216 |
| mesopore | 70 | 150 | 181 | 172 | 231 |
| meso/total pore ratio (%) | 11.9 | 27.7 | 44.8 | 40.8 | 51.7 |
| pore volume (mL/g) | 0.415 | 0.419 | 0.471 | 0.472 | 0.5 |
| micropore | 0.264 | 0.204 | 0.128 | 0.131 | 0.113 |
| mesopore | 0.15 | 0.22 | 0.34 | 0.34 | 0.39 |
| average pore size (Å) | 28.2 | 31.0 | 46.5 | 44.6 | 44.7 |

Table 1. Textural Properties of the Zeolites and the Catalysts

2.2. X-Ray Diffraction Measurements of the Zeolites and the Catalysts. The measured data of the zeolites and the catalysts are shown in Figures 5 and 6, respectively. Some main results of the zeolites and the catalysts are summarized in Table 2. With the SiO₂/Al₂O₃ molar ratio increase, the relative crystallinity of the zeolites decreases from 81.1 to 64.4%. From the bulk and framework SiO₂/Al₂O₃ molar ratio, the ratio of non-framework aluminum in total aluminum in the zeolite can be calculated by bulk Al subtracting framework Al, which is calculated by Breck equation. Due to only being hydrothermally treated (the dealuminated Al is deposited in the channels or cages of the zeolite), Z-1 has 26.8% non-framework Al. After acid treatment, almost all of the non-framework Al is removed, and thus the non-framework of Z-2 becomes zero. For similar reasons, the proportions of non-framework Al of Z-3, Z-4, and Z-5 are 14.6, 8.9, and 0%. The presence of the non-framework Al can significantly change the acidity and textural properties of the zeolite.11–13 For low-Si/Al-ratio zeolites (Z-1 and Z-2), it is interesting to note that, when they were mixed in the catalysts, the crystallinity of the zeolites dramatically decreased and was much lower than expected. However, for high-Si/Al zeolites (Z-3, Z-4, and Z-5), their zeolite structure can be well maintained (the crystallinity is higher than expected values).

2.3. Acidity Properties of the Zeolites and the Catalysts. The acidity and acidity distribution of the zeolites and the catalysts were characterized by the ammonia temperature-programmed desorption (NH₃-TPD). The results are summarized in Figures 7 and 8, and Table 3. In this study, based on the ratios of the amount of the NH₃ desorbed at 300, 300–500, and >500 °C to the total NH₃ desorbed, categorization was done as weak acid sites, medium acid sites, and strong acid sites, respectively. With the SiO₂/Al₂O₃ molar ratio increasing from 5 to 30, the total acidity of the zeolites increased from 1.21 to 1.47 mmol NH₃/g, while with further increase in the SiO₂/Al₂O₃ molar ratio to 80, the total acidity decreased to 0.86 mmol NH₃/g. The acidity distribution reveals that the weak, medium, and strong acid sites take about 74.1−83.0, 16.9−23.9, and 0.1−6.1%, respectively. Z-4 has the highest ratio of strong acid sites. It is well known that the acidity and its distribution are closely related to the Al content and what species of the aluminum are in zeolites. Although Z-1 has the highest Al amount, as expected, it should have the highest total acidity. However, probably due to the presence of increased from 36.4 to 77.4%, while the ratio of surface area to total surface area increased from 11.9 to 51.7%. As a result, the average pore size increased from 28.2 to 46.5 Å. When the SiO₂/Al₂O₃ molar ratio is equal or higher than 30 (Z-3), the textural properties for Z-3, Z-4, and Z-5 are quite similar. Interestingly, when these zeolites are mixed with metals, with a large-pore-size alumina matrix, the difference of the textural properties of the catalysts becomes much less than that among the zeolites. Contrary to the zeolites, the catalysts with lower-SiO₂/Al₂O₃-ratio zeolites have higher surface area and pore volume than that of the higher Si/Al molar ratio.
the high proportion of non-framework Al, its acidity is lower than that of Z-2 and Z-3. After the hydrogenation metals and alumina (most in the form of binder) are added, the acidity of the corresponding catalysts is greatly enhanced, and follow the same trend as the zeolites. The higher the SiO2/Al2O3 molar ratio of the zeolite, the more pronounced the enhancement. Among all catalysts, HC-60 possesses the highest percentage of strong acid sites.

