

Catalytic Pyrolysis of Fuel Oil Blended Stocks (FOBS) to Hydrogen and Methane using Mo/ZSM-5 Catalyst

Wan Nur Anis Amira Wan Ranizang^a, Huzaimah Mazlan^a, Mohd Asmadi Mohammed Yussuf^a, Mazura Jusoh^c, Zaki Yamani Zakaria^{a,b,*}

^aFaculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, UTM, 81310, Skudai, Johor, Malaysia

^bCentre for Engineering Education, Universiti Teknologi Malaysia, UTM, 81310, Skudai, Johor, Malaysia

^cInstitute Bioproduct Development, Universiti Teknologi Malaysia, UTM, 81310, Skudai, Johor, Malaysia
 zakiyamani@utm.my

There was an abundance of very poor-quality oil such as fuel oil blended stocks (FOBS) that caused numerous environmental problems. In this study, FOBS conversion to higher value-added products was achieved through catalytic pyrolysis in a pyrolytic reactor system, producing hydrogen (H₂)-rich and methane (CH₄)-rich gas. The impact of varying weight percentage of molybdate (Mo) on HZSM-5 (1 %, 3 % and 5 %) and ratio of catalyst-to-feedstock (1:5, 1:10 and 1:15) was explored using pyrolysis reactions. The catalyst was synthesized by using the impregnation method and characterized by using XRD, SEM, FTIR and BET. The characterization results showed that catalyst containing 3 % Mo was more dispersed in ZSM-5 particles. The 3Mo/ZSM-5 catalyst exhibited uniform morphology, a large specific surface area, and good pore size distribution, leading to favorable results in H₂ and CH₄ gas production. Using 3Mo/ZSM-5, the highest H₂ yield of 90.68 % was achieved at a catalyst-to-feedstock ratio of 1:10, while the highest CH₄ yield of 83.75 % was obtained at a ratio of 1:5.

1. Introduction

Fuel oil blended stock (FOBS) is made up of a variety of hydrocarbons refined from crude oil refineries. FOBS were available in all refineries worldwide and consisted of various low-quality refined oil, making them difficult to be further processed. The abundance of FOBS caused many environmental problems. Pyrolysis was the thermal breakdown of long-chain polymeric compounds into shorter, less complex molecules in the presence or absence of catalysts in an inert or oxygen-deficient atmosphere. The ratio of solid, liquid, and gas products produced by pyrolysis could change depending on the feedstock and operating conditions (Velebná et al., 2015). The thermal pyrolysis of polymers was an energy-intensive endothermic process. Typically, the reaction requires temperatures of between 350 °C and 500 °C. In certain experimental tests, temperatures as high as 700–900 °C have been needed to get desired product yields. The drawbacks of thermal pyrolysis have led to the development of catalytic pyrolysis. The temperature needed for the pyrolysis reaction to occur is greatly reduced when a catalyst such as zeolite is added since it decreases the activation energy needed for the reaction (Hafeez et al., 2018). Hydrated aluminium silicates are frequently utilised as catalysts in the cracking of crude oil. Zeolites, also known as molecular sieves, are hydrated aluminosilicates with very porous crystal structures that trap water molecules (Reese, 2020). Zeolite's small pore size, limits its utility as a catalyst. Because of this, the mass transfer process will be challenging for reactant components with big molecules (Widayat and Annisa, 2017). There have been several studies up to this moment into the modification of zeolites to metal-zeolites can improve the catalytic activity (Sriatun et al., 2019). It is also said that the addition of Mo to modify ZSM5-zeolite improves the yields of aromatic hydrocarbons (Sun et al., 2020). Mo/ZSM-5 was the most active catalyst out of many that were examined (Velebná et al., 2015). Transition metal dopants were believed to alter the oxygen exclusion pattern, by generating more carbon oxides and less water, allowing more hydrogen to be integrated into hydrocarbons. To determine whether metal-promoted low acid zeolites produce higher hydrocarbon yield and less coke than the commercial ZSM-5 catalysts previously tested, a variety of metal-modified ZSM-5 catalysts (CeZSM-5, Co-ZSM-5, FeZSM-5, Ga-ZSM-5, HZSM-5, and Ni-ZSM-5) have been used in biomass

