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CATALYTIC CRACKING OF USED PALM OIL USING COMPOSITE ZEOLITE

(Peretakan Bermangkin Minyak Kelapa Sawit Terguna Menggunakan Zeolit Komposit)

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Abstract

The rapid expansion of human society implies greater energy demand and environmental issues. In face of depletion energy resources, research is being carried out widely in order to convert the plant oil into biofuel. In this research, the production of liquid biofuels via catalytic cracking of used palm oil in the presence of composite zeolite was studied. The performance of composite zeolite of different properties in the reaction has been evaluated. The catalytic cracking reactions were carried out in a batch reactor at reaction temperature of 350°C for an hour. In the present study, adjusting the ratio of mesoporous coating to microporous zeolite and magnesium loading on composite zeolite catalyst were found to be able to increase the gasoline fraction and overall conversion of the reaction.

Keywords: Catalytic cracking, used palm oil, composite zeolite

Abstrak

Perkembangan pesat masyarakat manusia menyebabkan permintaan tenaga yang lebih tinggi dan isu-isu alam sekitar. Untuk menghadapi masalah kehabisan sumber tenaga, penyelidikan sedang dijalankan secara meluas untuk menghasilkan bahan api hijau daripada minyak tumbuhan. Dalam kajian ini, pengeluaran bahan api hijau cecair daripada peretakan bermangkin minyak sawit terguna dengan kehadiran zeolit komposit telah dikaji. Prestasi sifat zeolit yang berbeza dalam tindak balas ini telah dinilai. Tindak balas peretakan bermangkin telah dijalankan dalam reaktor kelompok pada suhu 350°C selama satu jam. Dalam kajian ini, penyelarasan nisbah salutan berliang-meso kepada zeolit berliang-mikro dan muatan magnesium pada mangkin zeolit komposit didapati boleh meningkatkan pecahan gasolin and penukaran keseluruhan tindak balas.

Kata kunci: Peretakan bermangkin, minyak kelapa sawit terguna, zeolit komposit

Introduction

Biofuel production is undergoing rapid technological reforms in industries and academia. This has become more obvious with the growing awareness of the issues of environmental sustainability and the fossil fuel over-dependency. The feedstock for biofuel production is mainly vegetable oil. Vegetable oil can be divided into edible and non-edible oil. Edible oil such as crude palm oil and soybeans oil and non-edible oil such as used palm oil, are commonly accepted as raw material to produce biofuel. Used palm oil is used as the utilization of used edible oil would not divert resources from the food supply [1]. Conversion of biofuel from vegetable oil via catalytic cracking process has been carried out. Catalytic cracking is preferable compared to thermal cracking as catalytic cracking can take place at a much lower temperature, produces high octane gasoline and lowers the yield of heavy fuel oils and light gases [2].

Zeolite with microporous structure, ZSM-5 is commonly used as a catalyst to boost the gasoline octane number. Various types of zeolite catalysts were reported in catalytic cracking for the production of biofuels from vegetable oil. These findings show that zeolite possess a great potential as solid acid cracking catalyst due to its structure, acidity and high selectivity for the production of biofuels from vegetable oils. Catalytic cracking of palm oil over HZSM-5 was found to produce organic liquid rich in gasoline fraction from the catalytic cracking of palm oil based

fatty acid mixture [3] but the selectivity for gaseous products was also high [4]. It was found that MCM-41, a mesoporous catalyst is more selective for C_{5+} olefin products producing high octane fuels comparing to the performance with ZSM-5 [4]. The selectivity of MCM-41 mesoporous materials towards particular liquid hydrocarbons such as gasoline, kerosene or diesel in the cracking of palm oil was found strongly depended on the pore size and the surface area of mesoporous material. Due to the higher accessibility of reactants in mesoporous MCM-41 as compared to zeolite, it is suitable for catalytic reactions dealing with large molecules. However, the cracking activity of MCM-41 is lower than ZSM-5 zeolite due to lower acidity and shape selectivity of the mesoporous materials [4].

