Malaysian Journal of Catalysis 5 (2021) 10-18

Malaysian Journal of Catalysis

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MJCat

Research Article

Development of zeolites for zeoforming reaction of naphtha

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Article history:
Received 16 August 2021
Accepted 4 October 2021

ABSTRACT

High octane naphtha production is the primary purpose of the zeoforming process that is genuinely needed in our modern life. Sulfur-containing compounds in gasoline are causing environmental pollution and catalysts deactivation. The metal function supplied by non-noble promoters such as Fe, Mn, Ni, Co, Cu, and Zn is deposited on the ZSM-5 type of zeolite. ZSM-5 zeolites were prepared by successive hydrothermal treatment following by impregnation of promoters on ZSM-5 type zeolite. The catalysts were characterized, utilizing XRD, N_2 physisorption, FESEM, TEM, TPR-H_2, and TPD-NH_3. Bibliometric results show that feed conversion concerns are the primary focus in naphtha and zeolite topic studies. Particular attention has been paid to ZSM-5 and performance that may be crucial for improving the naphtha reforming reaction. The experimental results verified that different promoters' use has a profound effect on zeolites' physicochemical properties. It found that Fe interacts strongly with the ZSM-5 zeolite producing growth in the metal function activity. The zeoforming results indicate that the highest research octane number (RON) belonged to the Fe promoter. A Fe promoter's existence increased the stability and selectivity for C_{7+} isomers and aromatics, thus reducing the formation of sulfur and low-value products like methane and gases.

Keywords: Non-precious metal; bibliometric; ZSM-5; zeoforming reaction; naphtha

| eISSN 0128-2581 |

1. INTRODUCTION

Refineries must also manufacture sustainable goods to comply with the strict global regulations surrounding air emissions. One of the primary sources of achieving human necessity for energy is fossil fuels, accompanied by pollutant agents such as sulfur that are not environmentally sustainable and may cause serious public health problems when inhaled or exposed. New sulfur part common values, as well as the octane number in gasoline, have been developed. Sulfur-containing compounds in fuel are linked to SOx and particulate matter (PM) emissions from gasoline generators, which cause contamination and acid rain in the environment. During the burning or fermentation of fuels, sulfur can be converted to other sulfurous compounds such as SO_2 and H_2S. The intense need to preserve the living ecosystem supports the publication of rigorous pollution legislation and prohibits harmful organisms (S, aromatics, and polyaromatics) in fuel requirements. According to the new regulations, industrial units must limit sulfur yields to no more than 10 mg/kg and raise RON values to at least 90. As a result, the operating units must quickly adjust their products to the new requirements [1]. Consequently, it is critical to consider starting a long-term strategy for reducing the negative effects of fuels to achieve an environmentally friendly process.

The sulphur portion in gasoline was eliminated from the feedthrough hydrodesulfurization (HDS) method before the octane number enrichment process. In the manufacturing sector, HDS is one of the methods for removing sulfur from petroleum products. New inexpensive and effective strategies for desulfurization of refractory organic sulfur are needed by strict new legislation to reduce sulfur content in fossil fuels. There are significant research efforts have been dedicated to improving the HDS process by developing bimetallic and trimetallic catalysts [2-13] to stop radioactive waste in the atmosphere and contamination of the transforming catalyst as a result of the reaction. HDS of such substances is very expensive and necessitates high temperatures and pressures during operation [14]. Other scientists employed zeolite to strip sulfur from naphtha as a catalyst. For instance, Sharifi et al. [1] produced the W/HZSM-5 catalyst for octane improvement and desulfurization at the same time. They discovered that the catalyst with a SiO_2/Al_2O_3 ratio of 60:1 had the most excellent output in the corresponding octane improvement phase. Sulfur compounds were reduced by 67.5 percent, and octane increased by 90 percent. Sulfur components in naphtha, on the other side, prove to be a cause of catalyst deactivation and high-octane fuel output concerns. Non-noble metals, such as Ni, Fe, Mn, Co, Cu, Zn, have been deposited onto W-HZSM-5 as a conventional metal in HDS industrial catalysts [15]. According to some studies, the ZSM-5 catalyst is highly effective at aromatizing and upgrading gasoline [1, 16-19]. As a result, the benefits of zeolite as a catalyst for the zeoforming phase with non-noble metals are its environmental friendliness and sulfur activity. According to these studies, the collaboration between acid zeolite catalysts like ZSM-5 and non-precious metals as promoters could significantly increase the sequential desulfurization-aromatization process performance.

In this context, it is clear that there is no consensus in the literature on the zeoforming process. This process is crucial for adequately planning future research designs but is currently unavailable. In our previous research [20], we sincerely reviewed hydrodesulfurization, catalysts used for the naphtha reforming process, and how the zeoforming process would decrease the sulfur component without using the conventional hydrodesulfurization process. There is no paper has been published on promoters' impact on the catalytic behavior of the zeoforming reaction, as far as we know. Thus, this study aims to systematically examine reports of “naphtha” and “zeolite” and the primary trend and focus of research from 1970 to 2021, containing journals, research topics, widely quoted articles, and often used keywords; and to determine the effect of non-noble metal promoters on the properties of the acid and metal functions of ZSM-5 type zeolite for zeoforming reaction. The zeolites synthesized in this study have been characterized through XRD, N_2 physisorption, FESEM, TEM, TPR-H_2, and TPD-NH_3 analysis. The catalysts' catalytic behavior has been explained accordingly, and the proposed reaction mechanism of the zeoforming process was drawn.

