[AMT02] Composite MCM-41/ZSM-5 as a cracking catalyst for the production of liquid fuel from used palm oil

Yean-Sang Ooi, Ridzuan Zakaria, Abdul Rahman Mohamed, Subhash Bhatia

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Seberang Prai Selatan Penang, Malaysia.

Introduction

The gradual depletion of fossil fuel and drastically increase of the price of petrol have driven researchers looking into a new source of sustainable energy resources. Biofuel production from vegetable oils such as canola oil (Idem *et al.*, 1996) and palm oil (Twaiq *et al.*, 2003) are recently being studied over different types of cracking catalysts. With biofuel produced from the vegetable oil, the green house effect and air pollution can be minimized due to the recycling of carbon source from the air to the plant in closed cycle compare to the fossil fuels. Nevertheless, the high cost of the vegetable oil in comparison to the price of fossil fuel was one of the main reasons for not taking off the growth of biorefinery for production of fuels and chemicals from sustainable resources. Therefore, palm oil based fatty acids mixture available as the residue from oleochemical industries was explored as raw materials by Ooi *et al.*(2004) instead of crude palm oil for the production of biofuel. Besides, the used palm oil (fried oil) obtained from the fast food restaurant can be utilized as the raw material. The utilization of these materials will not only help in cleaning up the waste but by converting them into value added chemical products. The consistent supply of these materials should not pose any problem in the near future.

Catalytic cracking of vegetable oil for liquid hydrocarbon production was studied over various microporous catalysts (Idem *et al.*, 1997; Twaiq *et al.*, 1999) as well as mesoporous catalysts (Twaiq *et al.*, 2003). Different types of catalysts show different activity and selectivity for cracking of saturated and unsaturated fatty acids present in the vegetable oil. The product distribution varied due to the shape selectivity effect and accessibility to the active sites. In the current study, the used palm oil discarded from the restaurants was utilized as raw material. Composite catalyst consists of mesoporous material MCM-41 and microporous material ZSM-5 was synthesized with two different methods in order to study their performance in used palm oil cracking in terms of the yield of gasoline fraction.

Experimental

MCM-41/ZSM-5 via seeding method

The MCM-41 was synthesized using the method reported by Lindlar *et al.*(2000) with a Si/Al ratio of the synthesis gel of 39. The mixture was stirred for 1 h at room temperature before heated at 373 K for 24 h without stirring. The mixture was then cooled to room temperature and the pH was adjusted to approximately 11 by dropwise addition of acetic acid under vigorous stirring. The reaction mixture was heated again to 373 K for 24 h and this procedure for pH adjustment and heating was repeated twice. The product obtained was filtered, washed with deionised water and dried at room temperature overnight before calcined at 823 K for 6 h.

The composite material was prepared by coating ZSM-5 by a layer of mesoporous material using cetyltrimethyl ammonium chloride (C_{16}TMACl) as templates following the procedure reported by Kloetstra *et al.* (1996) with some modifications. The procedure of pH adjustment and subsequent heating for three times was included as in the synthesis of MCM-41. The composite of pure siliceous MCM-41 with HZSM-5 was coded as CMZX where C referred to composite, M to MCM-41, Z to HZSM-5 and X referred to the mesophase weight percent (20, 30 and 40) in the composite synthesis gel.

MCM-41/ZSM-5 via two-step crystallization

5.3 g of tetrapropyl ammonium bromide (TPABr) was dissolved in 13.5 g of deionized water before added to sodium aluminate solution (0.16 g of sodium aluminate in 14.0 g deionized water) under mild stirring. Subsequently, 22.3 g of sodium silicate was added to the mixture. The mixture was stirred for another 30 min and then heated to 413 K for 48 h, 96 h and 144 h respectively to obtain colloidal ZSM-5. After cooling to room temperature, the colloidal ZSM-5

was added dropwise in to a cetyltrimethyl ammonium bromide solution (5.8 g of C_{16}TMA-Br and 57.6 g of water) with stirring. The pH of the mixture was adjusted to 9.6 or 8.6 with 50 wt% acetic acid under vigorous stirring. The mixture was again heated to 373 K for 48 h in the reactor before filtered and washed thoroughly with deionized water. The resultant solid was dried overnight at room temperature and calcined at 823 K for 6 h. The composites were coded as CMZI48 where I refers to *in situ* (aging for 48h), CMZI96 (aging for 96 h) and CMZI144 (aging for 144 h).

