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Research paper

Aromatization of Heavy Naphtha using Modified Zeolite Supported Catalyst

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Abstract

Growing population has increased the dependency toward sustainable energy sources. Research industries have groomed their facilities to find alternative sources of energy. Heavy naphtha can be converted to value added fuel such as gasoline via catalytic conversion. Modified zeolite supported catalyst was employed for aromatization of heavy naphtha to gasoline like liquid. The catalyst was impregnated with 3 wt.% Fe via wet impregnation method. The catalysts prepared were send for characterization using BET, FESEM-EDX and TPD. Catalytic activity was performed at 430-480 °C, LHSV 1 hr^{-1} and 14 bar in a fixed-bed continuous reactor. The result revealed that the by adding Fe onto the zeolite supported catalyst provides slight improvement of yield.

Keywords: *Aromatization; catalytic conversion; gasoline; heavy naphtha; modified zeolite*.

1. Introduction

Urbanization of the world has put the demand on the supply of energy at the stake to support the growth of the world population. World consumption of energy has forecast to expand from 2.5 Tb/d to 3.7 Tb/d however, the supply measured by the energy world bank currently at 31 Mb/d in 2012 to 2040 period [1]. Due to this current state, rapid researches have been conducted to find the solution. Sustainable energy sources have been one of the popular research niches nowadays. Many researches have rapidly innovated formulation and operational processes for alternative energy source and supply.

Malaysia is blessed by abundancy of potential alternative energy sources to be explored and utilized. Heavy naphtha has been extensively used for producing high octane gasoline and it is also being used as heavy oil thinner, light fluid additive and metal cleaner solvent. Naphtha is a petroleum refineries intermediate product. It is a liquid intermediate between the light gases in the crude oil and the heavier liquid kerosene. Upgrading heavy naphtha to gasoline involving the reforming process which catalytic conversion of low octane naphtha to higher octane gasoline supported by zeolite catalyst [1-3].

Bifunctional catalyst incorporated by a metal function and has an acidity function is a widely used [4]. The competency of zeolite in cracking oil product has make it one of the preferred catalysts to start off. Several previous study used bifunctional zeolite-based catalyst for aromatization process via catalytic cracking of hydrocarbons [5, 6]. Cracking rate of olefins will produced more isoparaffins instead of aromatics when the silica alumina ratio is higher, resulting higher yield and RON of gasoline produced [6-8].

Besides that, the aromatization of heavy naphtha also can promote the yield of product by modification of zeolite-based catalyst via metal impregnation [6-8]. All transition metals have ability to promote more carbon oxide and inhibit water production by rejection of oxygen in the system, thus facilitate hydrogen to incorporate into the hydrocarbon [8].

In this present study we evaluated the performance of tailored zeolite-based catalyst compare to the blank zeolite-based catalyst in naphtha reforming reactions at 430-480 °C, LHSV 1 hr^{-1} and 14 bar to produce a better gasoline.

2. Methodology

2.1. Material

The commercial blank zeolite catalyst is brought from ACS Materials, LLC was chosen to serve as support catalyst. The metal oxide used was iron (III) nitrate nonahydrate brought from Merck Sdn. Bhd and the feedstock obtained and purchased from Petronas Penapisan (Melaka) Sdn Bhd.

The blank zeolite catalyst is impregnated with 3 wt.% iron metal following the impregnation work done by Anita & Farooq [9]. The catalysts are prepared using incipient wetness impregnation method where a required amount of iron (III) nitrate is first dissolved in sufficient amount of deionized water. The soaked catalyst was left for 24 h at room temperature in shaker bath and later dried at 120 °C for 24 h and calcined at 550 °C for 6 h.

2.2. Catalyst Characterization

The catalysts produced were characterised using variable pressure field emission scanning electron microscopy – energy dispersive X-ray (Ziess Supra 55VP) was used to investigate the morphology of the catalyst.