2. EXPERIMENTS

It started with a bibliographical quest in the WOS directory of periodicals. A few keywords were used to conduct this research, and these keywords were incorporated into the WOS search engines by following the form of the Boolean "AND". The program EndNotes X 5TM was used to index these archives, and the raw research was kept there. Accordingly, bibliometrics was carried out using the mathematical study of publication peaks and keyword networking. The experimental study was carried out in line with the pattern in experiments and study void found.

2.1 Catalyst preparation

The synthesis of ZSM-5 zeolite was performed from a sol-gel intermediate with the chemical compositions of Al_2O_3: 120 SiO_2: 3 TPAOH:6 TPABr: 1.5 Na_2O: 1000 H_2O in the following order and using a hydrothermal treatment which also described elsewhere [21, 22]. Initially, NaOH pellets and aluminum isopropylate were melted in distilled water (solution I), supplemented by distilled water with a measured amount of TPAOH and TPABr (solution II), and finally, distilled water with a source of silica (solution III). To achieve homogeneity, each solution was stirred for 4 hours. Then, the solutions (I) and (II) were added drop-wise to the solution (III) under dynamic mixing. The resulting mixture was blended for 12-16 h at room temperature to ensure homogeneity. The synthesized gel was transferred into a stainless-steel autoclave hydrothermal reactor with PTFE lining (200 mL) and maintained at an appropriate temperature of 150 ^{o}C for 48 h. The solid stock was purified and washed with deionized water until the washing water's pH hit 6, then dried for 24 hours at 110 ^{o}C. The outcome was calcined for 5 h at 600 ^{o}C. Using the impregnation technique, the promoters/ZSM-5 catalysts (all elements from Aldrich) were developed. The impregnation process has the benefit of producing a large concentration of active substances on the catalyst surface. [23, 24]. To prepare the catalysts, 1 wt.% non-noble promoters such as Fe, Ni, Co, Cu, Zn, and Mn with 99 wt.% of ZSM-5 were mixed in 200 mL deionized water. The mixture was heated to 90 °C and mixed with a hot plate until it thickened into a viscous paste. The paste was cured overnight in an oven at 110 °C. The catalyst was then calcined at 600°C overnight in a furnace before being cooled to room temperature. The mixture was heated to 90 °C and mixed with a magnetic stirrer until it became an extremely viscous paste. The paste was cured overnight in an oven at 110 °C. The catalyst was then calcined at 600 °C overnight in a furnace before being cooled to room temperature. Prepared ZSM-5 samples are shown in Figure 1 and were named Fe/ZSM-5, Ni/ZSM-5, Co/ZSM-5, Cu/ZSM-5, Zn/ZSM-5, and Mn/ZSM-5. Samples were grinded and fermented on 2 phases of 35 and 34 mesh before the experiment reaction test to achieve particles with a scale of 1.0 mm to 1.4 mm.

Figure 1 Prepared ZSM-5 samples with different promoters

2.2 Catalyst characterization

The X-ray diffraction (XRD) of the samples was carried out on an X-ray diffractometer by Ni filtered Cu K α radiation with a scanning angle (2θ) of 5 to 80° with a step size of 0.02° and a step time of 49 s. Furthermore, the Brunauer–Emmett–Teller (BET) procedure was extended to the isotherms of N_2 adsorption to measure reduced catalyst entire surface region, estimated at liquid nitrogen temperature on a Beckman Coulter SA3100^{TM} apparatus at 200 °C for 2 h on outgassed samples. A JEM-ARM200F microscope was used for transmission electron microscopy (TEM). The acidity of the formulated catalysts was calculated using a Micromeritics Chemisorb 2720 chemisorption analyzer. To determine the total acidity of catalysts, 35 mg of the sample was kept at 600 °C for 60 minutes under a 30 mL/min argon flow rate, then cooled to 25 °C and held under a 20 mL/min helium flow rate for 30 minutes. The catalyst was saturated with NH_3 for 30 minutes at a rate of 20 mL/min in argon containing 5% (vol.) NH_3.

2.3 Zeoforming reaction

There have been many approaches for designing the reactor and processes comparable to other catalytic materials production. We previously demonstrated that fluid bed reactors could accommodate massive feed and catalyst volumes in a previous study [20]. On the other hand, fixed bed reactors were extensively used in earlier tests of the catalytic reforming mechanism with strong catalysts. The fixed bed reactor is the most popular method for studying gas-phase reactants with a strong catalyst to synthesize large quantities of appropriate chemicals and intermediates [25, 26]. Fixed-bed reactors have been primarily used for the disposal of radioactive and hazardous compounds in recent years, in addition to the synthesis of valuable chemicals [25]. The experimental setup for the zeoforming process is depicted in Figure 2. A total of 0.1 g of catalyst was included in the activity samples. The catalyst bed was installed in a 0.5-inch OD quartz tubular reactor with a coaxially focused thermocouple. Before the reaction, the catalyst bed was flooded with nitrogen at 300 °C, then reduced in situ for 1 hour at 600 °C with 30 mL/min pure hydrogen. As n-heptane is a significant component in naphtha, it was chosen as a typical feed for this set of experiments to give a realistic picture of the industrial reforming process [27]. Until combining with carrier N_2, N-heptane was fed separately into the pre-heater using an HPLC pump (Bio-RadTM, Series 1350) at 0.1 mL/min. At a temperature of 400 °C and a pressure of 10 bar, the reduced materials were checked for n-heptane. The reaction last for an hour and stability test last for 24 continues hours for the optimum catalyst. The reaction products were studied using a GC with TCD (Agilent 6890N) and a Carboxen Plot 1010 capillary column (Fused silica, 30 m x 0.53 mm) attached in sequence argon as the carrier gas. Meanwhile, a GC-FID with a Petrocol-DH column (100 m 0.25 mm ID) and a flame ionisation detector are used to test the liquid product. By utilizing specific solutions and the table included with the panel, the peaks in the chromatograms received from the GC were established. In each catalytic experiment, the study octane number (RON) for the finished product was determined as:

$$RON = \sum_{i=1}^{K} y_i RON_i$$

where RONi represents the analysis octane amount of each pure ingredient i in the end product, and y_i represents the mole fraction of particle i [28, 29].

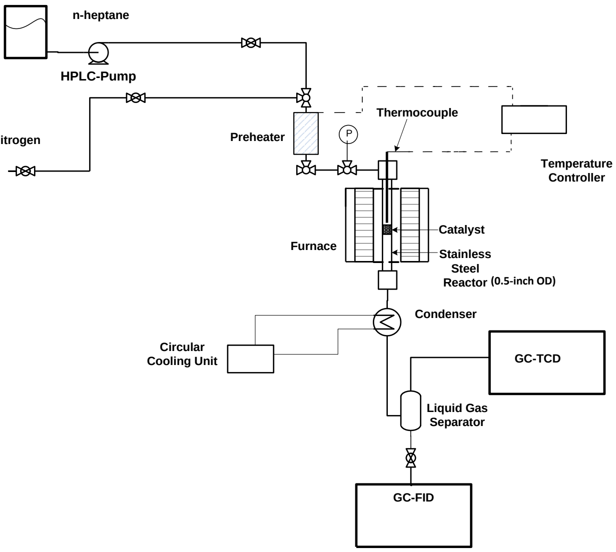

Figure 2 A fixed bed reactor system utilized in this research

3. RESULTS AND DISCUSSION

3.1 Catalysts characterization

Various methods were used to classify the synthesized zeolites. XRD analysis was used to analyze the composition of zeolites. Figure 5 displays the zeolites' XRD trends in the 2-theta radiation angle range and the 5–80° angle range after calcination. The index peaks for this sample in 2-theta are 7.78, 8.68, 23.09, 23.49, 23.77, and 24.29, which were detected in all catalysts ZSM-5 zeolite development before and after promoter processing, according to JCPDS results with reference code 00-037-0359 for ZSM-5 Zeolite. The XRD patterns of ZSM-5 and HZSM-5 showed peaks at 7–30° and 22.5–24°, representing the crystal plane of orthorhombic and monoclinic phase structure, respectively. The sharpness of the peaks shows the crystalline nature of the silicone samples. The findings indicate that during the impregnation phase, the promoters' crystallinity did not alter dramatically in the crystalline structure, mechanism change, or harm to the catalysts. The absence of any peaks linked to metal species means that the promoter is distributed uniformly in the catalyst system [30, 31].

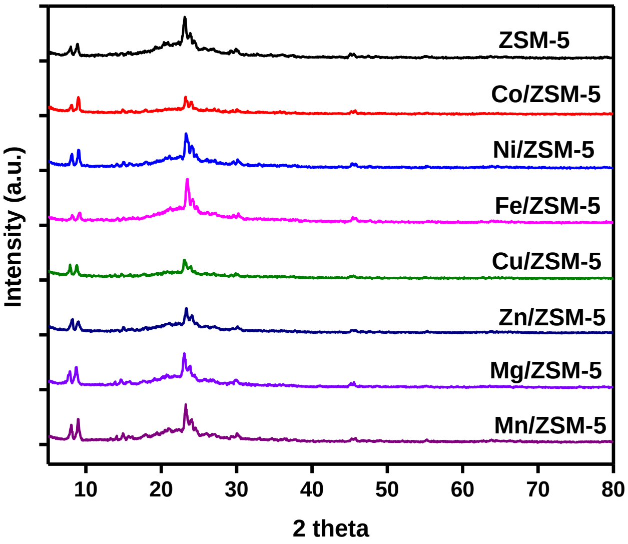

Figure 3 XRD pattern of zeolites

The Brunauer-Emmett-Teller (BET) method was employed to analyze all catalysts' textural properties, including surface area (S_{BET}), pore depth, and pore diameter. Table 2 displays the SBET surface area and total acidity (measured by TPR-NH_3) of ZSM-5, Fe/ZSM-5, Ni/ZSM-5, Co/ZSM-5, Cu/ZSM-5, Zn/ZSM-5, and Mn/ZSM-5 zeolites. Among the zeolites, the Zn/ZSM-5 exhibited a higher surface area, followed by Mn/ZSM-5. Nevertheless, in Fe/ZSM-5, the strong acidity needed for the isomerization reaction is high. The SBET was reduced from 413 to 284 m^2/g after loading 1wt% Fe on ZSM-5 due to heavy Fe contact with ZSM-5, suggesting that Fe was mainly deposited on the exterior surfaces could have prevented some of ZSM-5's micropores [32]. The S_{BET} reduced when 1 wt% Co, Ni, and Cu were introduced, but not as significant as when 1 wt% Fe was added. The drop in surface area of supported catalysts as compared to unpromoted catalysts may be attributed to the fact that certain metals, such as Fe, may increase the agglomeration of certain zeolite species, causing a drop in surface area [33].