Characterization

The catalyst was characterized by XRD to determine the structure and composition of crystalline material using a Philips diffractometer with Cu-Kα radiation at 2θ values of 1.5–90° with a step of 0.04-degree/10 sec. The BET surface area and pore volume were measured by nitrogen adsorption using an Autosorb I (Quantachrome Automated Gas Sorption System). The samples were degassed for 5 h under vacuum at 300°C prior to the analysis. The acidity of the catalyst was measured using temperature programmed desorption (TPD) of ammonia. The temperature programmed desorption was carried out using a Chembet 3000 instrument (Quantachrome) equipped with TPRWin, version 1 software to calculate the acidity. Transmission electron microscopy (TEM) was performed with a Philips CM12 Transmission Electron Microscope operated at 80 kV. SEM photographs were taken using a Leica Cambridge S-360 scanning electron microscope.

Activity test

The catalytic cracking activity of composite materials was measured at reaction temperature of 450°C and a feed rate of used palm oil (weight hourly space velocity, WHSV) of 2.5 h$^-$^{1} at atmospheric pressure in a fixed-bed micro-reactor rig reported elsewhere (Ooi *et al.*, 2004). 1.0g of composite catalyst was loaded over 0.2g of quartz wool supported by a stainless steel mesh in the micro-reactor (185 mm ×10 mm I.D.) placed in the vertical tube furnace (Model No. MTF 10/25/130, Carbolite). The liquid product was collected in a glass liquid sampler, while the gaseous products were collected in a gas-sampling bulb once the steady state was reached in the reactor. The residue oil was separated from the liquid product by distillation in a micro-distillation unit (Buchi B850, GKR)

at 200°C for 30 min under vacuum (100 Pa) with the pitch as the residual oil. The gaseous products were analyzed over a gas chromatograph (Hewlett Packard, Model 5890 series II) using a HP Plot Q capillary column (Divinyl benzene/styrene porous polymer, 30 m long × 0.53 mm ID × 40 μm film thickness) equipped with a thermal conductivity detector (TCD) and nitrogen as a carrier gas. The organic liquid product (OLP) was analyzed using a capillary glass column (Petrocol DH 50.2, film thickness 0.5 micron, 50 m long × 0.2 mm ID) at a split ratio of 1:100, using a FID detector. The composition of OLP was defined according to the boiling range of petroleum products in three categories i.e. gasoline fraction (333–393 K), kerosene fraction (393–453 K) and diesel fraction (453–473 K). The spent catalyst was washed with acetone prior to the coke analysis. The amount of coke was determined by the difference in weight before and after calcination in muffle furnace.

Results and Discussion

Catalyst characterization

Zeolite ZSM-5 was used as the microporous component for the synthesis of composite material via seeding method. The effect of the silica amount in the coating was investigated. In the two-step crystallization, ZSM-5 structure-directing agent, tetrapropyl ammonium cations (TPA$^+$) were first mixed with silica source followed by a variation in the aging period of 48, 96 and 144 h respectively before adding cetyltrimethyl ammonium bromide (C_{16}TMA-Br) to promote the formation of MCM-41. Table 1 summaries the physicochemical properties of the catalysts synthesized and the physical mixture of MCM-41/ZSM-5 with 40 wt.% MCM-41. It can be seen from the table that when the siliceous MCM-41 coating was increased from 20 to 40 wt.%, the BET surface area of the composites was increased from 367 to 614 m^2/g. This confirmed that MCM-41 was growing accordingly when different amount of synthesis gel was added. As compared with the physical mixture of MCM-41/ZSM-5, the BET surface area of CMZ40 was 122 m^2/g lower. This suggested that not 100% of the synthesis crystalline to form MCM-41. The total acidity of the catalyst was calculated by assuming that one molecule of ammonia reacted with only one acid site. The pure siliceous MCM-41 did not

contribute to the acidity. Therefore, the acidity was deceased from 0.13 to 0.09 mmol H^+/g cat with the increase of the coating layer of MCM-41 for the composite synthesized via seeding method.

