



CATALYTIC CRACKING OF PALM OIL TO GASOLINE OVER PRETREATED Cu-ZSM-5

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Abstract. The catalytic conversion of palm oil to gasoline using hydrogen pretreatment on H-ZSM-5 with different copper loadings is discussed in this paper. The Cu-ZSM-5 catalysts were prepared using incipient wetness impregnation technique. The crystallinity, acidity and surface area were examined by X-ray diffraction (XRD), Pyridine adsorption - infra red spectroscopy (Py-IR), and Nitrogen Adsorption (NA). The results revealed that the crystallinity, acidity, and surface area of catalyst decreased with increasing copper loading. The catalytic testing was carried out in a fixed bed reactor at atmospheric pressure with hydrogen flow rate of 1 L/h for an hour for hydrogen pretreatment on catalysts. Then, the cracking process was continued at 500°C and weight hourly space velocity (WHSV) of 2.5 h⁻¹ for four hours. Loading copper on the ZSM-5 catalyst showed adverse effects on catalytic activity. The highest gasoline component was aromatics, which was about 11.45 wt% (all consisted of alkyl benzene) followed by 10.53 wt% of naphthenes and 4.06 wt% of isoparaffins for 6 wt% Cu-ZSM-5. Gas as side product consisted mainly of C₃ compounds with 53.30 mol% followed by 29.84 mol% of C₄ and 0.62 mol% of C₅ compounds.

Keywords: Zeolite, H-ZSM-5, Cu-ZSM-5, hydrogen pretreatment, cracking

Abstrak. Pemecahan bermangkin minyak sawit kepada gasolin menggunakan rawatan mangkin zeolit H-ZSM-5 yang dimasukkan dengan pelbagai kepekatan kuprum dibincangkan dalam hasil kerja ini. Cu-ZSM-5 disediakan melalui teknik *incipient wetness impregnation*. Kehabluran, keasidan dan luas permukaan mangkin dikaji secara pembelauan sinar X-ray (XRD), spektroskopi infra merah menggunakan penjerapan piridin (Py-IR), dan penjerapan nitrogen (NA). Hasil kajian mendapati bahawa kehabluran, keasidan dan luas permukaan Cu-ZSM-5 berkurang dengan penambahan kuprum. Aktiviti mangkin telah diuji menggunakan reaktor mangkin terpadat pada tekanan atmosfera dan kadar alir hidrogen 1 L/jam selama sejam untuk mengaktifkan mangkin secara rawatan hidrogen. Seterusnya, proses pemecahan mangkin diteruskan pada 500°C dan kelajuan berat per jam (WHSV) sebanyak 2.5 jam⁻¹ selama empat jam. Peningkatan kuantiti kuprum dalam mangkin memperlihatkan kesan yang negatif ke atas aktiviti mangkin. Komposisi gasolin tertinggi adalah aromatik, iaitu sebanyak 11.45% (terdiri daripada alkil benzena sahaja), diikuti pula oleh 10.53% naftena dan 4.06% isoparafina dengan 6 peratus berat Cu-ZSM-5. Hasil sampingan yang terdiri daripada gas pula mempunyai 53.30 %mol gas C₃, 29.84 %mol gas C₄, dan 0.62 %mol gas C₅.

Kata kunci: Zeolite, H-ZSM-5, Cu-ZSM-5, rawatan hidrogen, pemecahan

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1.0 INTRODUCTION

Zeolites have been creating a growing interest because of their application as catalysts in industries. The conversion of hydrocarbons to valuable chemicals such as gasoline and aromatic compounds in catalytic processes has been investigated and progressively improved. Currently, some researchers are concentrating on developing alternative and renewable sources of an environmental friendly liquid fuel.

The excellent shape-selectivity of zeolite catalysts that governs the movement of molecules within the pore structure has attracted researchers to investigate its application in converting vegetable oil feedstock into chemicals and fuel products. The medium pore zeolite, ZSM-5 with a pore diameter of 4.5-6.0 Å is a crystalline shape-selective zeolite [1-2] that has been widely investigated in catalytic conversion of plant oil to fuels and chemicals [3-8].

Malaysia is the largest producer of palm oil in the world. In 2004, the palm oil production was about 14 000 million tons [9]. Palm oil is enriched with triglycerides that can be converted to clean premium fuels and chemicals. Catalytic cracking using H-ZSM-5, gives high gasoline yield with high aromatic contents [10]. By passing palm oil vapor through H-ZSM-5, high gasoline selectivity enriched with paraffin and olefin compounds can be obtained [11]. However, the gas yield was high whereas more liquid products are desired.

The effect of hydrogen pretreatment on the catalytic activity of zirconium oxide modified with sulfate ion and platinum ($\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$) for cumene cracking was studied by Shishido and Hattori [12]. They found that pretreatment of the catalyst with hydrogen gave high activity for cumene cracking. Bernas *et al.* [13] studied the isomerization of linoleic acid for Ni/H-MCM-41 and Ru/C, and found that isomerization was dramatically enhanced with hydrogen activation. Nevertheless, further explanation on this phenomenon was not discussed. Cu/SiO₂ activated with hydrogen for hydrogenation of rapeseed oil showed good activity and excellent selectivity towards formation of high oleic derivatives [14].