pyrolysis (Ding et al., 2020). Precipitation, impregnation, precipitation impregnation, sol-gel, and chemical deposition are some of the techniques used to prepare heterogeneous catalysts. In this study, impregnation method was chosen as it is less complicated and efficient compared to other methods. The objective of this study was to synthesize 1, 3 and 5 wt. % Mo/ZSM-5 by impregnation method and characterize the catalysts. Subsequently, catalytic pyrolysis testing was performed to produce H₂ and CH₄ gases at ratio of catalyst-to-feedstock; 1:5, 1:10 and 1:15. Despite the promising results observed with Mo/ZSM-5 catalyst in this study, there remained significant room for further exploration in treating FOBS through pyrolysis with presence of Mo/ZSM-5 catalyst, particularly in optimizing catalyst composition and process condition to enhance H₂ and CH₄ gas yields.

2. Methodology

2.1 Materials

HZSM-5 catalyst (Si/Al ratio of 30), ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), distilled water, FOBS obtained from local petrochemical refinery were employed for this study.

2.2 Catalyst Preparation

The Mo/ZSM-5 catalyst was synthesized via the impregnation method. Commercial zeolite HZSM-5 (Si/Al: 30) was purchased from Zeolyst International and ammonium heptamolybdate tetrahydrate, ((NH₄)₆Mo₇O₂₄·4H₂O) was purchased from Qrec for the synthesis of Mo/ZSM5. The Mo/ZSM-5 was prepared at variant weight percentages: at 1 %, 3 % and 5 %. The catalysts were labeled as 1Mo/ZSM-5, 3Mo/ZSM-5 and 5Mo/ZSM-5. During the synthesis, the HZSM-5 was dissolved in 100 ml of distilled water and stirred until it was fully dissolved. Next, (NH₄)₆Mo₇O₂₄·4H₂O was added to the HZSM-5 and the mixture was stirred at 80 °C until the water evaporated. The drying process continued in the oven overnight at 110 °C. After drying, the impregnated catalyst was crushed into fine particles size and then calcined in a furnace for 5 hours at 550 °C.

2.3 Catalyst Characterization

X-Ray Diffraction (XRD) was utilized to identify the catalyst compositions using Cu K α radiation (Yu et al., 2018), and the XRD patterns were recorded at 30 mA and 40 kV for $2\theta = 10^\circ - 40^\circ$ at a scan rate of 5 °/min. For visualizing the microstructure and morphology of materials, scanning electron microscopy (SEM) was done using JEOL JSM-5510LV. It uses a tungsten filament and operates between 0.5 and 30 kV of accelerating voltage. Brunauer-Emmett-Teller (BET) was done to study the surface area of the catalysts. Samples were degassed at 350 °C for 4 h for analysis and N₂ adsorption was carried out at -196 °C. Time taken is 4 h with degassing temperature of 350 °C. The reference of surface area of HZSM5 is 400-480 m²/g, Mo/ZSM-5 is 300 - 350 m²/g and Mo with surface area of 6-36 m²/g. Fourier Transform Infra-Red (FTIR) analysis was done to analyze material's ability to absorb infrared light. The model used was Frontier (Perkin Elmer) with the wavelengths used were between 4,000 cm⁻¹ to 650 cm⁻¹.

2.4 Catalytic Pyrolysis

To conduct the experiment, the quartz boat was filled with Mo/ZSM-5 catalyst and FOBS and placed in the center of the quartz tube reactor. Nitrogen gas was then purged into the tube at a flow rate of 150 mL/min for 10 min to create an inert atmosphere for the experiment. The furnace was turned on and held until 500 °C and experiment set for 60 min. One of the condenser's outlets was connected to a round-bottom flask to collect the liquid product while the other outlet was connected to a gas bag to collect the gas product. The gas product was analyzed using gas chromatography (GC) at the 10th, 30th and 60th minutes of the experiment. After the heating area had cooled to room temperature, the remaining solid products placed in the quartz boat were collected and weighed to measure the yield. To ensure the reliability and consistency of the data, each experiment was performed in triplicate.