2.4. Reaction Performance of the Five Hydrocracking Catalysts. The catalysts were evaluated in a pilot plant unit. The liquid product properties and product distributions of the five catalysts are summarized in Table 4. Density of the total liquid products is a good indicator of the product hydrocarbon structure (for example, the more aromatics the product contains, the higher the density is) and product distribution (the more lighter the fractions, the lower the density). HC-5 catalyst has the highest density among the five catalysts, due to the higher percentage of >180 °C fractions than that of other catalysts. Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) conversions are >99.2 and >96.1 wt % for all catalysts because majority of the sulfur and nitrogen is removed by the hydrotreating catalysts loaded on the top of the catalysts studied.

The separate pilot plant testing with hydrotreating catalysts only and using the same feedstock indicated that hydrotreating catalysts removed 98.0 wt % of sulfur and 94.2 wt % of nitrogen. HC-60 exhibits the best HDS and HDN activity, and highest <180 °C product yields (naphtha plus gas) over other catalysts. Heavy fraction conversion is well correlated with the catalyst acidity and acidity distribution. HC-60 catalyst not only has higher total acidity, but also 41.6% of the acid sites are strong and medium, which made the catalyst exhibit the best heavy fraction conversion. On the contrary, HC-5 has the lowest total acidity, and most of them are weak and medium acid sites. As a result, it gave a lower heavy fraction conversion. The large molecules in >540 °C fraction can be easily cracked.
on weak and medium acid sites. However, to further crack the 180−540 °C fraction to lighter fractions such as naphtha (C5−
180 °C) and gas, more medium and strong acid sites are required.

In the crude oil, there is 14.6 wt % of >540 °C fraction, which includes the largest molecules and majority of organic sulfur and nitrogen compound. To convert these molecules, the first step is that these molecules are able to contact active sites on the catalysts. Most of these active sites are located inside the catalysts, especially inside the zeolite. Therefore, the zeolites and the catalysts with a large pore opening can ensure that these molecules are efficiently diffused into the channel or cages of the zeolites. After modification, some mesoporosity was generated for all of the zeolites studied, and the catalysts with higher mesoporosity revealed a higher conversion of >540 and 350−540 °C. The gas and naphtha yields can be taken as the indicator of the catalyst activity and are related to strong acidity sites. With the SiO2/Al2O3 increase (the strong acid site increase), the gas plus naphtha yields increase from 31.64% (for HC-5) to 70.43 wt % (HC-60). The larger mesoporosity of HC-30 to HC-80 contributes more conversion of >540 and 350−540 °C fractions compared with HC-5 and HC-12. For
VGO hydrocracking, the pore sizes of zeolite-Y are big enough to make the molecules in the range diffuse in and out of the zeolites; the zeolites’ and catalysts’ acidity become a decisive factor to determine the catalyst reaction performance. However, for crude or heavy oil, due to larger molecules in the oils, the diffusion of these molecules in and out of the zeolites becomes another critical factor for the heavy-oil hydroconversion, besides the acidity. Therefore, it can be highlighted that the acidity and mesoporosity of the zeolite and the catalysts play critical roles in determining the final catalyst performance in crude-oil or heavy-oil hydrocracking.

3. CONCLUSIONS

In the present study, the authors modified zeolite-Y-based hydrocracking catalyst on crude hydroconversion; five catalysts were synthesized with the various zeolites; the synthesized catalysts were characterized using N₂-adsorption, XRD, and NH₃-TPD, and were evaluated with a crude oil under the same operation conditions in a pilot plant unit. Based on the results, the following conclusions can be drawn:

- With the SiO₂/Al₂O₃ molar ratio increase of the modified zeolites, the pore volumes and surface areas of the zeolites increased, and more mesopores were created. When the SiO₂/Al₂O₃ molar ratio is higher than 30, the textural properties became similar. The difference in the textural properties between the zeolites and catalysts made from these zeolites becomes less. The catalysts with lower-SiO₂/Al₂O₃-ratio zeolites have a higher surface area and pore volume. After the zeolites were mixed with other components to become the catalysts, due to the presence of the mesoporous
### Table 3. NH3-TPD Results of the Zeolites and the Catalysts

| samples | total acidity (mmol NH3/g) | acidity distribution (%) |
|---------|----------------------------|--------------------------|
|         |                            | weak acid | medium acid | strong acid |
| Z-1     | 1.21                       | 83.0      | 16.9        | 0.1         |
| Z-2     | 1.35                       | 74.1      | 23.9        | 2.0         |
| Z-3     | 1.47                       | 78.9      | 18.7        | 2.5         |
| Z-4     | 1.22                       | 74.7      | 19.2        | 6.1         |
| Z-5     | 0.86                       | 76.7      | 18.0        | 5.4         |
| HC-5    | 1.46                       | 66.9      | 28.3        | 4.8         |
| HC-12   | 1.85                       | 67.3      | 28.0        | 4.7         |
| HC-30   | 2.28                       | 67.2      | 28.1        | 4.7         |
| HC-60   | 2.12                       | 58.4      | 32.8        | 8.8         |
| HC-80   | 1.75                       | 72.4      | 25.7        | 2.0         |

### 4. EXPERIMENTS

#### 4.1. Preparation of the Modified Five Zeolite-Y and Five of the Catalysts

Five zeolites were synthesized by NH4+ ion-exchanging the parent NaY zeolite (i.e., Na2O: 13 wt %, SiO2/Al2O3: 5.1, unit cell size: 24.65 Å) followed by hydrothermal and acid leaching treatments. The hydrothermal treatment of the zeolites was conducted at 550 °C for 1 h in the presence of 0.1 MPa steam. The hydrothermal treatment did not change the SiO2/Al2O3 molar ratio of the zeolite. However, due to dealumination, the unit cell was only decimally reduced. To increase the SiO2/Al2O3 molar ratio of the zeolite, the extra-frame Al needed to be removed by acid leaching with 2.5 M HCl aqueous solution at 60 °C. The basic information of the five zeolites is shown in Table 5. The sodium content (wt %) of the benchmark zeolite or base zeolite (0.2 wt %) is higher than that of other zeolites (<0.05 wt %), which may have some effect on zeolite acidity and catalyst cracking activity. Due to the shorter bond length of Si–O (1.59–1.64 Å) than Al–O (1.73 Å),14 with more aluminum removed from the framework, the SiO2/Al2O3 molar ratio of the zeolite increases from 5.2 to 80, and the unit cell size slightly or decimally decreases from 24.53 to 24.24 Å.

The zeolite was mixed with large-pore alumina (Sasol PURALOX TH100/150, pore volume 0.96 mL/g, specific surface area 201.6 m2/g), MoO3, nickel nitrate hexahydrate, and binder (partially acid-peptized alumina, SASOL, CATAL-PAL B), extruded to form a cylinder-shaped extrudate, dried at 110 °C overnight, and then calcined in air at 500 °C for 4 h. The catalysts with zeolites Z-1, Z-2, Z-3, Z-4, and Z-5 were designated as HC-5, HC-12, HC-30, HC-60, and HC-80, respectively. The number in HC-x represents the SiO2/Al2O3 molar ratio of the zeolite used for the catalyst preparation. All