Activity and selectivity of the catalysts are governed by several factors, such as their acidity, surface area, and pore size. The objective of this research is to investigate the effect of acidity, surface area, pore size, and metal loading of hydrogen pretreated Cu-ZSM-5 for palm oil cracking.

2.0 EXPERIMENTAL

2.1 Materials

The raw material was a refined, bleached, and deodorized (RBD) commercial grade palm oil "Vesawit" that was purchased from the local market. The chemicals used in this research were hydrogen and nitrogen gas with 99.99% of purity from SIG company; while the catalyst used was NH₄-ZSM-5 (Si/Al=30) with 99.98% of purity

from Zeolyst International and code no. of CBV 3024 E. The copper (II) nitrate-3-hydrate employed was from Riedel de Haen with a purity of 99%.

2.2 Catalyst Preparation

H-ZSM-5 was prepared by drying the ammonium forms of the zeolite overnight and was subsequently calcined at 550°C for five hours. Copper was impregnated on the H-ZSM-5 by the incipient wetness technique. An aqueous solution containing copper ammonium nitrate salt with a suitable volume of water was added into H-ZSM-5 and stirred for 15 minutes. The paste was then dried overnight, recalcined at 550°C for four hours, and finally screened to about 35 mesh (0.5 mm diameter). The schematic diagram of the preparation method is shown in Figure 1.