In highlight, the temperature, reaction time and gas flow rate were set as fixed variables in this experiment. This was supported by previous study which mentioned that the pyrolysis reaction takes place at a very rapid heating rate to a desired temperature of 400 to 600 °C for a very short residence period (Gong, 2021). It was reported that the pyrolysis vapors were produced at 500 °C (Yung et al., 2019). As the temperature increased, coke selectivity gradually increased. Between 600 and 700 °C, the coke selectivity was around 10 %, but it increased significantly when the temperature exceeded 750 °C (Kosinov et al., 2019). As coke formation should be avoided and we want to collect gas product from this study, temperature of 500 °C is chosen. At the same time, 60 min retention time was selected due to the liquid and gaseous yield climbing steadily while the yield remained constant afterwards. The pyrolysis process works best when the pyrolysis lasts for 60 minutes (Bett et al., 2022). Then, the yield of gas produced varied at different N₂ flow rates. The gas yield was higher at a medium flow rate 60 to 100 mL/min and lowest at 20 mL/min. The maximum gas yield occurred at N₂ flow rate 150 mL/min

(Wulandari et al., 2020). Flow rate 150 mL/min was chosen for this study, considering the size of quartz tube and based on preliminary tests.

3. Results and Discussion

3.1 Catalyst Characterization

Figure 1 displays the XRD patterns of the Mo/ZSM5 with Mo loadings 1 %, 3 % and 5%, along with the parent HZSM-5 and Mo. The fact that the modified zeolite's XRD patterns resemble those of the parent HZSM-5 zeolite suggests that the HZSM-5 structure was still preserved during the solid-state reaction (Tursunov et al., 2019). The presence of Mo was observed in range of 23° to 24.6° . As the Mo species loading grew, the peak intensities of the Mo/ZSM5 pattern fell in comparison to the HZSM-5 pattern. The presence of Mo with varying weight percentages was evident through the observed changes in peak morphology, with a broader base observed as the Mo loading increased. This phenomenon is likely attributed to the high dispersion of MoO_3 within HZSM-5 (Thangalazhy-Gopakumar et al., 2012). Figure 1 was indicated that upon catalyst modification, the emergence of new peaks became discernible, coinciding with the disappearance of the sharp peak characteristic of the parent catalyst.

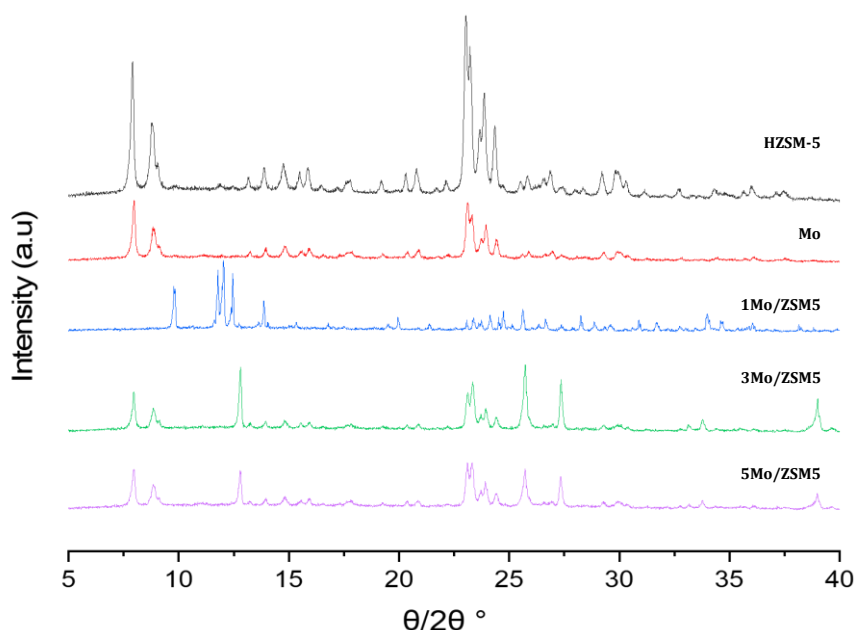


Figure 1: X-Ray Diffraction (XRD) patterns of HZSM-5, Mo, 1Mo/ZSM5, 3Mo/ZSM5 and 5Mo/ZSM5

Figure 2 displays the SEM images of the HZSM-5, Mo and Mo/ZSM-5 catalysts. The Mo/ZSM5 catalysts maintain the cubic form of HZSM-5 zeolites in contrast to the morphologies of HZSM-5. As a result of the Mo species dispersed on the Mo/external HZSM-5's surface, tiny crystal particles are dispersed on the surface of HZSM-5 catalysts, increasing their Mo content from 1 wt. % to 5 wt. %. HZSM-5 and Mo/ZSM-5 catalysts share a similar surface look, as seen in the SEM image. As revealed by XRD study, the metal clusters are tiny, which makes it difficult to discern them in the SEM image. It is notable to assume that the metals are scattered on catalysts because the metal clusters are small. It is proposed that the metal clusters are small and distributed on the catalysts based on the XRD study and supported by the SEM image.