N_2 adsorption-desorption isotherm used to determine the surface properties of the catalysts using Micromeritics ASAP 2020 at 196 °C and the samples were degassed at 250 °C for 4 h. Surface area analysis was determined by the method of Brunauer–Emmett–Teller (BET) while the pore volume was calculated at a relative pressure P/Po = 0.98 and the pore size and pore volume were determined from desorption isotherms via Barrett-Joyner-Halenda (BJH) analysis method

The acidity of catalysts was investigated by temperature programmed desorption of ammonia (TPD) using TPDRO1100 (Thermo Scientific). The TPD was carried out in a micro reactor made of pyrex with 0.2 g of the catalyst at atmospheric pressure. The adsorption of ammonia was carried out at 120 °C for 30 min and heat up to 600 °C for another 30 min with a heating rate 10 °C/min.

2.3. Catalyst Screening

The impregnated catalyst and blank were screening for the performance of catalyst for upgrading naphtha to gasoline. The screening activities were carried out by using lab scale continuous fed batch reactor which operational setting varied at 430 to 480 °C under 14 bar with LHSV of 1 h^{-1}. 100 ml fresh impregnated and blank catalyst are fed into the catalyst gasket and heavy naphtha fed at 75 ml/h flowrate. Collected gasoline product is analysed using FID gas chromatography to evaluate the gasoline yield and RON.

3. Result & Discussion

Fig. 1 shows the morphology of the catalysts produced. FESEM-EDX allow us to study the surface morphology and elemental composition of the catalyst. Both catalysts seem to have an irregular shape and porous zeolite structure. There are also a present of deposited particles at Fig 1(b) due to the iron impregnation which measured to be around 25 – 50 nm.

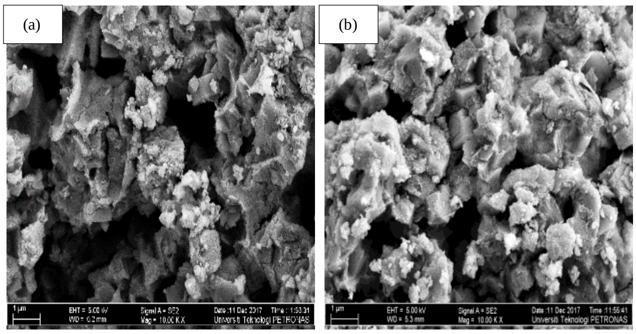

Fig.1: FESEM images of catalyst prepared under 10kX magnification for (a) zeolite-based support catalyst and (b) 3 wt.%Fe/ zeolite-based support catalyst.

Surface area, pore size and pore volume of the catalysts were tabulated in Table 1 based on the result obtain from Brunauer-Emmett-Teller (BET) equation. The general trend was observed where, there is decline in a surface area with impregnation of Fe in zeolite support. The reduce of surface is explained by binding of iron particle onto the framework of the support catalyst and occupied the pore of the catalyst.

There is no significant different on the results obtained since we only impregnated with low iron concentration of 3 wt.%. The activity of the catalyst will be affected by the increase in pore size and pore volume as the Fe will enhance the active sites on the surface of zeolite support.

Table 1: The surface area, pore size and pore volume of blank and 3 wt.% Fe catalyst.

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^2/g)	Pore Size (nm)
Blank	313.02	0.23	5.08
3% Fe	312.38	0.24	5.25

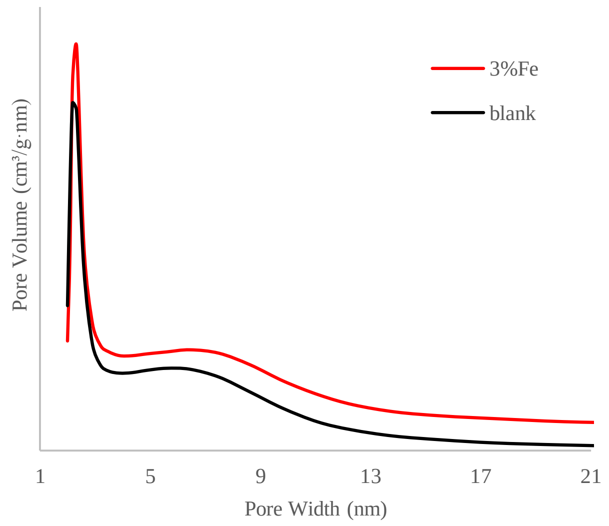

Fig. 2: Pore distribution of blank and impregnated catalyst.