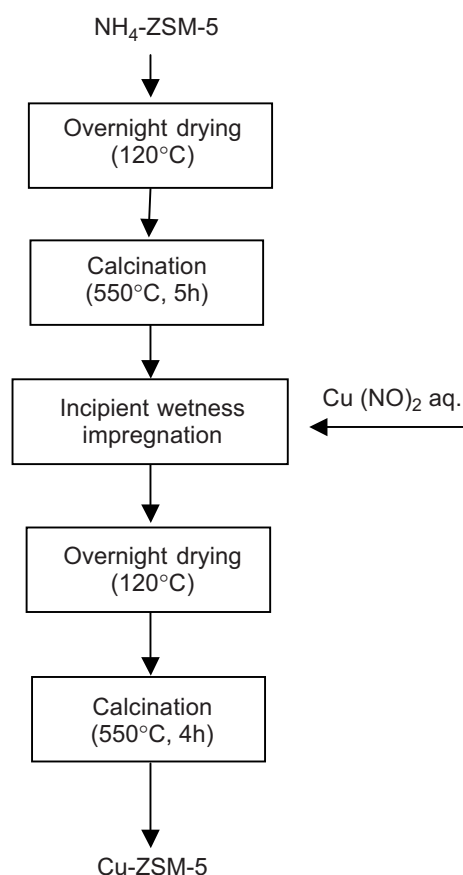


Figure 1 Schematic diagram showing the preparation procedures of Cu-ZSM-5

2.3 Catalyst Characterization

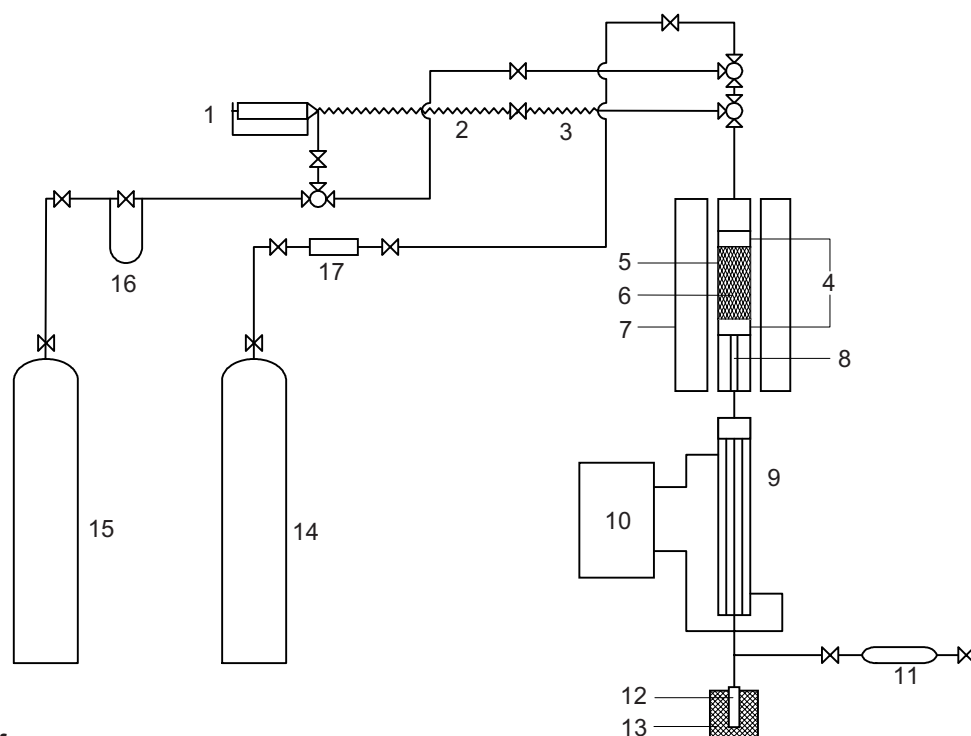
The calcined and hydrotreated catalysts were characterized with XRD, Py-IR, and NA. XRD measurements were performed using a Philips 1840 with $\text{CuK}\alpha$ radiation with $\lambda = 1.54056 \text{ \AA}$ at 40 kV and 30 mA in the 2θ range of 5° to 50° at a scanning speed of 0.05° per second, with a vertical goniometer at room temperature (20°C). The sample was placed on a mountain sample holder, and then grounded before mounting on a glass slide. Py-IR was used to identify types of acid sites in the catalysts. About 10 mg of samples were pressed at 5 ton for a minute to get a 13 mm die. The samples were introduced in the infrared cell with calcium fluoride, CaF_2 windows and were heated at 400°C under vacuum condition for four hours. The samples were then cooled to room temperature before pyridine was adsorbed for a minute, which was then desorbed at 150°C for an hour under vacuum. The infrared spectra was collected at room temperature using a Shimadzu 2000 FTIR spectrometer with 2 cm^{-1} resolution. The infrared spectra was monitored at room temperature in the wave number range of $1400 - 1700 \text{ cm}^{-1}$. Adsorption and desorption of nitrogen were performed using a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2010 at 120°C under vacuum conditions for six hours prior to the adsorption-desorption process. The data obtained included the BET surface area, pore size, micropores volume, and micropores area. The type of pores was determined by comparing the sample's isotherm with the standard isotherm from the literature [15].

2.4 Experimental and Analytical Procedures

All experiments were conducted in a fixed bed reactor at atmospheric pressure, as shown schematically in Figure 2 and carried out using the scheme shown in Figure 3.

The reactor was loaded with 1 g of catalyst that was calcined and screened to 35 mesh particle size. It was plugged by 0.2 g of glass wool, which was supported by a pin over a stainless steel pipe. The reactor placed in a vertical furnace and was preheated at 450°C for an hour, flushed with N_2 (100 ml/min) for 15 minutes and fed with H_2 at 1 L/h for an hour for activation of catalyst. The reactor was then heated to the desired temperature. Palm oil was injected by a syringe pump with weight hourly space velocity (WHSV) of 2.5 h^{-1} . It was preheated at 120°C and 250°C respectively before entering the reactor. The experiment was conducted for four hours with the N_2 flowing at 1 L/h. Furthermore, the syringe pump was turned off, while the N_2 was flowed for another hour to continue the reaction of the excess palm oil in the rig. The reactor was then flushed with N_2 only for 30 minutes at 30 ml/min to remove the remaining products.

The products exiting the reactor were cooled to 40°C with a condenser system to prevent solidification of the residual oil. It was then separated into liquid and gas fractions. The liquid fraction was collected in a liquid collecting flask while the gas



References

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| 1. Syringe pump | 7. Vertical furnace | 13. Ice trap |
| 2. Heating coil 1 | 8. Supporting rod with pin | 14. Hydrogen gas tank |
| 3. Heating coil 2 | 9. Condenser | 15. Nitrogen gas tank |
| 4. Glass wool | 10. Water bath | 16. Manometer |
| 5. Reactor | 11. Gas sampling port | 17. Flowmeter |
| 6. Catalyst | 12. Liquid collector | |

Figure 2 The experimental rig for palm oil cracking and *in situ* hydrogen pretreatment catalyst

fraction was collected in a gas sampling port. The aqueous phase was separated from the condensed liquid product using a syringe. It consisted mainly of water and some organic components that are soluble in water. Among the components that are soluble include alcohols and acid carboxylic chains. The organic liquid product (OLP) was then distilled in a micro distillation unit at atmospheric pressure and at gasoline boiling point range of 40-170°C for an hour and heavy liquid product (which contains kerosene, jet oil and diesel) boiling point range from 171 to 250°C for another hour. The products remaining after the distillation were termed as residue.

The gaseous products (C_1 - C_4 , CO and CO_2) were analyzed with a Hewlett Packard Agilent 6890N GC system equipped with a thermal conductivity detector (TCD) and 4 series column (UCW 982, DC 200, Porapak Q and Molecular Sieve 13A). The gasoline product was analyzed with a gas chromatograph (Perkin Elmer, Auto System) using capillary column (100 m long \times 0.25 mm width, model no: SGE 100QC2.5 BPI PONA) with a flame ionization detector (FID).