Zeolite can be more effective for larger reactant molecules by combining their microporous structure with mesoporous materials having higher adsorption capacity. The role of HZSM-5 in catalytic cracking unit was an octane-boosting additive due to its higher selectivity towards aromatic hydrocarbons [4]. However, HZSM-5 has tendency to produce gaseous product compare to other zeolite catalysts in palm oil cracking [4]. Hence, mesoporous materials were introduced as a diluting component to moderate the activity of the zeolite. Composite catalyst of mesoporous and microporous zeolite is desired as it contains the characteristic of both the mesoporous molecular sieve and microporous zeolite [4]. It is reported that MCM-41/Beta zeolite composite catalyst was more selective towards liquid fuel gasoline and enriched with olefins [5]. Composite material (MCM-41/ZSM-5) gave similar yield as HZSM-5 but lower gaseous products [4].

The modification of zeolite with Zn, Cu and rare earth metal (RE) could increase the total acidity of zeolite [6]. ZSM-5 zeolites modified with transition metals, such as Cu, Zn, and Ag increase the yield of aromatics. The loading of rare earth metal into Y zeolite catalyst improved the ability of the catalyst to withstand high temperature, leading to the catalytic stability and increasing the catalyst activity and gasoline selectivity [7]. Introducing rare earth metal in zeolite USL, was believed to increase the yield of total liquid products (LPG, gasoline and diesel) and improving the quality of gasoline. It has not only enhanced the content of isoparaffins, aromatic hydrocarbons and RON number in gasoline, but also decreased the olefin content in gasoline [8].

The objective of the present study is to develop a suitable metal loaded composite zeolite catalyst for catalytic cracking of used palm oil to produce liquid fuel.

Materials and Methods

Catalyst preparation

Metal loaded zeolite catalyst

Metal loaded zeolite catalyst was prepared by impregnation method. Zeolite catalysts loaded with three different metals (magnesium, zinc, copper) were prepared in the present study. To load magnesium on zeolite, first, magnesium chloride, $MgCl_2$ (Merck) was dissolved in decationized water and mixed with zeolite. The mixture was stirred at room temperature for 12 hrs. Then, the mixture was dried in an oven at 120^oC for 24 hrs. Next, the mixture was calcined in a muffle furnace at $550\ ^0C$ for 2 hrs. The same procedure has been used to load zinc and copper on the zeolite by using zinc chloride, $ZnCl_2$ (Merck) and copper (II) nitrate, $Cu(NO_3)_2.3H_2O$ (Merck) as the metal precursor, respectively.

Composite zeolite (CMZ)

The composite materials were prepared by coating commercially obtained zeolite ZSM-5 (Acros) by a layer of mesoporous material. The procedure was based on Twaiq et al. [4]. First, cetyltrimethylammonium hydroxide, CTMA-OH (Acros, 25% in methanol) and $SiO_2.NaO$ (Aldrich, 20% in water) was dissolved in deionized water. Then another mixture of metal loaded ZSM-5 and cetyltrimethylammonium chloride (CTMA-Cl) (Aldrich, 25% in methanol) which undergo medium mixing rate for overnight to form gel was added to the solution. 0.15 wt% of $Al_2O_3.NaO$ (Aldrich) aqueous solution was added to the reaction gel mixture after 15 mins. The amount of chemical used, CTMAOH: H_2O: $SiO_2.NaO$: $Al_2O_3.NaO$ followed the mole ratio of 1:97.23:1.15:0.058. The reaction gel mixture was stirred vigorously for 1 hr. The resulting mixture was loaded in a Teflon liner autoclave and kept for 24 hrs at 150^oC under 150 rpm. The solid was filtered and washed by water, followed by drying overnight at room temperature. The solid was then calcined at $440\ ^0C$ for 6 hrs.