### Table 4. Liquid Product Properties and Product Distribution of the Five Catalysts

| catalyst | density (g/mL) | HC-5 | HC-12 | HC-30 | HC-60 | HC-80 |
|----------|----------------|------|-------|-------|-------|-------|
|          |                | 0.8301 | 0.7736 | 0.7906 | 0.7716 | 0.7823 |
| S (wppm) | 28.5           | 145.0 | 7.2   | 3.4   | 10.6  |
| N (wppm) | 15.8           | 13.0  | 32.8  | <1    | 0.8   |
| H2S      | 1.80           | 1.80  | 1.80  | 1.80  | 1.80  |
| NH3      | 0.08           | 0.08  | 0.08  | 0.08  | 0.08  |
| C1–C4    | 7.88           | 10.91 | 4.82  | 13.40 | 7.52  |
| C5–180 °C| 23.76          | 51.16 | 51.54 | 57.03 | 52.48 |
| 180–350 °C| 43.04          | 15.21 | 38.63 | 20.92 | 37.67 |
| 350–540 °C| 23.46          | 20.90 | 6.13  | 8.37  | 3.95  |
| >540 °C  | 1.98           | 2.74  | 0     | 2.40  | 0     |
catalysts have the same composition: 15 wt % of MoO₃, 5 wt % of NiO, 50 wt % of zeolite, and 30 wt % of alumina.

4.2. Characterization of the Zeolites and the Catalysts. The sample texture property (e.g., surface areas, pore volumes, pore sizes, and distributions of pore size) was characterized using a physisorption analyzer of Quantachrome Autosorb iQ instrument. Before adsorption, the samples were calcined at 823 K for 4 h. Approximately, 30–40 mg of powder samples was degassed in a sample preparation station under 473 K and 1.33 × 10⁻³ Pa for 15 h, then switched to the analysis station for adsorption and desorption under liquid nitrogen at 77 K with an equilibrium time of 2 min. The surface area was calculated with the multipoint Brunauer–Emmett–Teller (BET) equation with a linear region in the P/P₀ range of 0.05–0.35. Pore volume was calculated from the maximum adsorption amount of nitrogen at P/P₀ = 0.99. The distribution of pore size was determined based on the Barrett–Joyner–Halenda (BJH) method and the desorption branch of the isotherm. The micropore analysis was conducted with the t-plot method.

The test was conducted with Quantachrome Chemstar instrument. Prior to the measurements, the sample was pre-treated with helium carrier gas at 500 °C for 60 min and cooled down to 50 °C. After that, the sample was exposed to 10% NH₃ in He for 30 min, followed by purging with helium gas at 100 °C for 60 min to remove the physisorbed ammonia. The thermal conductivity detector run was then conducted from 50 to 700 °C at a heating rate of 10 °C per minutes. A TCD detector was used to record the signal generated by desorbed NH₃.

The synthesized zeolite catalysts were independently and manually ground by an agate mortar and a pestle for several minutes to achieve a fine particle size, and mounted onto the X-ray diffractometer sample holders by front pressing. Subsequently, high-resolution data were measured using the Rigaku ULTIMA-IV multi-purpose X-ray powder diffractometer, with a copper X-ray tube, scan range 5–50° 2θ, a step size of 0.04°, and a scan rate of 1° per minute. Moreover, all of the data sets were identified and quantified (i.e., crystallinity percentage) by High Score Plus software combined with the ICDD PDF-4+ database of the standard reference materials. Additionally, the details of the small-angle X-ray scattering are given by Ding et al. The silicon, aluminum, and sodium contents (wt %) in the samples were analyzed by the PANalytical AXIOS Advanced Wavelength-Dispersive X-ray fluorescence spectrometer. The samples were manually ground to a fine powder and mixed thoroughly. Then, 0.25–1.5 g of the homogenized sample was mixed well with 0.9 g of binder (Liqowax C micropowder PM (Hoechstwax)) using the Spex 8000 mixer/mill. The homogenized mixture was pressed to form a pellet. The pellet sample was irradiated with X-ray photons from the X-ray tube. The intensity of the X-rays was processed by the PANalytical instrument’s software (i.e., Omnian) to determine semiquantitatively the concentrations of the detected elements.

4.3. Reaction Performance Testing of the Hydrocracking Catalysts. The reaction performances of the catalyst were evaluated in a pilot plant unit using a crude oil as feedstock. The main properties of the crude oil are summarized in Table 6. Residue hydrotreating catalysts (120 mL) were loaded on the top of a reactor to remove majority of the impurities (e.g., metals, sulfur, and nitrogen) in the crude oil. At the bottom of the reactor, 30 mL of the catalyst was loaded. The catalysts were presulfided with 2 wt % of dimethyl disulfide in straight-run diesel at 230 °C for 4 h and 350 °C for 8 h. After the presulfiding, the crude oil was introduced into the reactor. After the catalyst initial activity was stabilized (about 7 days), the samples were taken and analyzed for density, simulated distillation, nitrogen, and sulfur. All catalysts were evaluated under the same conditions: reaction temperature 390 °C, total liquid hourly space velocity 0.16 h⁻¹, reaction pressure 150 bar, and H₂/oil volume ratio 1500:1.