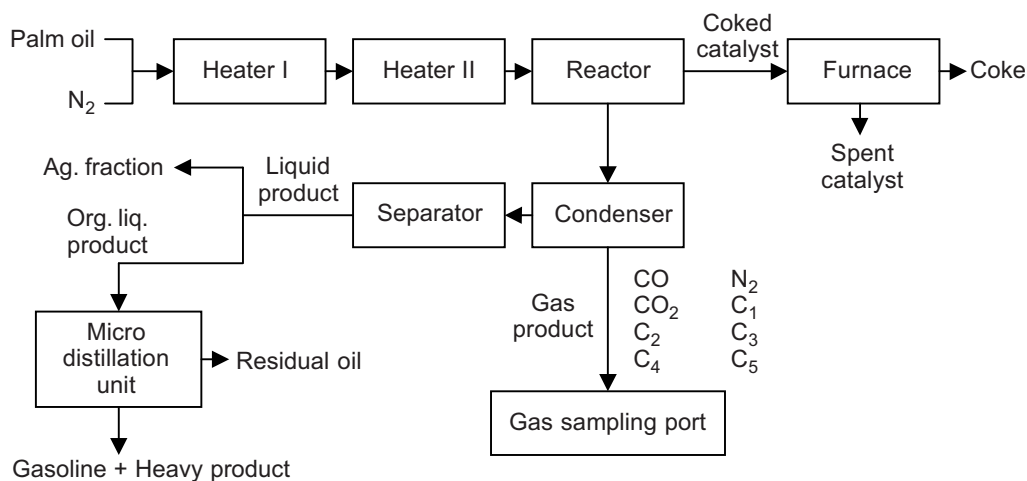


Figure 3 Schematic diagram of the catalytic cracking process

A substantial amount of coke was accumulated on the catalyst after each experiment. The spent catalyst was weighed using a microbalance. It was then heated to 500°C in a furnace for five hours. The spent catalyst was then re-weighed. The difference in the weight of the spent catalyst before and after heating is termed as the weight of coke that was burned off.

3.0 RESULTS AND DISCUSSION

3.1 Catalyst Characterization

The XRD patterns of Cu-ZSM-5 at various percentages of copper loading are shown in Figure 4.

The entire Cu-ZSM-5 patterns (Figure 4(b) - 4(e)) had two high intensity diffractograms at $2\theta = 7.9$ and 8.9° and three high intensity diffractograms at $2\theta = 23 - 25^\circ$. These patterns were similar to the parent H-ZSM-5 pattern (Figure 4(a)), which is similar to simulated ZSM-5 pattern [16, 17]. This phenomenon indicates that the structure crystal of Cu-ZSM-5 did not change drastically. The peaks at $2\theta = 35.5^\circ$ and 38.7° correspond to the (002) and (111) planes of divalent copper oxide (CuO) (JCPDS Pattern No. 2-1040). CuO peak appeared for 6 wt% and 8 wt% Cu-ZSM-5. Increasing the copper loading on H-ZSM-5 increased the intensity for CuO peak, thus indicating the copper did not enter the zeolite's framework [18].

The diffractogram of parent H-ZSM-5, 6 wt% Cu-ZSM-5 and pretreated 6 wt% Cu-ZSM-5 are shown in Figure 5.

After hydrogen pretreatment, the CuO peak in Cu-ZSM-5 disappeared. Another peak at $2\theta = 43.3^\circ$ appeared. This peak corresponds to the (111) plane of metallic copper species (JCPDS Pattern No. 4-836) [18, 19].