Acidification of zeolite
The zeolite was acidified by reflux zeolite with 0.1M of ammonium chloride aqueous solution with solution to solid ratio of 20 at 80 ^{0}C with continuous overnight stirring. The zeolite was then recovered and dried in air overnight, followed by calcination at 550 ^{0}C for 4 hrs. The prepared composite catalyst was coded as *X*-CMZ (*W*, *Y*)- P% where *X* referred to the metal, *W* referred to the mesophase to zeolite ratio in the synthesis gel, *Y* referred to Al/Si ratio in the mesophase and *P* referred to metal loading.

Catalyst characterization
BET surface area was measured by nitrogen adsorption-desorption analysis using Micromeritics ASAP 2020 at 77 K. XRD patterns of catalysts were carried out in a range of 20°-80° with Cu target Kα-ray by using a Philips diffractometer.

Catalyst activity test
The feedstock, used palm oil (UPO) for the catalytic cracking reaction was waste cooking oil obtained in local café. The catalyst performance in catalytic cracking was evaluated in a batch reactor (Parr 4570). 100 ml of used palm oil and 0.5 wt% of catalyst were loaded into the reactor. The reactor was purged with nitrogen before heated up to 350°C and maintained for 1 hr. The stirrer speed was set at 350 rpm after the reactor temperature reach 350°C. After 1 hr, the reactor was cooled down to room temperature by passing water through the cooling coil. Then, the liquid and solid product was recovered. The coke formation was defined as the acetone insoluble after dried in oven at 100°C for 24 hrs.

The liquid products boiling points distribution were analyzed by using ASTM D86 distillation. The composition of cracking liquid product was defined according to boiling range of petroleum products such as gasoline (< 180°C), kerosene (180°C - 240°C), diesel (240°C - 340°C) and palm oil residue (>340°C). The performance of catalysts was evaluated in terms of conversion, product yield and liquid product fraction distribution. The conversion and liquid product fraction are defined as follow:

$$\text{Conversion (wt \%)} = \frac{\text{residue (>340°C) in feedstock - residue (>340°C) after cracking}}{\text{residue (>340°C) in feedstock}} \times 100\ \% \qquad (1)$$

$$\text{Liquid product yield (wt \%)} = \frac{\text{weight of distillate}}{\text{weight of liquid before distillation}} \times 100\% \qquad (2)$$

$$\text{Liquid product fraction (vol \%)} = \frac{\text{volume of distillate fraction}}{\text{total volume of distillate obtained}} \times 100\% \qquad (3)$$

Results and Discussion

Result of UPO analysis
The feed, UPO was analyzed for its boiling range fraction. The result is given in Table 1. There is no gasoline boiling range fraction obtained in the UPO. The largest volume fraction was diesel (72 vol%) followed by palm oil residue (22 vol%) and kerosene (6 vol%).

Table 1. UPO boiling range fraction

Temperature (^{0}C)	Liquid fraction (vol %)
<180 (gasoline)	0
180-240 (kerosene)	6
240-340 (diesel)	72
>340 (palm oil residue)	22

Catalytic cracking of UPO with different metal loaded HZSM-5 catalyst

Three metals i.e. magnesium, zinc and copper was loaded on zeolite and tested for their respective activity in catalytic cracking of UPO. These metals were reported to increase the total acidity of zeolite and thus increase the gasoline fraction [6]. The product yield of different catalyst in the catalytic cracking of used palm oil is shown in Table 2. As expected, the liquid product yield (72.11 wt%) for thermal cracking of used palm oil was the lowest. Meanwhile, the gas yield (16.65 wt%) was the highest. However, when comparing the catalytic cracking reaction with the presence of different catalyst, ie. H-ZSM5, Cu-HZSM5, Zn-HZSM5, Mg-HZSM5, there was negligible coke formation in thermal cracking of used palm oil. Coke formation was observed for all catalytic cracking of used palm oil. Similar observation was also reported by Ong and Bhatia [2].