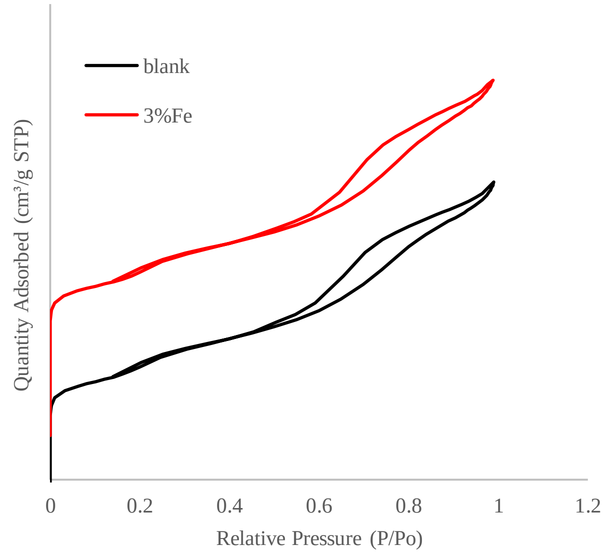

Fig. 3: The nitrogen adsorption (cm^3/g) for specific surface area of blank and impregnated catalyst.

Fig. 2 shows pore size distribution plot for both of catalysts. The catalysts show the attribute of small mesopores with an intense peak found in between 2 and 3 nm. Besides that, Fig. 3 shows isotherm plot for the catalyst where it is representing the type IV isotherm with H2 hysteresis loop.

The isotherm type features the catalyst having porous and ordered structure. However, the hysteresis loop in impregnated catalyst is broader due to the blocking of iron particles in the support catalyst. The impregnating of metal to the support catalyst leads to slight pores blockage due to metal bind at the framework of support catalyst and consequently supporting the reduction of the catalyst surface area.

Acidity analysis was carried out using temperature programmed desorption of ammonia (TPD) pictured in Fig. 4 has showed that the blank catalyst has one strong acid site at 407 °C while the impregnated catalyst has two acid sites at 126 °C representing weak acid site and 474 °C for strong acid site. Based on study done by Shirazi et. al, and Santa et. al, they classified the weak acid site and strong acid as low temperature peak at 200-300 °C and high temperature peak at 370-550 °C respectively [10, 11].

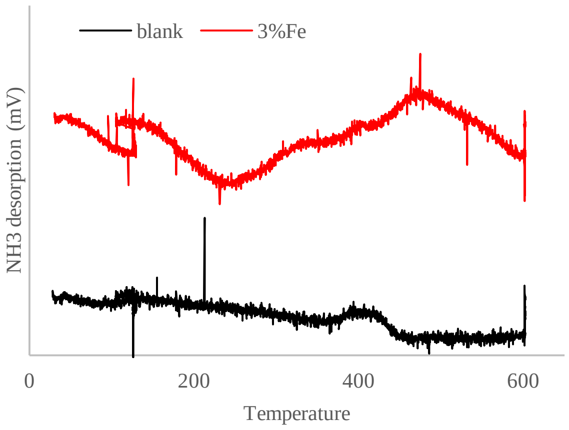

Fig. 4: NH_3 – TPD analysis for blank and impregnated catalyst

The XRD pattern of both catalysts is shown in Fig. 5. The intense peak for the present of blank can be seen at 2θ = 8°, 8.85°, 9.16°, 23.11°, and 23.98° (ICSD 98-006-7667) but after the catalyst is impregnated with 3 wt.% iron there are new peaks form which can be observed at 2θ = 24.56°, 36.24°, and 55.16° (ICSD 98-009-8088) due to the impregnated Fe also have their crystallite structure and contributed to the overall crystallite size of produced catalyst. The crystallite sizes of the catalysts were calculated by Debye Scherr Equation where represented by Table 2.