Table 1 BET surface area, pore-volume, average pore diameter and acidity data of catalysts

Zeolites	S_{BET} (m^2/g)	V_P (cm^3/g)	D_P (nm)	Acidity (m.mol NH_3/g)
ZSM-5	413	0.38	3.68	0.37
Co/ZSM-5	308	0.45	5.84	0.42
Ni/ZSM-5	305	0.54	7.08	0.39
Fe/ZSM-5	284	0.48	6.76	0.53
Cu/ZSM-5	301	0.26	3.46	0.45
Zn/ZSM-6	378	0.44	4.66	0.41
Mn/ZSM-8	326	0.37	4.54	0.43

According to Gorzin et al. [31], the decreased surface area of promoted catalysts may be due to micropore damage or pore blockage. This result approves that partial structural damage may occur during the parent catalyst's impregnation; for example, the promoted samples lost some crystallinity, and the catalysts' crystal and particle sizes grew larger. The Zn/ZSM-5 catalyst behaved badly in terms of acidity, but it has a greater surface area than other promoted catalysts. As a result, it'll be important to see how low-acidity porosity affects the isomerization reaction.

FESEM imaging performed to investigate the morphology of catalysts in it is presented in Figure 4. FESEM micrographs of the catalysts show relatively uniform spherical aggregation. The pictures show that the support was an irregular particle and was made of porous sphere particles ranged from 16–38 nm. The promoted and pure ZSM-5 catalysts had identical surface morphologies and particle size distributions, suggesting no major morphology shift or structural disruption attributable to impregnation, which mirrored the XRD findings.

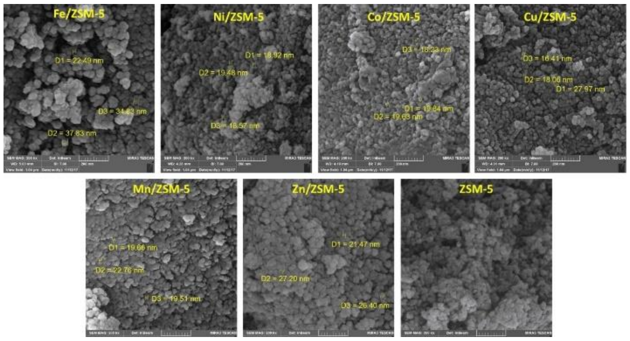

Figure 4 FESEM images of catalysts

The dispersion of metal in the zeolite support and promoters' impact on delivery were investigated using TEM on pure zeolite and the same catalysts. Results are shown in Figure . The products' high porosity is visible in the TEM, and these nano-sized characteristics are more readily noticed. ZSM-5 zeolites appeared to be hexagonal or spherical crystals with 1–5 m diameters and smooth surfaces, common in the ZSM-5 style [34-36]. The incorporation/deposition of the promoter molecules, depicted as dark-grey regions (10–30 nm), could be seen in the impregnated catalysts. In the impregnated samples, the incorporation/deposition of promoter particles may be seen as dark grey regions (10–30 nm). The TEM photos showed pale spots on mesoporous substrates' surfaces, which were traced to non-precious metal nanoparticles. On the other side, the metal nanoparticles were scattered in the help in a somewhat uneven fashion. As seen in the graphs, certain zeolite areas were heavily packed with metal particles, whilst others had just a few metal particles. The catalysts that have been promoted, as seen in TEM images of Fe/ZSM-5, Cu/ZSM-

5, and Mn/ZSM-5 a relatively better metal dispersion was observed.

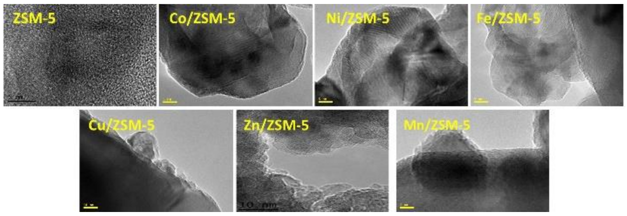

Figure 5 TEM images of zeolites

The reducibility of metals promoted ZSM-5 catalysts was investigated using H_2–TPR experiments. In Figure , the TPR curves for Fe/ZSM-5, Ni/ZSM-5, Co/ZSM-5, and Cu/ZSM-5 catalysts are displayed. The catalysts' TPR curves vary, suggesting an incompatible relationship between active phases [23, 24, 36, 37] and the difference in reducibility of the metal oxides in the zeolite.

In the temperature range tested, the H_2-TPR of pure ZSM-5 did not indicate hydrogen usage [38]. The prominent reduction peak at 462 °C corresponds to the Fe metal phase reduction. Ni and Co promoters' addition to ZSM-5 zeolite moved the H_2-TPR peaks to higher reduction temperatures, with the H2-TPR peak at 416 and 731 °C, respectively. That may be due to a more significant proportion of Ni and Co ions in the Ni and Co samples being completely depleted. With the Zn promoter in the ZSM-5, no major TPR peaks were observed. It was previously stated that the TPR profiles of zinc oxides are close to those of zinc-free iron oxides [39].