Table 2. Performance of different catalyst on catalytic cracking of UPO

	Liquid product (wt%)	Residue (wt%)	Coke (wt%)	Gases (wt%)	Conversion (wt%)
UPO without catalyst	-	10.58	-	-	-
	72.11	11.24	Negligible	16.65	1.192
HZSM-5	83.28	10.46	0.48	6.26	22.67
Cu-HZSM-5	80.6	10.81	0.348	8.59	15.68
Zn-HZSM-5	75.94	8.2	0.056	15.804	26.74
Mg-HZSM-5	84.7	9.647	0.37	5.633	14.5

Reaction with the presence of Mg-HZSM5 catalyst gave the highest liquid product yield (84.70 wt%) and lowest gas yield (5.63 wt%) among the four catalysts used. Mg-HZSM5 catalyst gave the highest liquid product could be due to the low secondary cracking reaction to a low gas yield (5.63 wt%).

Among the catalyst studied, the highest gas yield (16.65 wt%) was obtained from the reaction running in the presence of Zn-HZSM5. This was followed by the reaction with Cu-HZSM5 as the catalyst (8.59 wt%). Zinc and copper are transition metals that were reported to increase the Lewis acid site of catalyst and promote the dehydrogenative cracking which leading to the yield of light olefins [7]. This could be reason for high gas yield obtained in these two reactions.

As shown in Table 2, thermal cracking of UPO at 350°C gave the lowest conversion (1.19 wt%). Among the four catalyst, catalyst Zn-HZSM5 gave the highest conversion (26.74 wt%) followed by HZSM-5 (22.67 wt%) in catalytic cracking of UPO while Mg-HZSM and Cu-HZSM both gave lower conversion, at 14.5 wt% and 15.68 wt% respectively. It was reported that loading of magnesium did not decrease the strength of acidity but reduced the Bronsted acid sites and the conversion of UPO was influenced by the disappearance of Bronsted acidity [9].

The liquid product distribution that obtained with different catalyst is shown in Figure 1. Mg-HZSM5 gave the highest gasoline fraction which was 9 vol% compared to that of HZSM-5 (5 vol%), Cu-HZSM5 (4.5 vol%) and Zn-HZSM5 (2 vol%). The gasoline fraction obtained with the presence of Zn-HZSM5 catalyst is the lowest. It is believed that most of the gasoline fraction was cracked to gas product since highest gas yield was obtained in the reaction. H-ZSM5 catalyst gave the highest kerosene fraction (7 vol%) while Mg-HZSM5 catalyst had the highest diesel fraction (72.5 vol%) in the catalytic cracking reactions in the present study.
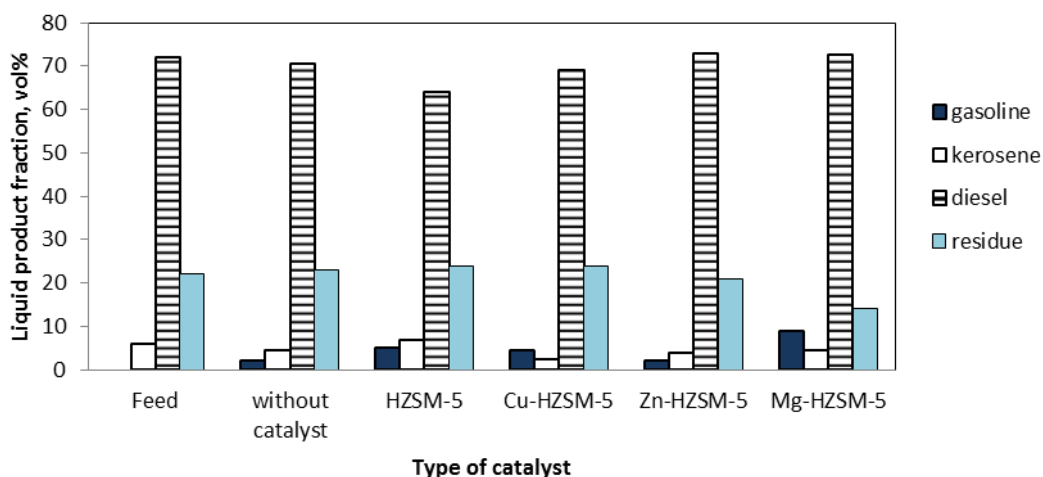
Figure 1. Liquid product fraction distribution for different catalysts (reaction condition: 350 ^{0}C, 1 atm, 0.5wt% catalyst and retention time 1 hour).