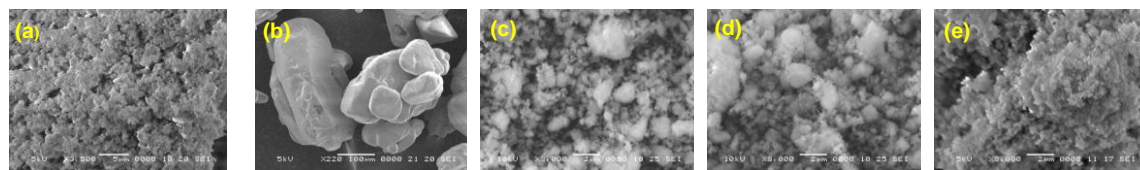


Figure 2: Scanning Electron Microscopy (SEM) images of (a) HZSM-5; (b) Mo; (c) 1Mo/ZSM5; (d) 3Mo/ZSM5 and (e) 5Mo/ZSM5

The specific surface area and pore volume of HZSM-5, Mo and Mo/ZSM-5 catalysts were shown in Table 1. The total specific surface areas of HZSM-5 and Mo were 350.58 and 6.95 m²/g while the specific surface area of 1Mo/ZSM-5, 3Mo/ZSM-5 and 5Mo/ZSM-5 increased compared with Mo catalyst but lower than specific surface area of HZSM-5.

Table 1: BET results of HZSM5, Mo, 1Mo/ZSM5, 3Mo/ZSM5 and 5Mo/ZSM5

Catalyst	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Mesopore volume (cm ³ /g)
HZSM-5	350.58	0.13370	0.12082	0.01288
Mo	6.95	0.02370	0.00298	0.02072
1Mo/ZSM-5	164.85	0.09990	0.09201	0.00789
3Mo/ZSM-5	168.63	0.08708	0.07592	0.01116
5Mo/ZSM-5	116.43	0.05301	0.05556	0.00255

Mo catalyst has the lowest surface area (6.95 m²/g). HZSM-5 catalyst has the maximum surface area (358.58 m²/g). After metal impregnation, the Mo/ZSM-5 catalyst's surface area resulted to 164.85, 168.63 and 116.43 m²/g. The differences in surface area on Mo/ZSM-5 catalysts were substantial. This variation was attributed to the distribution of Ni and Mo metals on the surface, which partially blocked the pores (Sriatun et al., 2019). The size of the Mo particles influenced the surface area, leading to its reduction. Microporous volume, and porous volume all changed after the addition of molybdate to HZSM-5. Indeed, the presence of active sites in mesopores, enhancing access to micropore openings and it was anticipated to have a positive impact on the catalytic performance of the catalyst in desired reactions. The augmented surface area was expected to lead to a higher count of external surface acid sites (Foster et al., 2012).