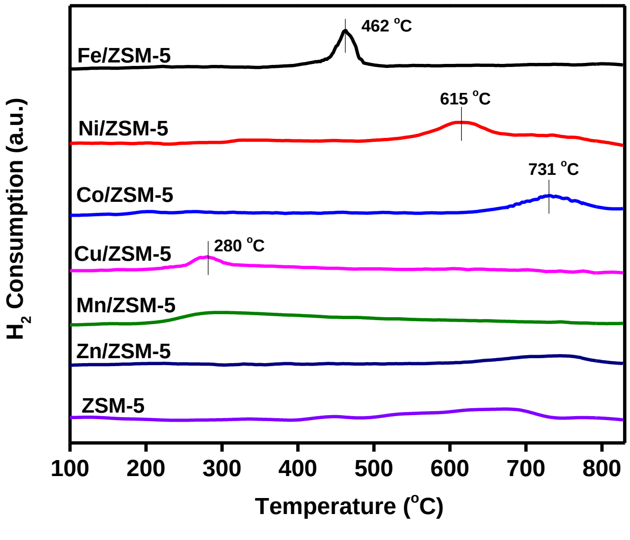

Figure 6 H_2-TPR profiles of the catalysts

3.2 Zeoforming reaction

The bifunctional catalysts, which consist of an acid function of ZSM-5 type zeolite and non-noble Fe, Mn, Ni, Co, Cu, and Zn metals function used for zeoforming reaction. The acidity of catalysts-controlled cyclization and isomerization reactions, while the metal function controlled the dehydrogenation and hydrogenation reactions. To achieve the best catalytic activity in zeoforming reactions, an appropriate equilibrium between such functions is essential. As shown in Table 3, the n-heptane conversion and catalytic activity of zeoforming have matched the acidity and surface area of catalysts. The catalyst's operation was assessed by converting n-heptane in a constant flow, a high-pressure micro-reactor system under reaction conditions of 400 °C and 10 bar pressures. The data from sulfur and n-heptane conversion and isomerization, octane number improvement, and the isomer composition were used to analyze the catalyst's activity. Sulfur was mixed as dimethyl disulfide (DMDS) at 1 wt% with n-heptane in the feed. The table shows that the increased yield from 12.22 wt.% (for pure ZSM-5) to 67.6 wt.% for the isomer when the Fe promoter impregnated.

Conversely, the cracked paraffin amount (C_1-C_6) decreased when the promoters applied for ZSM-5 zeolite. The product obtained for Fe/ZSM-5 catalyst appears to be reasonable for octane number enhancing (from 13 to 48.8) and zeoforming reaction. This reaction which increases 35.8 units in RON, could be used for blending of gasoline purpose. The Fe/ZSM-5 catalyst achieved the highest n-heptane conversion and sulfur portion, according to the results. The Fe/ZSM-5 catalyst's high activity is due to the addition of metal, which increases the acidity of the catalyst. It is also proved by previous studies, which revealed that the conversion of reactants is mainly determined by the acidity of the catalyst [40, 41].

There are few sequential reaction steps such as dehydrogenation (step 1), isomerization (step 2), and hydrogenation (step 3) for the isomerization reaction might involve. Reaction pressure could influence dehydrogenation and hydrogenation because these two reactions include various numbers of reactants to products. On this occasion, the low pressure enables the dehydrogenation reaction, and the high pressure allows the hydrogenation one. An intense observation of data given predicts that the reaction pressure slightly increased isoparaffin yields and the conversion. That may be attributed to the more successful conversion of iso-heptane olefin to hydrogenation in the third stage of the reaction relative to cracking. High n-heptane conversion (82.5 wt.%) and isoparaffin yield (73.05 wt.%) and 51.3 units for octane number were obtained at 20 bar; this is because the desorption and diffusion of molecules are more complex in high pressure.

The refining of hydrocarbons is followed by the deposition of carbonaceous deposits on the catalyst surface, a mechanism known as coking, which is the most common cause of catalyst deactivation. Deactivation happens in most catalytic processes and is affected by a combination of factors such as catalyst active site reactivity to foreign molecules such as sulfur and nitrogen compounds, alteration of reaction parameters, sintering (decrease in metallic, active surface area), and heavy metal deposition, which is calculated at the end. In the last part of the experiment, time on stream behavior during n-heptane conversion was examined for the Fe/ZSM-5 at 10 bar pressures for 24 h, and the results are shown in Table . It can be seen that the feed conversion was decreased from 76.2% to 67.7% after 24 h of TOS. Catalyst selectivity, the yield of C6 crushed substance alkanes, and catalyst deactivation were both influenced by the solvent row's duration. In general, the Fe/ZSM-5 catalyst was selective for 1-hexene oligomerization due to the cracking reaction were blocked. The octane number also seems to be stable during 24 h of TOS (48.8-46.8).

During the zeoforming reaction, many reactions arise to transform n-heptane to paraffin, aromatic hydrocarbons, hydrogen sulfide, and sulfur-containing species to paraffin, aromatic hydrocarbons, and hydrogen sulfide. A simple reaction mechanism for the conversion of sulfur components in the zeoforming reaction is shown in Figure 7. The C–S bonds of mercaptans, sulfides, thiophenes, or their products are split, releasing hydrogen sulfide and olefin particles, as we discovered in previous studies [20]. The intermediate olefins are then transformed to paraffin and aromatics, while hydrogen sulfide, a gaseous C1–C4 species, is isolated along with side products of the whole phase.