TABLE 1   Physicochemical properties of the catalysts.

Catalyst ID	BET Surface Area, m^2/g	Mesophase APS*, nm	Acidity, mmol H^+/g cat
ZSM-5	367	-	0.25
CMZ20	400	2.87	0.13
CMZ30	439	2.87	0.12
CMZ40	614	2.89	0.09
CMZI48	533	2.50	0.24
CMZI96	311	2.83	0.33
CMZI144	301	-	0.27
MCM-41	1100	2.89	-
MCM-41/ZSM-5	736	2.89	-

* APS = Average pore size determined using BJH method.

BET surface area for CMZI48 was in the range between mesoporous MCM-41 and microporous ZSM-5. The other composite materials synthesized via two-step crystallization gave BET surface area lower than ZSM-5 revealing low crystallinity of the material due to the synthesis conditions. The thickness of MCM-41 decreased with the increase of aging time suggested too long aging time discouraged the growth of MCM-41. The acidity was lower because MCM-41 was presented in the composite materials. Since Si/Al ratio of 16 was employed in the synthesis gel and the acidity obtained for the samples without mesophase was higher than ZSM-5 with a Si/Al ratio of 40. Although the high aluminum loading improved the acidity, but ZSM-5 with a lower BET surface area rendered the active sites available for the reactants.

Since the characteristic of MCM-41 derived from the nitrogen adsorption measurements did not give complete picture of the structural order, XRD patterns of the synthesized composite materials were studied and presented in Figure 1. The figure shows three peaks at 2θ lower than 5° which correspond to the hexagonal structure of MCM-41. The intensity of the peak increased

as the coating percentage of MCM-41 was increased as shown in Figure 1a. All the XRD patterns exhibited five peaks characteristic of ZSM-5 in the 2θ range of 8–25° proved that ZSM-5 was preserved during the hydrothermal synthesis especially for the catalyst prepared via seeding method.
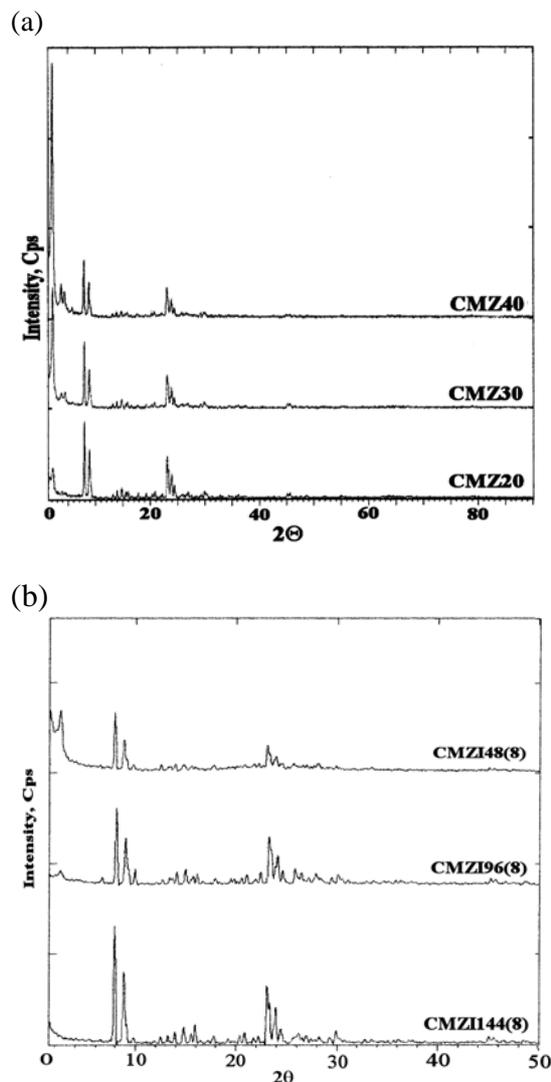
(a)

(b)

FIGURE 1   XRD images of composite MCM-41/ZSM-5 synthesized via (a) seeding method and (b) two-step crystallization.