Effect of ratio of mesophase to microphase in composite zeolite for catalytic cracking of UPO

As illustrated in Table 3, the ratio of mesophase to microphase in composite zeolite had not much effect on the liquid product yield. As the ratio of mesophase to microphase in composite zeolite increase, the conversion of UPO was found to decrease. The gasoline fraction obtained was also having the similar trend, decrease with increasing of the ratio. This was in agreement with the result reported by Twaiq et al. [4] that increasing the coating in the composite catalyst would decrease the gasoline fraction while increase the kerosene fraction as lower ratio of mesophase coating in composite zeolite can improve the gasoline fraction. Lower ratio of mesophase coating increase the conversion as thinner coating layer is preferable in order to allow reactants to access the micropores [4]. Although the liquid product yield in the presence of HZSM-5 is higher than another three composite zeolites, the conversion is lower.

Table 3. Effect of mesoporous/microporous ratio in composite zeolite and HZSM-5 on liquid and gas yield and conversion

	Liquid product (wt%)	Residue (wt%)	Coke (wt%)	Gases (wt%)	Conversion (wt%)
HZSM-5	83.28	10.46	0.48	6.26	22.67
CMZ (0.1, 0.15)	78.90	10.50	0.38	10.22	35.00
CMZ (0.15, 0.15)	79.20	10.47	0.39	9.94	33.00
CMZ(0.2,0.15)	79.31	8.97	0.41	11.31	26.7

As shown in Figure 2, when the ratio of mesophase to microphase in composite zeolite decrease, the gasoline fraction and diesel fraction increase while the kerosene fraction decrease. The gasoline fraction for three composite zeolite is higher than catalyst NZSM-5. The fraction of gasoline is higher than the fraction of kerosene in each of the composite zeolite. CMZ(0.10, 0.15) composite catalyst even gave a gasoline fraction as high as 18 vol%.
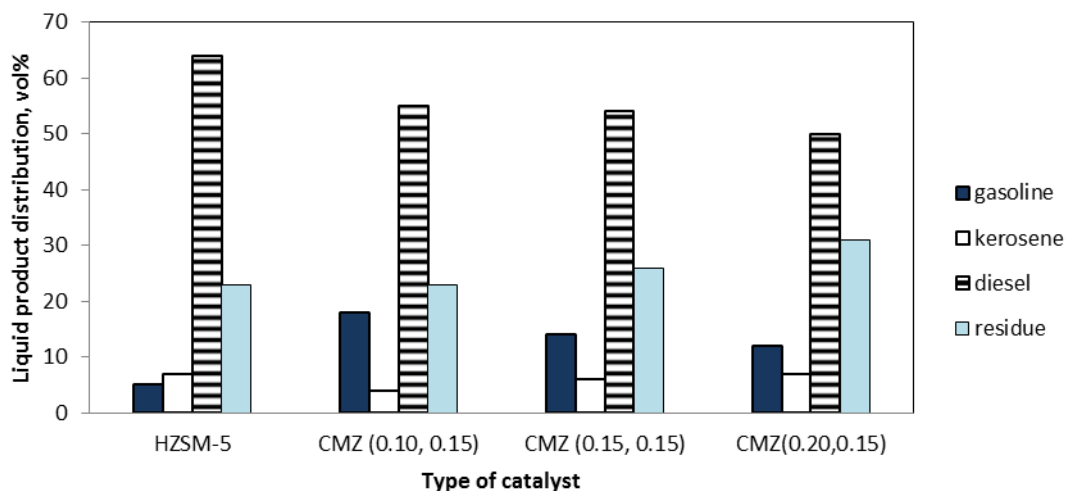
Figure 2. Effect of ratio of mesoporous to microporous in composite zeolite on product fraction (reaction condition: 350 ^{0}C, 1 atm, 0.5wt% catalyst and retention time 1 hour)