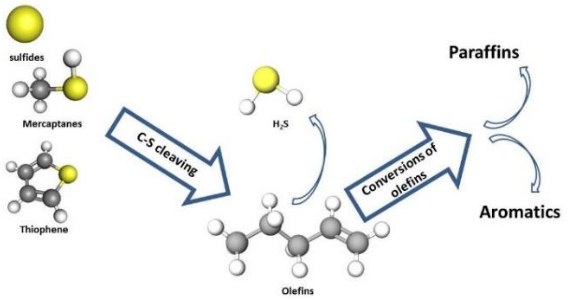

Figure 7 Proposed transform of sulfur-containing organisms in the zeoforming reaction

Table 2 Effect of promoters of ZSM-5 zeolite on zeoforming

Catalysts	**ZSM-5**	**Co/ZSM-5**	**Ni/ZSM-5**	**Fe/ZSM-5**	**Cu/ZSM-5**	**Zn/ZSM-5**	**Mg/ZSM-5**	**Mn/ZSM-5**
Conversion (wt %)	21.9	37.5	28.8	76.2	69.4	42.6	74.2	72.7
Gas yield (wt%)	5.8	4.5	7.9	15.3	5.1	14.3	3.6	3.6
Liquid yield (wt%)	94.2	95.5	92.1	84.7	94.9	85.7	96.4	96.4
Total Paraffins	86.86	69.17	80.44	28.92	37.33	67.49	31.17	34.47
(i)Cracked Paraffins (C1-C6)	3.3	4.9	7.9	9.3	6.1	5.38	8.6	7.6
(ii) n-heptane	83.56	64.27	72.54	19.62	31.23	62.11	22.57	26.87
Total i-Paraffins	12.22	26.31	17.58	67.6	61	31.52	65.73	62
(i)Lower i-paraffins (iC4-iC6)	3.8	5.31	5	9.6	9.4	7.9	9.6	7.7
(ii) C7+ i-paraffins	8.42	21	12.58	58	51.6	23.62	56.13	54.3
a) Mono-branched	7.4	18.2	11.3	43.4	41.1	19.6	43.1	42.4
b) Di-branched	1.02	2.8	1.28	13.1	10.4	4	12.43	11.4
c) Multi-branched	0	0	0	1.5	0.1	0.02	0.6	0.5
Olefins	0	1.2	0.1	0.1	0.1	0	0	0.1
Naphthenes	0	2.3	1	2.4	0.7	0	2.2	2.5
Aromatics	0	0.4	0.2	0.9	0.6	0.6	0.8	0.8
Sulfur	0.92	0.62	0.68	0.08	0.27	0.39	0.1	0.13
Total	100	100	100	100	100	100	100	100
RON	13	25.5	16.4	48.8	45.5	35.2	47.5	47.5

Table 3 Effect of pressure on zeoforming reaction

Pressure (bar)	10	15	20	25
Conversion (wt %)	76.2	78.3	81.9	82.5
Gas yield (wt%)	15.3	12.8	12.8	14.1
Liquid yield (wt%)	84.7	87.2	87.2	85.9
Total Paraffins	28.92	25.76	25.32	23.04
(i)Cracked Paraffins (C1-C6)	9.3	4.1	4.1	4
(ii) n-heptane	19.62	21.66	21.22	19.04
Total i-Paraffins	67.6	70.6	71.4	73.05
(i)Lower i-paraffins (iC4- iC6)	9.6	8.4	7.5	6.6
(ii) C7+ i-paraffins	58	62.2	63.9	66.45
a) Mono-branched	43.4	46.8	46.8	47.2
b) Di-branched	13.1	13.9	15.4	17.5
c) Multi-branched	1.5	1.5	1.7	1.75
Olefins	0.1	0.1	0	0.1
Naphthenes	2.4	2.5	2.2	2.7
Aromatics	0.9	0.98	1.05	1.1
Sulfur	0.08	0.06	0.03	0.01
Total	100	100	100	100
RON	48.8	49.5	49.8	51.3

Table 4 Time on stream for Fe/ZSM-5

Time (h)	1	4	8	12	16	20	24
Conversion (wt %)	76.2	74.8	69.3	68.7	67.8	67.9	67.7
Gas yield (wt%)	15.3	14.9	14.1	15.1	14.3	14.1	14.6
Liquid yield (wt%)	84.7	85.1	85.9	84.9	85.7	85.9	85.4
Total Paraffins	28.92	29.1	29.2	29.7	29.8	29.8	29.8
(i)Cracked Paraffins (C1-C6)	9.3	9.2	9.1	8.9	8.9	8.7	8.6
(ii) n-heptane	19.62	19.9	20.1	20.8	20.9	21.1	21.2
Total i-Paraffins	67.6	67.44	67.32	67.14	67.04	67.27	67.46
(i)Lower i-paraffins (iC4- iC6)	9.6	9.74	10.32	9.74	9.34	11.97	12.96
(ii) C7+ i-paraffins	58	57.7	57	57.4	57.7	55.3	54.5
a) Mono-branched	43.4	43.1	42.9	43.5	44.1	42.1	41.8
b) Di-branched	13.1	13.1	12.9	12.8	12.7	12.5	12.1
c) Multi-branched	1.5	1.5	1.2	1.1	0.9	0.7	0.6
Olefins	0.1	0.1	0.2	0.1	0.3	0.1	0.1
Naphthenes	2.4	2.4	2.3	2.1	1.9	1.9	1.7
Aromatics	0.9	0.87	0.87	0.85	0.84	0.81	0.81
Sulfur	0.08	0.09	0.11	0.11	0.12	0.12	0.13
Total	100	100	100	100	100	100	100
RON	48.8	47.5	47.2	47.1	46.9	46.8	46.8