Table 6. Main Properties of the Crude Oil

| Property                  | Value       |
|---------------------------|-------------|
| Density at 16.5 °C (g/mL) | 0.8658      |
| Sulfur (S) (wppm)         | 18030       |
| Nitrogen (N) (wppm)       | 844.1       |
| Simulated distillation (SIMDIS) (°C) | 34 |
| Initial boiling point (IBP) | 723         |
| <180 °C (wt %)            | 21.0        |
| 180–350 °C (wt %)         | 31.1        |
| 350–540 °C (wt %)         | 33.3        |
| >540 °C (wt %)            | 14.6        |

At the bottom of the reactor, 30 mL of the catalyst was loaded. The catalysts were presulfided with 2 wt % of dimethyl disulfide in straight-run diesel at 230 °C for 4 h and 350 °C for 8 h. After the presulfiding, the crude oil was introduced into the reactor. After the catalyst initial activity was stabilized (about 7 days), the samples were taken and analyzed for density, simulated distillation, nitrogen, and sulfur. All catalysts were evaluated under the same conditions: reaction temperature 390 °C, total liquid hourly space velocity 0.16 h⁻¹, reaction pressure 150 bar, and H₂/oil volume ratio 1500:1.

### AUTHOR INFORMATION

**Corresponding Authors**

Lianhui Ding — Saudi Aramco, Research and Development Center, Dhahran 31311, Saudi Arabia; Email: lianhui.ding@aramco.com

Husin Sitepu — Saudi Aramco, Research and Development Center, Dhahran 31311, Saudi Arabia; Email: sitepuhx@aramco.com

**Authors**

Saad A. Al-Bogami — Saudi Aramco, Research and Development Center, Dhahran 31311, Saudi Arabia

Duhaiman Yami — Saudi Aramco, Research and Development Center, Dhahran 31311, Saudi Arabia

Mazin Tamimi — Saudi Aramco, Research and Development Center, Dhahran 31311, Saudi Arabia

Kareemuddin Shaik — Saudi Aramco, Research and Development Center, Dhahran 31311, Saudi Arabia

Essam Sayed — Saudi Aramco, Research and Development Center, Dhahran 31311, Saudi Arabia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03029

**Notes**

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

The authors would like to acknowledge the Saudi Aramco R&DC management for giving permission to publish the results. Thanks are also due to all employees who helped and encouraged this study; without their help, this paper would not have been possible.

REFERENCES

(1) Rigutto, M. S.; van Veen, R.; Huve, L. Zeolites in Hydrocarbon Processing. In Studies in Surface Science and Catalysis; 2007; Vol. 168, pp 855–913.

(2) Martinez, C.; Corma, A. Inorganic Molecular Sieves: Preparation, Modification and Industrial Application in Catalytic Processes. Coord. Chem. Rev. 2011, 255, 1558–1580.

(3) Ferraz, S.G.A.; Zotin, F.M.Z.; Araujo, L.R.R.; Zotin, J. L. Influence of Support Acidity of NiMoS Catalysts in the Activity for Hydrogenation and Hydrocracking of Tetralin. Appl. Catal., A 2010, 384, 51–57.

(4) Breyssse, M.; Portefaix, J. L.; Vrinat, M. Support Effects on Hydrotreating Catalysts. Catal. Today, 1991, 10, 489–505.

(5) Whitehurst, D. D.; Isoda, T.; Mochida, I. State of the Art and Future Challenges in the Hydrodesulfurization of Polyaromatic Sulfur Compounds. Adv. Catal. 1998, 42, 345–471.

(6) Gallezot, P. The State and Catalytic Properties of Platinum and Palladium in Faujasite-type Zeolites. Catal. Rev. 1979, 20, 121–154.