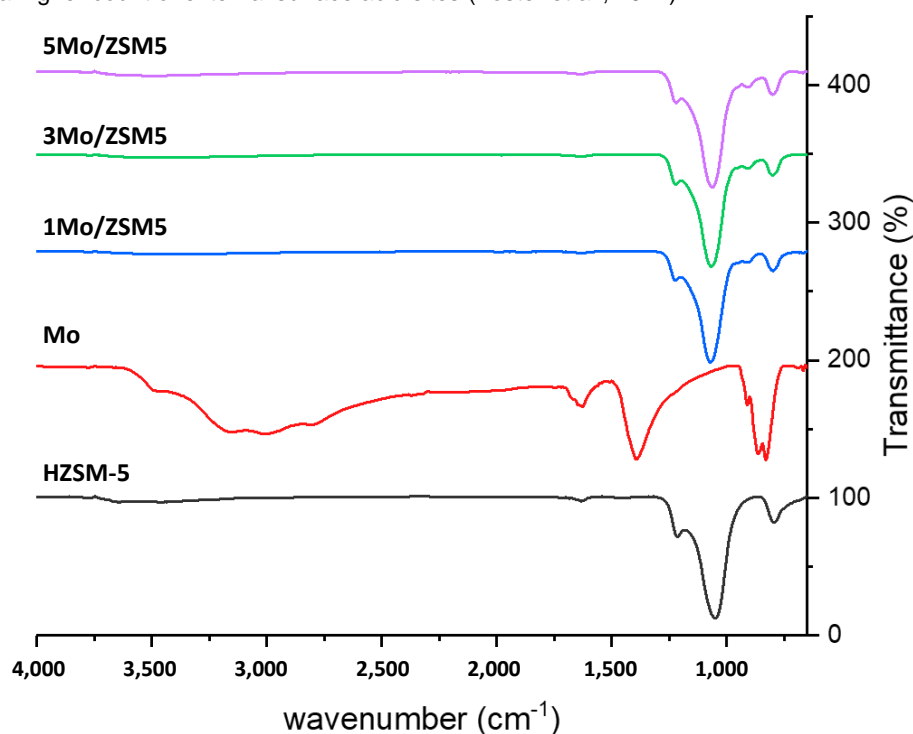


Figure 3: Spectra FTIR of ZSM-5, Mo, 1Mo/ZSM-5, 3Mo/ZSM5 and 5Mo/ZSM5

As shown in Figure 3, hydroxyl group produced from internal silanol is seen in HZSM-5's wide band at 3,500 cm⁻¹. Silanol insulation on the outside and silanol contained in the HZSM-5 crystals make up the absorbent band in the wave number range 3,800-3,700 cm⁻¹. The Brønsted acid site is where the band about 3,600 cm⁻¹ is absorbed. It can be shown in Figure 3 that the loading of Mo on the HZSM-5 results in a decline and nearly complete disappearance of absorption bands in the 3,500 cm⁻¹ regions. When Mo is present, they interact with one other through their intrinsic silanol groups and OH groups, producing MoOH⁺ species. Internal silanol groups and cations may interact. Then, Mo/ZSM-5 catalysts exhibited infrared absorbance peaks in the fingerprint area

that could be attributed to the stretching vibration of Si-O-Si (Barros et al., 2008). The presence of Mo metals interacted with these metals with OH groups and internal silanol groups, producing MoOH⁺ species. Cations were able to interact with internal silanol groups (Xu et al., 2020).

3.2 Data Analysis on Gas Production

Using a fixed basis of 10 grams of FOBS for the three ratio setups, the data from the study was presented in Table 2.

Table 2: Percentage of gas yield, H₂, CH₄ and hydrocarbon gases obtained through catalytic pyrolysis reaction

Catalyst	Yield of gas (%) at ratio 1:5			Yield of gas (%) at ratio 1:5			Yield of gas (%) at ratio 1:5		
	H ₂	CH ₄	C ₁ -C ₄	H ₂	CH ₄	C ₁ -C ₄	H ₂	CH ₄	C ₁ -C ₄
HZSM-5	45.49	18.89	35.62	37.60	56.29	6.11	42.08	22.78	35.14
Mo	52.83	4.18	42.99	54.59	41.86	3.55	55.52	4.94	39.54
1Mo/ZSM-5	60.04	39.96	0.00	84.57	5.08	10.35	37.37	60.98	1.65
3Mo/ZSM-5	16.25	83.75	0.00	90.68	2.82	6.50	36.55	61.46	1.99
5Mo/ZSM-5	20.63	10.14	69.23	49.84	43.57	6.59	56.67	23.05	20.29