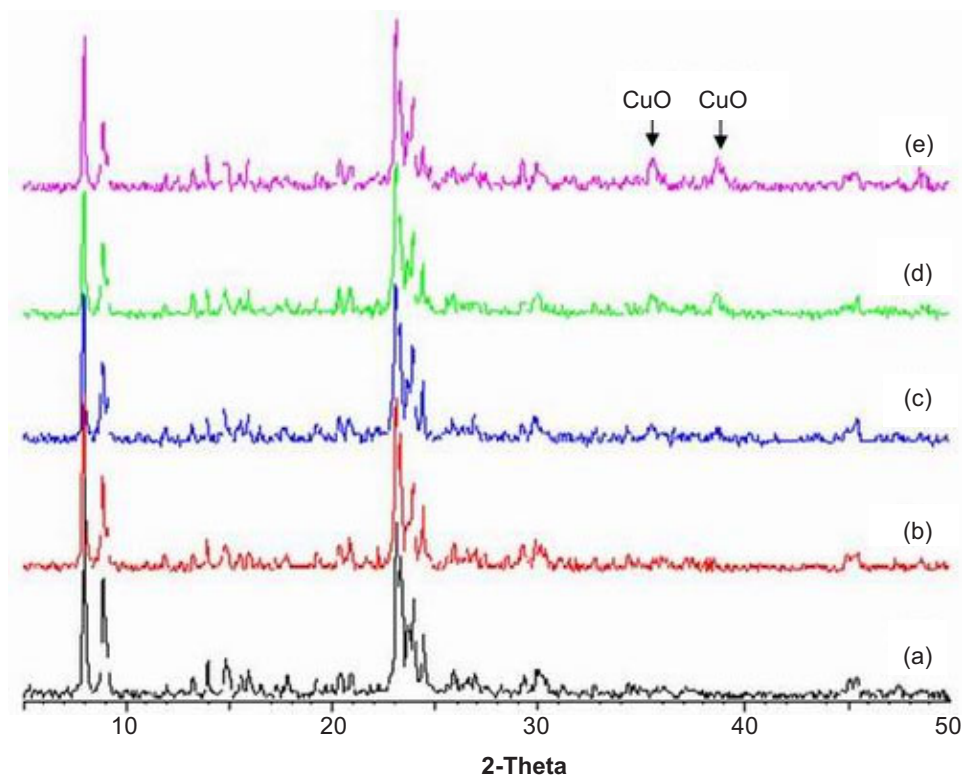


Figure 4 XRD pattern of (a) H-ZSM-5, (b) 2 wt% Cu-ZSM-5, (c) 4 wt% Cu-ZSM-5, (d) 6 wt% Cu-ZSM-5, and (e) 8 wt% Cu-ZSM-5

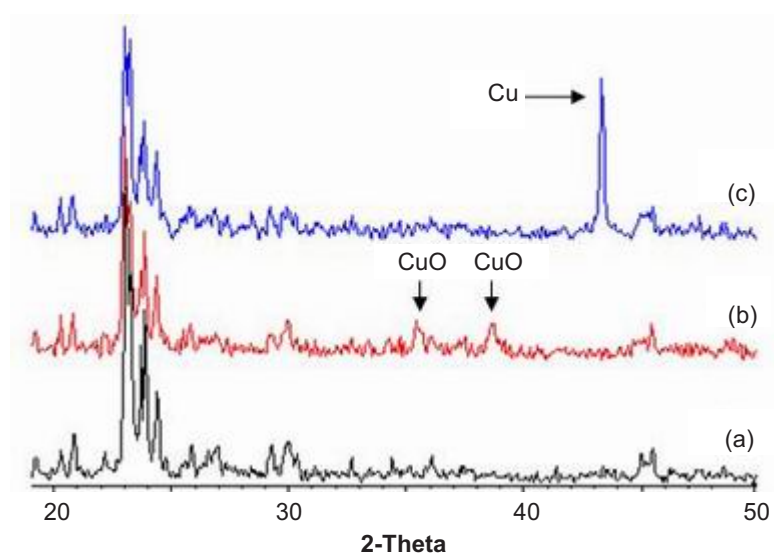


Figure 5 XRD pattern of (a) H-ZSM-5, (b) Cu-ZSM-5, and (c) pretreated Cu-ZSM-5

The Py-IR-spectrum of H-ZSM-5, Cu-ZSM-5, and pretreated Cu-ZSM-5 are shown in Figure 6. The IR of coordinated pyridinium frequencies at 150°C corresponds to the Brönsted and Lewis acidities, respectively [20]. The wavenumber of Brönsted acidity for H-ZSM-5 are 1545.8 cm⁻¹ and 1635.5 cm⁻¹. A slight shift to 1546.8 cm⁻¹ and 1648.1 cm⁻¹ for Cu-ZSM-5 and to 1547.8 cm⁻¹ and 1650.0 cm⁻¹ for pretreated Cu-ZSM-5 was observed. The Lewis acidity for H-ZSM-5 is at 1453.3 cm⁻¹ and 1622.0 cm⁻¹, while for Cu-ZSM-5 and pretreated Cu-ZSM-5, there was a slight shift to 1451.3 cm⁻¹ and 1611.4 cm⁻¹. The mixed Brönsted and Lewis acid sites of the three catalysts were shown at the same frequency of 1489.9 cm⁻¹. The results indicate that H-ZSM-5, Cu-ZSM-5, and hydrotreated Cu-ZSM-5 have both the Brönsted and Lewis acid sites.

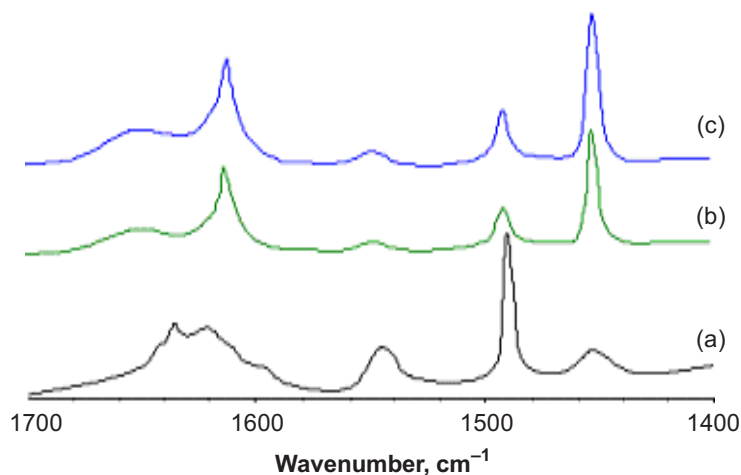


Figure 6 Pyridine absorption infra red (Py-IR) spectrum of (a) H-ZSM-5, (b) 6 wt% Cu-ZSM-5, and (c) pretreated 6 wt% Cu-ZSM-5

The physicochemical properties of H-ZSM-5, Cu-ZSM-5, and pretreated Cu-ZSM-5 are tabulated in Table 1.