The mesophase formed in CMZI48 can be confirmed from the XRD peaks in Figure 1b for the region of 2θ lower than 5°. This is the synergy effect of the aging time and pH adjustment and thus provided the strong interaction between CTA^+ and TPA^+ cation with the aluminosilicate species. The intensity of the peak corresponds to mesophase decreased once the aging time increased from 48 to 144 h. This

was due to a longer aging time converting the synthesis gel to crystalline ZSM-5. The addition of surfactant C_{16}TMA-Br was unable to promote the formation of mesophase. Hence, it is clear that synthesis of composite MCM-41/ZSM-5 via seeding method gave a better option in controlling the amount of mesophase presence.

Catalytic Cracking Performance

The performance of the catalysts synthesized was studied in terms of conversion, yield and selectivity as defined in equations (1) to (3):

$$\text{Conversion (wt.\%)} = \frac{\text{Total Product (g)}}{\text{Used Palm Oil Feed (g)}} \times 100\% \quad (1)$$

$$\text{Yield (wt.\%)} = \frac{\text{Desired Product (g)}}{\text{Used Palm Oil Feed (g)}} \times 100\% \quad (2)$$

$$\text{Selectivity (wt.\%)} = \frac{\text{Desired Product (g)}}{\text{Total Products (g)}} \times 100\% \quad (3)$$

where the total products are gas, water, organic liquid product (OLP) and coke. Table 2 presents the catalytic cracking activity of used palm oil over ZSM-5, composite catalysts and physical mixture of MCM-41/ZSM-5. The conversion of used palm oil over composite MCM-41/ZSM-5 synthesized via seeding method was comparable to the catalytic cracking of ZSM-5. The yield of gasoline fraction increased at the expense of diesel fraction after ZSM-5 was coated with silica MCM-41 due to the ease of accessibility. The pre-cracking of the bulky molecules before entering the core of the catalyst promoted the production of liquid product in the gasoline fraction. The mild acidity of MCM-41 prohibited over-cracking of the used palm oil to gas product. The maximum gasoline fraction yield was obtained when 20 wt.% of MCM-41 was loaded in ZSM-5. The coke formation slightly increased with the increase of MCM-41 content in the composite. This was due to the open structure of MCM-41 which encouraged the growth of coke precursor.

The conversion of used palm oil over the composite synthesized via two-step crystallization was lower than that of ZMS-5 but increased with the increase of the BET surface area of the catalysts. The yield of gasoline fraction was low but the coke deposition was higher than expected even the amount of mesophase

TABLE 2   Catalytic cracking activity of used palm oil over ZSM-5, composite catalysts and physical mixture of MCM-41/ZSM-5.

Catalyst	ZSM-5	CMZ 20	CMZ 30	CMZ 40	CMZI 48	CMZI 96	CMZI 144	MCM-41/ZSM-5
Conversion (wt.%)	95.9	94.7	91.2	95.8	62.3	59.8	37.1	96.4
Product Distribution (wt.%)								
Gas	27.3	27.6	17.3	26.2	13.4	9.6	7.1	27.1
OLP	59.3	57.8	63.7	59.8	39.7	42.0	23.4	48.0
Water	8.2	7.9	7.9	7.6	5.3	2.5	1.1	8.1
Coke	1.1	1.4	2.3	2.2	3.9	5.7	5.5	13.2
Yield of OLP (wt.%)								
Gasoline Fraction	40.9	45.1	43.9	47.1	26.0	22.3	14.0	29.5
Kerosene Fraction	15.9	11.2	15.9	11.8	10.9	13.4	6.4	15.0
Diesel Fraction	2.5	1.5	3.9	0.9	2.8	6.3	3.0	3.5
Aromatics content in OLP (wt.%)								
Benzene	5.7	7.8	6.2	6.7	1.5	5.4	2.1	5.5
Toluene	22.0	27.3	21.3	23.0	5.5	21.7	8.3	18.9
Xylene	21.5	23.2	19.9	20.8	5.8	18.0	7.4	18.4
BTX	49.2	58.3	47.4	50.5	12.8	45.1	17.8	42.8