(7) Breyssse, M.; Cattenot, M.; Kougionas; V.; Lavallely, J.-C.; Maugé, F.; Portefaix, J.-L.; Zotin, J. L. Hydrogenation Properties of Ruthenium Sulphide Clusters in Acidic Zeolites. J. Catal. 1997, 168, 143–153.

(8) Sato, K.; Nishimura, Y.; Honna, K.; Matsubayashi, N.; Shimada, H. Hydrocracking of Heavy Oils. J. Catal. 2001, 208, 288–297.

(9) Kazakov, M. O.; Nadeina, K. A.; Danilova, I. G.; Dik, P. P.; Klimov, O. V.; Pereyma, V. Yu.; Gerasimov, E. Yu.; Dobryakova, I. V.; Kayzavev, E. E.; Ivanovab, I. I.; Noskov, A. S. Hydrocracking of vacuum gas oil over NiMo/Y-Al2O3: Effect of Mesoporosity Introduced by Zeolite-Y Recrystallization. Catal. Today 2018, 305, 117–125.

(10) Chang, X.; He, L.; Liang, H.; Liu, X.; Yan, Z. Screening of Optimum Condition for Combined Modification of Ultra-Stable Y-Zeolites using Multi-hydroxyl Carboxylic Acid and Phosphate. Catal. Today 2010, 158, 198–204.

(11) Shertukde, P. V.; Hall, W. K.; Dereppe, J. M.; Marcelin, G. Acidity of H-Y Zeolites: Role of Extralattice Aluminum. J. Catal. 1993, 139, 468–481.

(12) Kubelkov, L.; Beran, S.; Malecka, A.; Mastikhin, V. M. Acidity of Modified Y-zeolites: Effect of Non-skeletal Al, formed by Hydrothermal Treatment, Dealumination with SiCl₄, and Cationic Exchange with Al. Zeolites 1989, 9, 12–17.

(13) Qin, Z.; Shen, B.; Yu, Z.; Deng, F.; Zhao, L.; Zhou, S.; Yuan, D.; Gao, X.; Wang, B.; Zhao, H.; Liu, H. A Defect-Based Strategy for the Preparation of Mesoporous Zeolite-Y for High-Performance Catalytic Cracking. J. Catal. 2013, 298, 102–111.

(14) Auerbach, S. M.; Carrado, K. A.; Dutta, P. K. Handbook of Zeolite Science and Technology; MARCEL D. KEEHIN; 2003; Chapters 3 and 4.

(15) Sitepu, H.; O’Connor, B. H.; Li, D. Y. Comparative Evaluation of the March and Generalized Spherical Harmonic Preferred Orientation Models Using X-ray Diffraction Data for Molybdate and Calcite Powders. J. Appl. Crystallogr. 2005, 38, 158–167.

(16) Khanfar, H. S.; Sitepu, H. A Lab Case Study of Microbiologically Influenced Corrosion and Rietveld Quantitative Phase Analysis of X-Ray Powder Diffraction Data of Deposits from Refinery. ACS Omega 2021, 6, 11822–11831.

(17) Ding, L.; Haboubi, H. H.; Sayed, E. A.; Sitepu, H.; Badairy, H. H.; Al-Ghamdi, R. A. Study on Mesoporous Al-SBA-15 with Enhanced Acidity and Hydrothermal Stability for Heavy Oil Hydrocracking Conversion. Am. J. Mater. Synth. Process. 2018, 3, 39–46.

(18) Sitepu, H.; Kopylopa, M. G.; Quirt, D. H.; Cutler, J. N.; Kotzer, T. G. Synchrotron micro-X-ray Fluorescence Maps of Natural Diamonds: First Steps in Identification of Mineral Inclusions In-situ. Am. Min. 2005, 90, 1170–1174.

(19) O’Connor, B. H.; Li, D. Y.; Sitepu, H. Strategies for Preferred Orientation Corrections in X-ray Powder Diffraction Using Line Intensity Ratios. Adv. in X-ray Anal. 1991, 34, 409–415.