Table 1 Physicochemical properties of H-ZSM-5, Cu-ZSM, and pretreated Cu-ZSM-5

Catalyst	Crystallinity	BET surface area (m ² /g)	BET pore size (Å)	Brönsted acidity (μ mol / g)	Lewis acidity (μ mol / g)
H-ZSM-5	100	333.32	25.11	134	61
Cu-ZSM-5	96	295.83	26.58	68	363
Pretreated Cu-ZSM-5	85	289.83	26.99	81	328

The crystallinity of the zeolites from their XRD diffractograms (as shown in Figure 5) can be calculated [21]. The crystallinities of H-ZSM-5, 6 wt% Cu-ZSM-5, and pretreated 6 wt% Cu-ZSM-5 were 100%, 96%, and 85% respectively. The Brönsted and Lewis acidity can be calculated following Huges and White's method [20]. The physicochemical properties of Cu-ZSM-5 were different compared to H-ZSM-5 in terms of their Brönsted and Lewis acidity. The Brönsted acidity of Cu-ZSM-5 decreased drastically whereas the Lewis acidity increased. This is probably due to increase amount of non-framework aluminium or hydrogen cation that was replaced by the metal ion (Cu^{2+}). The decrease in H^+ ions decreases the Brönsted acidity. The Lewis acidity, meanwhile, was created by Cu^{2+} ions [18, 22]. The surface area of H-ZSM-5 was larger than Cu-ZSM-5 and the pore size of Cu-ZSM-5 was bigger than H-ZSM-5. The decrement in the surface area indicates that CuO covers the surface of H-ZSM-5 zeolite. The increment in the pore size of Cu-ZSM-5 might be due to copper species that are attached in the micropores of modified ZSM-5 [23].

The effect of hydrogen pretreatment on Cu-ZSM-5 towards the surface area, pore size, Brönsted and Lewis acidity were negligible. A small increment of Brönsted acidity after hydrogen pretreatment of Cu-ZSM-5 might be due to dissociated hydrogen (H^+ ion) associated with zeolite AlO_4 sites. This phenomenon could be interpreted by the presence of hydrogen spillover effect [24]. Consequently, the Lewis acidity decreased because H^+ ion reacted with oxygen atom of non-framework zeolite. Crystallinity of pretreated Cu-ZSM-5 decreased too, which might be related to the transformation of copper oxide to copper species.

3.2 Catalytic Activity

The performance of various pretreated Cu-ZSM-5 with a particle size of about 35 mesh was evaluated based on the selectivity of gasoline. The conversion, gasoline selectivity and yield are defined as follow:

$$\text{Conversion (wt\%)} = \frac{F - R}{F} \times 100\% \quad (1)$$

$$\text{Selectivity (wt\%)} = \frac{P}{F - R} \times 100\% \quad (2)$$

$$\text{Yield (wt\%)} = \frac{P}{F} \times 100\% \quad (3)$$

where F is the palm oil feed weight (g), R is the residual oil weight (g), and P is the product weight (gasoline, heavy product, residue product, gas and coke).

Palm oil conversion decreased with increasing copper loading on H-ZSM-5, as shown in Figure 7. At 8 wt% Cu-ZSM-5 loading, the conversion fell nearly 20 to 76.25 wt%. The conversion of palm oil cracking using pretreated H-ZSM-5 is much