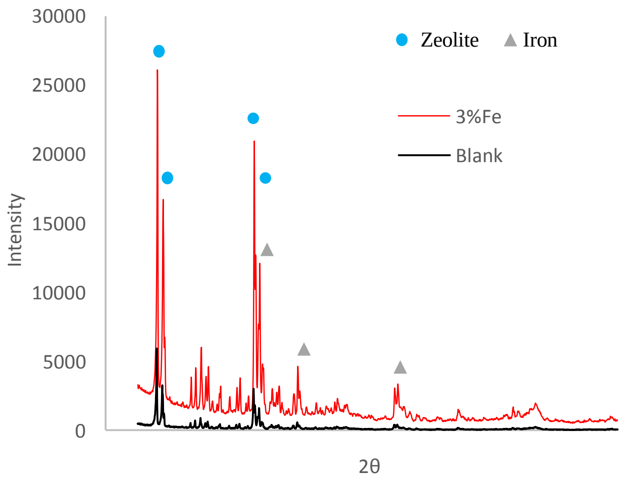

Fig. 5: XRD patterns of blank and impregnated catalyst.

Table 2: Crystallite size of the catalysts using Scherr Calculator.

Catalyst	**B obs. [°2θ]**	**B std. [°2θ]**	**Peak pos. [°2θ]**	**B struct. [°2θ]**	**Crystallite size [Å]**
Blank	0.1405	0.025	23.108	0.115	705
3% Fe	0.148	0.0336	22.936	0.114	713

Yield and RON are the significant points for indication of quality degree of gasoline produced. Yield measure the successful of catalytic conversion as it increases the profitable of the process while, RON evaluate the quality of good performance gasoline. The trend of relationship of yield and RON is reciprocal as there is an increase in yield, RON will be reduced. Catalytic performance in the gasoline production fed by heavy naphtha reforming via zeolite-based catalysts is shown by Fig.4.

Fig. 6 showed the gasoline yield and RON obtained at operational temperature of 430, 450 and 480 °C. The yield 3 wt.% Fe is higher compared to blank catalyst. From the Fig. 6, the highest yield recorded is 58.7 wt.% at 450 °C however, the highest RON recorded at 101.4 at 480 °C. As the working temperature increased the yield produce by using blank catalyst is reduced, even though in the impregnated catalyst, it showed that the increase in yield then it reduced. This could be explained due to the present of two acid site in 3 wt.% Fe has maximized and selective in promoting dehydrogenation and hydrogenation of hydrocarbons in the process, producing more gasoline yield [4, 12].

The RON of gasoline produce shows the increase trend across the operation temperature increase. However, the RON recorded almost the same reading at 450 °C. The higher RON recorder in impregnated catalyst is because the acid function of the impregnated catalyst encourage the isomerization and cyclization which indication to the successful of aromatization process [4].

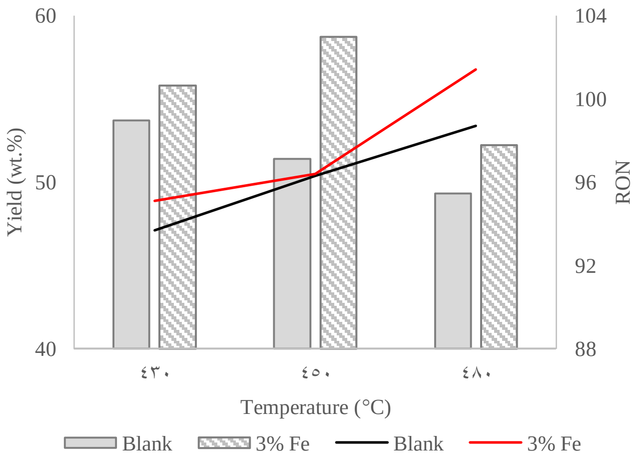

Fig. 6: Performance of catalysts at different operational temperature

4. Conclusion

In conclusion, the impregnation of metal oxide can improve the yield of gasoline produced. The temperature programmed desorption shows that by adding metal the acidity of the support catalyst can be tailored and eventually will promote aromatization of the heavy naphtha. The surface area of the impregnated catalyst is slightly lowered while the pore size and pore volume is little bit higher. 3 wt.% Fe impregnated zeolite-based catalyst more effective than the blank catalyst.

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