Magnesium loaded composite zeolite for catalytic cracking of UPO
The liquid yield for CMZ(0.1,0.15) catalyst (78.9 wt%) and Mg-CMZ(0.1,0.15)-5% (77.8 wt%) were almost similar. However, Mg-CMZ(0.1,0.15)-5% catalyst gave lower yield of coke (0.3 wt%) and lower yield of residue (10.5 wt%) compared to CMZ(0.1,0.15) catalyst.

As shown in Figure 3, the gasoline fraction for CMZ(0.1,0.15) catalyst (18 vol%) and Mg-CMZ(0.1,0.15)-5% catalyst (17 vol%) were similar but higher than feed which does not have any gasoline fraction. The diesel fraction for Mg-CMZ(0.1,0.15)-5% (60 vol%) was higher than CMZ(0.1,0.15) catalyst which gave 55 vol% of diesel. The feed contains the highest diesel fraction which is 72 vol%. The conversion for the catalytic cracking reaction in the presence of Mg-CMZ(0.1,0.15)-5% catalyst (58.89 wt%) was higher than CMZ(0.1,0.15) catalyst (35 wt%).
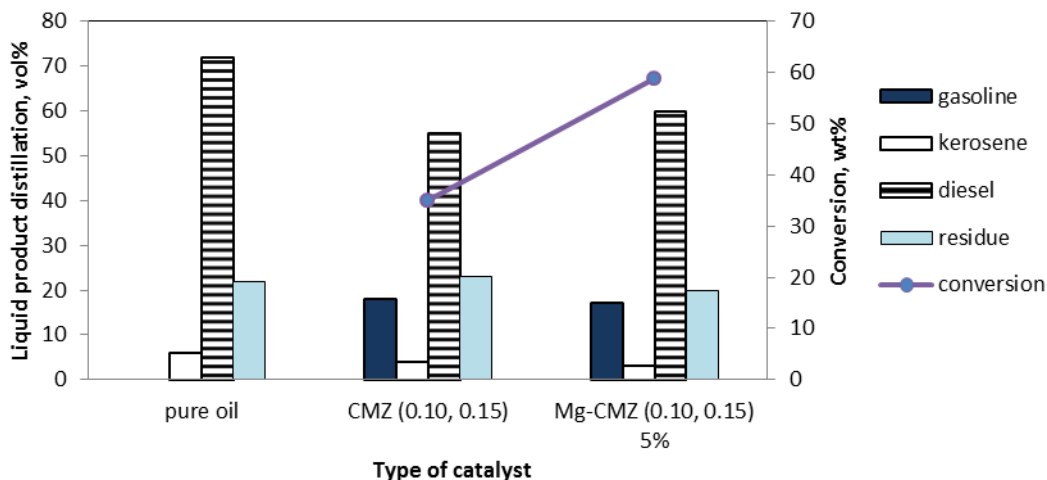

Figure 3. Effect of 5% magnesium loaded in composite zeolite CMZ(0.10,0.15) on product fraction and conversion (reaction condition: 350 ^{0}C, 1 atm, 0.5wt% catalyst and retention time 1 hour).

Properties of catalyst

The physical properties of CMZ(0.10, 0.15) catalyst was obtained from the nitrogen adsorption-desorption analysis. The result is presented in Table 4. The composite catalyst zeolite was found to have large BET surface area of 272 m^2/g and also large average pore size of 29 nm.

Table 4. Physical properties of CMZ(0.10, 0.15) catalyst.