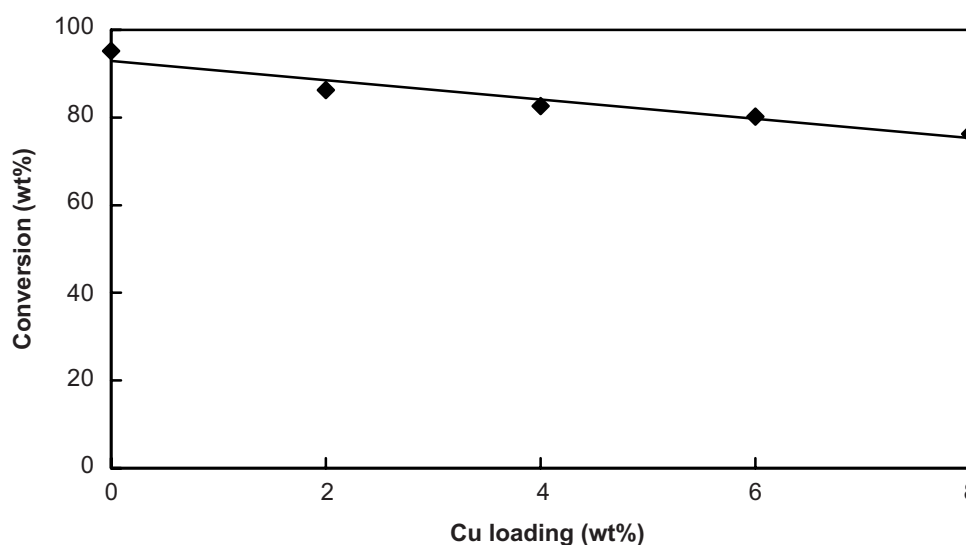


Figure 7 The conversion of pretreated Cu-ZSM-5 at various weight percent of copper. Operating conditions: 500°C, WHSV = 2.5 h⁻¹ and F_{H2} = 1 L/h for an hour

higher compared to pretreated Cu-ZSM-5. It is related to their surface area, Brönsted acidity, and crystallinity. The surface area of parent H-ZSM-5 was larger than copper loaded ZSM-5. Large surface area has more contact space for heterogeneous catalytic reaction [25]. Hence the conversion over H-ZSM-5 was higher than Cu-ZSM-5. In addition, the Brönsted acidity also plays an important role in hydrocarbon cracking [23]. Consequently, the cracking activity of Cu-ZSM-5 was reduced due to lower concentration of Brönsted acid sites.

Hydrogen spillover is a term used to describe migration of hydrogen atoms from a metal. This metal is active for dissociative adsorption of hydrogen to an oxide or carbon surface, which by itself is inactive for dissociative hydrogen adsorption. The acid sites are acceptor for spilt over hydrogen, activated by metal phase. The number of spilt over acceptor sites is important for zeolites and activated carbon for hydrogen spillover effect to occur [26]. Hydrogen spillover phenomenon resulted in deactivation of catalyst for hydroisomerization of *n*-pentane [27]. Two factors are probably determining the decrement of catalytic activity (conversion and gasoline selectivity) of palm oil cracking over hydrogen pretreated Cu-ZSM-5. One of them was the reduction of Brönsted acidity as mentioned above and the other could be the hydrogen spill over effect. Hydrogen can be dissociated on metal sites, spills over CuO and then reduce them to copper species [27, 28].

Yield of products at various Cu-ZSM-5 catalysts are shown in Figure 8. OLP yield increased with increasing copper loading. The highest OLP obtained was 46.96 wt% with 8 wt% Cu-ZSM-5. Yield of gas and coke did not differ much with different copper loading. The gas product consisted mainly of C₃–C₄.

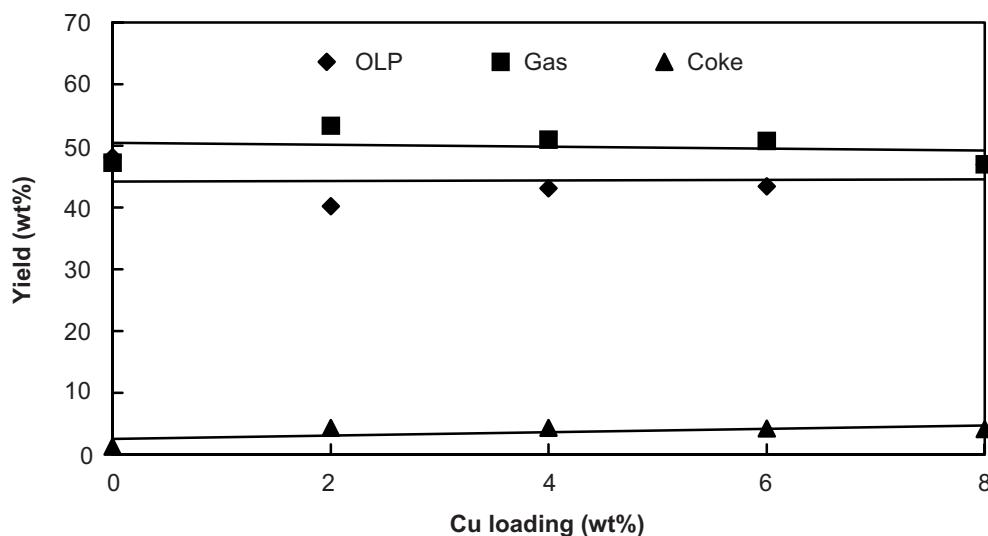


Figure 8 The yield product of pretreated Cu-ZSM-5 at various copper loading. Operating conditions: 500°C, WHSV = 2.5 h⁻¹ and F_{H2} = 1 L/h for an hour

Figure 9 shows the selectivity of different products in the cracking process. Selectivity towards gasoline declined with more copper loading, while selectivity towards residue rose significantly with increasing copper loading. Selectivity of heavy products did not change with increasing copper loading.