Table 2 showed that the primary gases produced throughout the pyrolysis process were CH₄ and H₂. The primary gases formation is typical product formed from catalytic pyrolysis of FOBS and sludge from refinery (Ranizang et al., 2022). Although other gases may have been generated during the reaction due to the inherent complexity and uncontrollable nature of pyrolysis, their quantities were relatively low and were considered insignificant. As reaction was at 500 °C, the optimal ratio gave the highest yield of gas products were identified. Based on the average gas yields for all tested ratios, the 1:10 catalyst-to-feedstock ratio using the 3Mo/ZSM-5 catalyst produced the highest H₂ yield, reaching 90.68 %. While, CH₄ yield was highest at the 1:5 ratio, with a percentage of 83.75 %. Mo/ZSM-5 has gained attention due to its ability to promote dehydrogenation, cracking, and aromatization reactions, which can enhance gas production, particularly H₂ and CH₄ (Ryu et al., 2023). According to previous study, it was found that Mo-modified ZSM-5 could effectively improve the yield of light hydrocarbons, including CH₄, due to the strong metal-acid interactions and the ability of Mo to facilitate carbon-carbon bond cleavage. The study demonstrated that Mo/ZSM-5 exhibited high activity in the catalytic conversion of hydrocarbons, resulting in significant CH₄ production (Sun et al., 2020). Then, the Mo/ZSM-5 enhanced production of hydrogen during pyrolysis. This is consistent with the work carried out by Ranizang et al (2023) that investigated the effect of Ni/ZSM-5 towards the catalytic pyrolysis of FOBS to hydrogen and light hydrocarbon. The incorporation of Mo into ZSM-5 alters the oxygen exclusion pattern and shifts the selectivity toward gas-phase products like H₂, by promoting the removal of oxygen from the feedstock in the form of H₂O and CO (Ding et al., 2020).

4. Conclusion

Catalytic pyrolysis of FOBS has shown great potential for upgrading FOBS into more valuable products, particularly in producing H₂ and CH₄ gases. The Mo/ZSM-5 catalyst was successfully synthesized and characterized, exhibiting superior performance in catalytic testing. Gas yields of H₂ and CH₄ were significantly higher with the Mo/ZSM-5 catalyst compared to the parent catalysts, HZSM-5 and Mo. Notably, the 3Mo/ZSM-5 catalyst delivered the best overall performance and, as a result, could play a crucial role in advancing catalytic pyrolysis technologies, contributing to more efficient and sustainable energy solutions. Future research will aim to further develop the applications of these products and demonstrate their competitiveness in the marketplace. This also include the effect of pressure and reactant diluent towards the catalytic pyrolysis reaction.

Acknowledgement

Thank you to Ministry of Higher Education Malaysia (MOHE) for the financial support through Fundamental Research Grant Scheme (FRGS/1/2020/TK0/UTM/02/97) and Universiti Teknologi Malaysia's Fundamental Research Grant (Q.J130000.3813.23H01).

References

- Barros I.C.L., Braga V.S., Pinto D.S., de Macedo J.L., Filho G.N.R., Dias J.A., Dias S.C.L., 2008, Effects of niobium addition on ZSM-5 studied by thermal and spectroscopy methods, *Microporous Mesoporous Materials*, 109, 485–493.
- Bett R.K., Kumar A., Siagi Z.O., Mibei Z.C., 2022, Thermal Pyrolysis of Used Tyres to Produce Liquid Fuel: Process Optimization and How It Compares to Microwave Pyrolysis, *Journal of Energy*, 2022, 1–12.