Properties	value
BET surface area (m^2/g)	272.55
Pore volume (cm^3/g)	0.10
Pore Size (nm)	29.58

Figure 4 shows the nitrogen adsorption desorption isotherms of CMZ(0.10, 0.15) catalyst. Type IV isotherm is observed. Type IV isotherm are very common and show characteristic hysteresis loops which arise from different adsorption and desorption mechanism in mesoporous. The sharp and steep initial rise in the first part indicated that the composite catalyst contains microporous material as the sharp and steep initial rise is associated with capillary condensation in micropores [10].
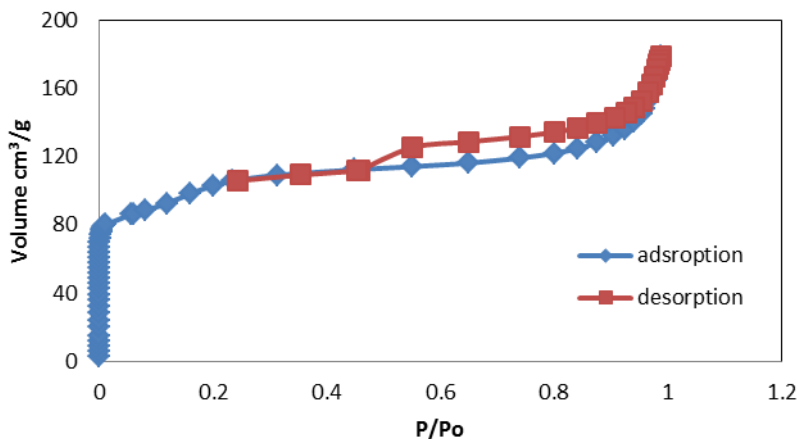

Figure 4: Nitrogen adsorption-desorption of CMZ(0.10, 0.15) catalyst.

The XRD pattern of Mg-CMZ(0.1, 0.15) -5% catalyst is presented in Figure 5. There are peaks that represent two components, which are zeolite and magnesium alumina silicate. The triangle symbol referring to the zeolite peaks while the peaks with a circle symbol referring to magnesium alumina silicate. The shape for zeolite was orthorhombic while for magnesium alumina silicate was hexagonal. From the XRD results, it showed that the active magnesium component on the zeolite is magnesium alumina silicate instead of magnesium oxide.
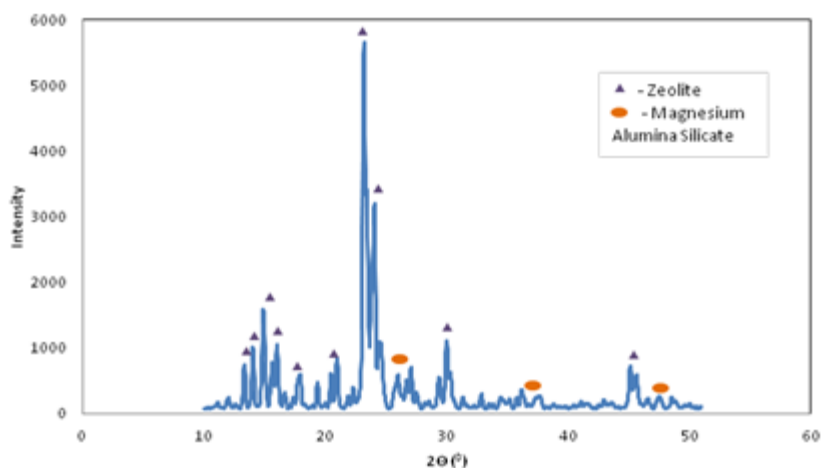
Figure 5. XRD pattern of catalyst Mg-CMZ(0.1, 0.15)-5%

Conclusion

Among the three metal loaded zeolite catalysts, Mg-HZSM5 gave the highest liquid product yield (84.7 wt%) and gasoline fraction (8 vol%). Zn-HZSM5 catalyst gave the highest conversion (26.74 wt%). Ratio of mesophase to microphase in composite catalyst plays an important role in increasing the gasoline fraction and conversion in catalytic cracking of UPO. When the ratio decreased, the gasoline fraction and the conversion of UPO was found to increase. In the present study, CMZ(0.1, 0.15) composite catalyst with 5 wt% of magnesium were found to be active in catalytic cracking of UPO.

Acknowledgement

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