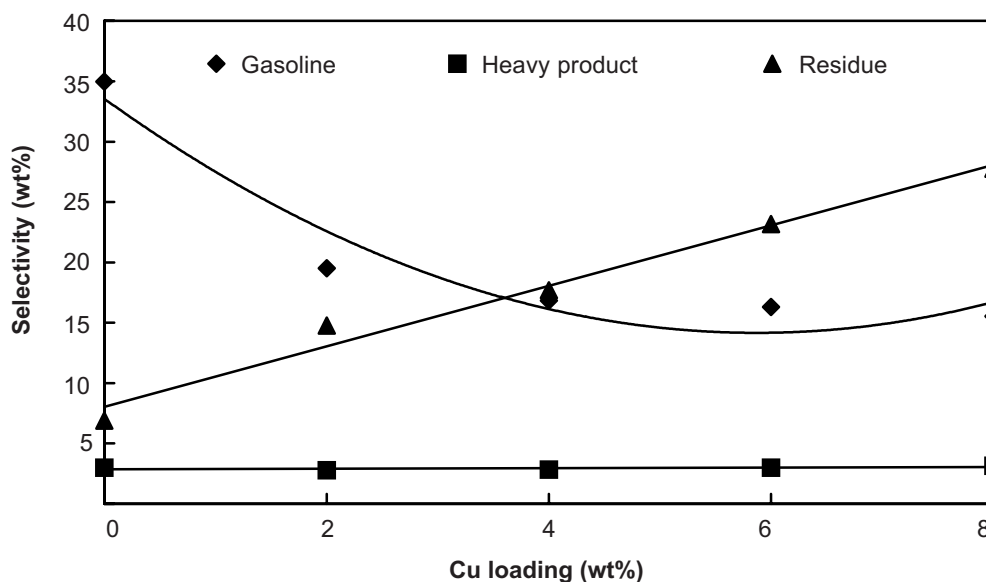


Figure 9 Different copper loadings effect on selectivity of products. Operating conditions: 500°C, WHSV = 2.5 h⁻¹ and F_{H2} = 1 L/h for an hour

The gasoline composition at various copper loading of pretreated Cu- ZSM-5 is tabulated in Table 2. The gasoline consisted mainly of naphthenes, aromatics, and isoparaffins. Aromatic contents were higher at higher copper loading compared to H-ZSM-5 without copper loading. As the copper loading increased, the naphthenes' composition decreased, yielding more aromatics. The aromatics were found to consist of alkylbenzene only. Pre-reduction of CuO to Cu (0) during hydrogen pretreatment of Cu-SiO₂ gave good activity and excellent selectivity towards the formation of high oleic derivatives for hydrogenation rapeseed oil [14]. This is in agreement with the olefin compositions observed in this study at higher copper loading. However, pre-reduction of CuO to Cu (0) showed reduced catalytic cracking activity of palm oil to gasoline. In other words, Cu-ZSM-5 was not selective towards palm oil cracking to gasoline.

Table 2 Gasoline composition of palm oil cracking with different copper loading percentage in Cu-ZSM-5. Operation condition: 500°C, WHSV = 2.5 h⁻¹ and F_{H2} = 1 L/h for an hour

Cu loading (wt%)	0	2	4	6	8
Gasoline composition (wt%)					
Paraffins	0.00	0.00	2.29	0.66	1.16
Olefins	0.00	1.05	4.09	3.47	8.05
Naphthenes	76.10	89.00	83.84	38.77	37.98
Aromatics	19.87	2.28	7.45	42.16	36.83
Isoparaffins	4.03	7.68	2.33	14.94	15.98

4.0 CONCLUSIONS

Catalytic cracking of palm oil over pretreated Cu-ZSM-5 catalyst showed that catalyst activity depended on the Brönsted acid sites. H-ZSM-5 without copper loading gave better performance than with copper loading at any weight percentage in terms of conversion, gasoline selectivity, and composition of gas product. Conversion and gasoline selectivity declined with increasing copper loading. This was due to the reduction of Brönsted acid sites. Crystallinity, surface area and pore size did not influence the catalyst's activity. The highest conversion and gasoline selectivity obtained were 95.18 wt% and 34.96 wt%, respectively with pretreated H-ZSM-5. The gasoline consisted mostly of naphthenes. At 6 wt% Cu-ZSM-5, the palm oil conversion decreased to 80.17 wt% while gasoline selectivity was 16.28 wt%. The most significant component in the gasoline was, however, aromatics with 11.45 wt% (all consisted of alkyl benzene) followed by 10.53 wt% of naphthenes and 4.06 wt% of isoparaffins. Gas as side product consisted mainly of C₃ compounds with 53.30 mol% followed by 29.84 mol% of C₄ and 0.62 mol% of C₅ compounds. Although OLP and gas product were increased with increasing copper loading, residue also drastically

increased while the coke was constant. Therefore, pretreated H-ZSM-5 alone is the most suitable catalyst for palm oil cracking to gasoline. However, Cu-ZSM-5 can be used to produce aromatics with high alkyl benzene composition.

ACKNOWLEDGEMENTS

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