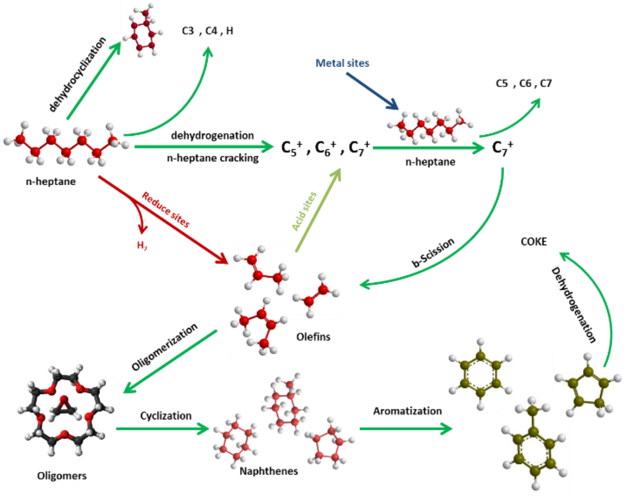

Figure 8 Proposed zeoforming reaction pathway

4. CONCLUSION

One of the essential processes in the processing industry is catalytic naphtha reforming. This system is generally used to make high-octane gasoline and aromatic materials. However, there are drawbacks in this technology such as sulfur emission, employing high costs units such as hydrodesulfurization (HDS) process, and high costs of catalysts. In this work, the bibliometric analysis found that conversion, performance, hydrocarbons, zsm-5, and zeolite have the highest total link strength and top occurrences by using keywords such as “naphtha” and “zeolite” search in the WOS database. In contrast, there is a lack of research in the title search of keywords such as “zeoforming” and “hydrodesulfurization” from 1970 to 2021. It is anticipated that scientists would be motivated to use and adapt these seeking methods and techniques to their study due to understanding that specific knowledge is right at their fingertips. Thus we carried out the zeoforming process using n-heptane as a model compound of naphtha over pure ZSM-5 type zeolite and promoted ZSM-5 such as Fe/ZSM-5, Ni/ZSM-5, Co/ZSM-5, Cu/ZSM-5, Zn/ZSM-5, and Mn/ZSM-5 zeolitic catalysts and examined their catalytic activities for zeoforming reaction and to produce high octane of mixed feedstocks such as naphtha. XRD, H_2-TPR, BET, TEM, and FESEM analyses enable the characterization of catalysts to elucidate the performance's reasonable compared to unpromoted ZSM-5 by showing non-noble metal ability to promote metal dispersion, catalyst crystallinity and provide the catalyst with the suitable acidity to enhance the octane number. The present study exemplified that the acid sites considerations for Fe/ZSM-5 catalyst play a vital role in the effective isomerization and octane number boosting. The catalyst can be economically viable in industrial applications. The addition of non-noble metals to the ZSM-5 helps increases both n-heptane conversion and aromatic selectivity. It may be due to the Fe promoter's existence raising the catalyst's dehydrogenation activity, resulting in higher availability of the olefin pool, which is the intermediate for aromatization. This indicates that Fe species are capable of dehydrating intermediates and turning them into aromatics.

ACKNOWLEDGEMENTS

The principal author, Walid Nabgan, is thankful for Universiti Teknologi Malaysia's support in the form of the Post-Doctoral Fellowship Scheme "Simultaneous heavy metals ions and organic pollutants photoredox reactions over SiO_2/ZrO_2 based catalysts under solar-light irradiation" (PDRU Grant number: 05E49). In addition, the authors acknowledge the financial support given for this work by Universiti Teknologi Malaysia (UTM) under the Collaborative Research Grant (CRG) number 07G61 and the University Laboratory Management Unit (UPMU).