- Ding Y.L., Wang H.Q., Xiang M., Yu P., Li R.Q., Ke Q.P., 2020, The Effect of Ni-ZSM-5 Catalysts on Catalytic Pyrolysis and Hydro-Pyrolysis of Biomass, *Frontiers in Chemistry*, 8, 1–11.
- Foster A.J., Jae J., Cheng Y.T., Huber G.W., Lobo R.F., 2012, Optimizing the aromatic yield and distribution from catalytic fast pyrolysis of biomass over ZSM-5, *Applied Catalysis A: General*, 423–424, 154–161.
- Gong W., 2021, Catalytic Fast Pyrolysis of Lignocellulosic Biomass to Benzene, Toluene, and Xylenes, *Recent Perspectives in Pyrolysis Research*, In book: *Recent Perspectives in Pyrolysis Research*, Edited by Mattia Bartoli and Mauro Giocelli, Intechopen.
- Hafeez S., Pallari E., Manos G., Constantinou A., 2018, Catalytic conversion and chemical recovery, Editor(s): S.M. Al-Salem, In *Plastics Design Library, Plastics to Energy*, William Andrew Publishing, 147-172,
- Kosinov N., Uslamin E.A., Meng L., Parastaev A., Liu Y., Hensen E.J.M., 2019, Reversible Nature of Coke Formation on Mo/ZSM-5 Methane Dehydroaromatization Catalysts, *Angewandte Chemie International Edition*, 58, 7068–7072.
- Wan Ranizang W.N.A.A., Mohammed Yussuf M.A., Mohamed M., Jusoh M., Zakaria Z.Y., 2022, Catalytic Pyrolysis of Fuel Oil Blended Stock for Bio-Oil Production: A Review, *Chemical Engineering Transactions*, 97, 373-378.
- Ranizang W.N.A.A.W., Shukri S.S.M., Zakaria Z.Y., Jusoh M., Yussuf M.A.M., 2023, Catalytic Pyrolysis of Fuel Oil Blended Stock to Methane and Hydrogen Gases Products Using Ni/ZSM-5 catalyst, *Chemical Engineering Transactions*, 106, 43-48.
- Reese C.D., 2020, Flammable and Combustible Liquids, *Handbook of Safety and Health for the Service Industry*, 4, 692–703.
- Ryu H.W., Lim Y.H., Jung W., Nam K., Hwang Y., Roh J.E., Kim D.H., 2023, Enhanced stability of CO₂-assisted shale gas aromatization through the introduction of Mg promoter on Mo/ZSM-5, *Chemical Engineering Journal*, 467, 143404.
- Sriatun, Susanto, H., Widayat, Darmawan A., 2019, Characteristic of ZSM-5 catalyst supported by nickel and molybdenum, *IOP Conference Series: Materials Science and Engineering*, 509, 012138, 1-8.
- Sun L., Wang Z., Chen L., Yang S., Xie X., Gao M., Zhao B., Si H., Li J., Hua D., 2020, Catalytic fast pyrolysis of biomass into aromatic hydrocarbons over Mo-modified ZSM-5 catalysts, *Catalysts*, 10, 1–10.
- Thangalazhy-Gopakumar S., Adhikari S., Gupta R.B., 2012, Catalytic pyrolysis of biomass over H+ZSM-5 under hydrogen pressure, *Energy and Fuels*, 26, 5300–5306.
- Tursunov O., Kustov L., Tilyabaev Z., 2019, Catalytic activity of H-ZSM-5 and Cu-HZSM-5 zeolites of medium SiO₂/Al₂O₃ ratio in conversion of n-hexane to aromatics, *Journal of Petroleum Science and Engineering*, 180, 773–778.
- Velebná K., Horňáček M., Jorík V., Hudec P., Čaplovičová M., Čaplovič L., 2015, The influence of molybdenum loading on activity of ZSM-5 zeolite in dehydroaromatization of methane, *Microporous Mesoporous Materials*, 212, 146–155.
- Widayat W., Annisa A.N., 2017, Synthesis and Characterization of ZSM-5 Catalyst at Different Temperatures, *IOP Conference Series: Materials Science and Engineering*, 214, 012032, 1-7.
- Wulandari Y.R., Chen S.S., Hermosa G.C., Hossain M.S.A., Yamauchi Y., Ahamad T., Alshehri S.M., Wu K.C.W., Wu, H.S., 2020, Effect of N₂ flow rate on kinetic investigation of lignin pyrolysis, *Environmental Research*, 190, 109976.
- Xu W., Chen B., Jiang X., Xu F., Chen X., Chen L., Wu J., Fu M., Ye D., 2020, Effect of calcium addition in plasma catalysis for toluene removal by Ni/ZSM-5: Acidity/basicity, catalytic activity and reaction mechanism, *Journal of Hazardous Materials*, 387, 122004.
- Yu J., Meng D., Zhang H., Gao J., Zhang Y., Jiao T., Liang P., 2018, Study on Modification and Sulfur-Resistance Characteristics of Dolomite Catalysts over Wash Oil Catalytic Cracking, *Industrial and Engineering Chemistry Research*, 57, 12973–12979.
- Yung M.M., Starace A.K., Griffin M.B., Wells J.D., Patalano R.E., Smith K.R., Schaidle J.A., 2019, Restoring ZSM-5 performance for catalytic fast pyrolysis of biomass: Effect of regeneration temperature, *Catalysis Today*, 323, 76–85.