REFERENCES

[1] Sharifi K, Halladj R, Royaee SJ, Nasr MRJ. Powder Technology. 2018;338:638-44.
[2] Klimov OV, Koryakina GI, Gerasimov EY, Dik PP, Leonova KA, Budukva SV, et al. Catalysis in Industry. 2015;7:38-46.
[3] Hein J, Gutierrez OY, Schachtl E, Xu PH, Browning ND, Jentys A, et al. ChemCatChem. 2015;7:3692-704.
[4] Huirache-Acuña R, Alonso-Núñez G, Paraguay-Delgado F, Lara-Romero J, Berhault G, Rivera-Muñoz EM. Catalysis Today. 2015;250:28-37.
[5] Klimov OV, Nadeina KA, Dik PP, Koryakina GI, Pereyma VY, Kazakov MO, et al. Catalysis Today. 2016;271:56-63.
[6] Liu YJ, Song SZ, Deng X, Huang W. Energy & Fuels. 2017;31:7372-81.
[7] Nikulshina MS, Mozhaev AV, Minaev PP, Fournier M, Lancelot C, Blanchard P, et al. Russian Journal of Applied Chemistry. 2017;90:1122-9.
[8] Boldushevskii RE, Guseva AI, Vinogradova NY, Naranov ER, Maksimov AL, Nikul'shin PA. Russian Journal of Applied Chemistry. 2018;91:2046-51.
[9] Dik PP, Pereima VY, Nadeina KA, Kazakov MO, Klimov OV, Gerasimov EY, et al. Catalysis in Industry. 2018;10:20-8.
[10] Behnejad B, Abdouss M, Tavasoli A. Petroleum Science. 2019;16:645-56.
[11] Valdes-Martinez OU, Santolalla-Vargas CE, Santes V, de los Reyes JA, Pawelec B, Fierro JLG. Catalysis Today. 2019;329:149-55.
[12] Abubakar UC, Alhooshani KR, Adamu S, Al Thagfi J, Saleh TA. Journal of Cleaner Production. 2019;211:1567-75.
[13] Villasana Y, Mendez FJ, Luis-Luis M, Brito JL. Fuel. 2019;235:577-88.
[14] Blanco-Brieva G, Campos-Martin J, Al-Zahrani S, Fierro J. Removal of refractory organic sulfur compounds in fossil fuels using MOF sorbents. Global Nest J. 2010;12:296-304.
[15] Zhao N, Li S, Wang J, Zhang R, Gao R, Zhao J, et al. Journal of Solid State Chemistry. 2015;225:347-53.
[16] Duan AJ, Li TS, Niu H, Yang X, Wang ZG, Zhao Z, et al. Catalysis Today. 2015;245:163-71.
[17] Harrhy JH, Wang A, Jarvis JS, He P, Meng S, Yung M, et al. Communications Chemistry. 2019;2:37.
[18] Yin C, Liu C. T, Petroleum Science and Technology. 2005;23:1153-6
[19] Yin C, Liu C. Applied Catalysis A: General. 2004;273:177-84.
[20] Nabgan W, Rashidzadeh M, Nabgan B. Environmental Chemistry Letters. 2018;16: 507–22..

[21] Soltanali S, Halladj R, Rashidi A, Bazmi M, Bahadoran F. Chemical Engineering Research and Design. 2016;106:33-42.
[22] Soltanali S, Halladj R, Rashidi A, Bazmi M. Crystal Research and Technology. 2014;49:366-75.
[23] Nabgan W, Tuan Abdullah TA, Mat R, Nabgan B, Gambo Y, Triwahyono S. International Journal of Hydrogen Energy. 2016; 41:22922-31.
[24] Nabgan W, Tuan Abdullah TA, Mat R, Nabgan B, Gambo Y, Moghadamian K. Journal of Environmental Chemical Engineering. 2016; 4:2765-73.
[25] Andrigo P, Bagatin R, Pagani G.. Catalysis Today. 1999; 52:197-221.
[26] Eigenberger G, Ruppel W. Ullmann's Encyclopedia of Industrial Chemistry: Wiley-VCH Verlag GmbH & Co. KGaA; 2000.
[27] Beltramini JN, Fang R. Studies in Surface Science and Catalysis. 1996; 100:465-75.
[28] Balaban A, Kier L, Joshi N. MATCH Commun Math Comput Chem. 1992; 28:13-27.
[29] Hasan M, Mohamed AM, Al-Kandari H. Molecular Catalysis. 2018;452:1-10
[30] Rostamizadeh M, Jalali H, Naeimzadeh F, Gharibian S. Physical Chemistry Research. 2019; 7:37-52.
[31] Gorzin F, Yaripour F. Research on Chemical Intermediates. 2019; 45:261-85.
[32] Kostyniuk A, Key D, Mdleleni M. Journal of Saudi Chemical Society. 2019; 23:612-26.
[33] Uykun Mangaloğlu D, Baranak M, Ataç Ö, Atakül H. Journal of Industrial and Engineering Chemistry. 2018; 66:298-310.
[34] Cheng K, Zhang L, Kang J, Peng X, Zhang Q, Wang Y. Chemistry – A European Journal. 2015; 21:1928-37.
[35] Moon S, Chae H-J, Park MB. Applied Catalysis A: General. 2018; 553:15-23.
[36] Nabgan W, Abdullah TAT, Mat R, Nabgan B, Jalil AA, Firmansyah L, et al. International Journal of Hydrogen Energy. 2017; 42:8975-85.
[37] Nabgan W, Tuan Abdullah TA, Mat R, Nabgan B, Triwahyono S, Ripin A. Applied Catalysis A: General. 2016; 527:161-70.
[38] Van der Borght K, Galvita VV, Marin GB. Applied Catalysis A: General. 2015; 492:117-26.
[39] Denardin F, Perez-Lopez OW. Fuel. 2019; 236:1293-300.
[40] Zhang X, Cheng D-g, Chen F, Zhan X. Chemical Engineering Science. 2017; 168:352-9
[41] Xu S, Zhang X, Cheng D-g, Chen F, Ren X. Frontiers of Chemical Science and Engineering. 2018; 12:780-9.
[42] Asaftei IV, Lungu NC, Sandu IG, Spac AF, Ignat M. Revista De Chimie. 2018; 69:2420-4.