presented was low (from the intensity of the peak correspondence to mesophase in XRD, Figure 1b). It was possible that the procedure used for the synthesis resulted in some degree of distortion in the pore structure. The distorted pore system prohibited the diffusion of the reactant as well as the product. The components accumulated inside the catalyst further oligo-merized and condensed to form coke. Therefore the composite prepared via this procedure would deactivate at a faster rate than the composite prepared via seeding method and gave a low conversion.

Figure 2 shows the selectivity of different fractions present in OLP over ZSM-5, the composite catalysts and the physical mixture of MCM-41/ZSM-5 in the cracking of used palm oil.
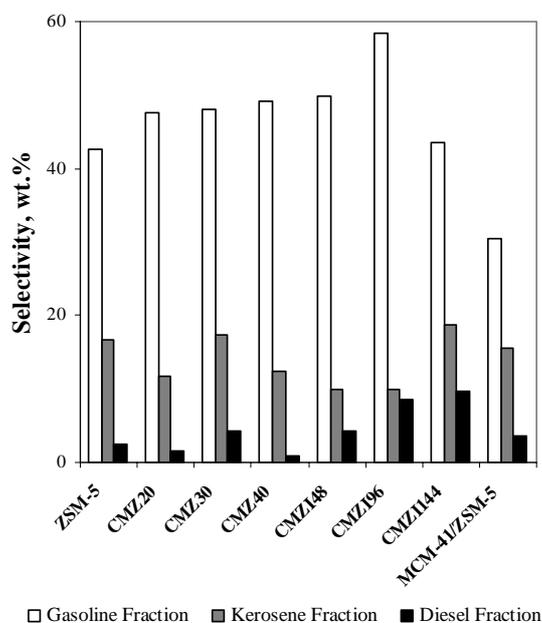

FIGURE 2 Selectivity of different fractions present in OLP over ZSM-5, the composite catalysts and the physical mixture of MCM-41/ZSM-5 in use palm oil cracking.

All the silica coated ZSM-5 (CMZs) gave a better selectivity towards gasoline fraction as compare to ZSM-5 alone. However, there was no obvious trend in the selectivity of the fractions in OLP with increased silica coating. Physical mixture of MCM-41 and ZSM-5 gave the conversion as high as 96 wt.% with high yield of gaseous product and coke. Therefore the selectivity towards the desired product, gasoline fraction in OLP turned out to be the lowest among the composite catalysts synthesized. The selectivity of the gasoline fraction was found to be dependent on the BET surface area and acidity for the composite synthesized via two-step crystallization. CMZI96 with the acidity of 0.33 mmol H^+/g cat and BET surface area of 311 m^2/g gave high selectivity (58 wt.%) towards gasoline fraction.

References

Idem, R.O., Katikaneni, S.P.R., & Bakhshi, N.N. (1997). Catalytic conversion of canola oil to fuels and chemicals: Roles of catalyst acidity, basicity and shape selectivity on product distribution. *Fuel Proc. Tech.* 51: 101-125.

Kloetstra, K.R., Zandbergen, H.W., Jansen, J.C. & Bekkum, H.V. (1996). Overgrowth of mesoporous MCM-41 on Faujasite. *Micropor. Mater.* 6: 287-293.

Lindlar, B., Kogelbauer, A. & Prins, R. (2000). Chemical, structural, and catalytic characteristics of Al-MCM-41 prepared by pH-controlled synthesis. *Micropor. Mesopor. Mater.* 38: 167-176.

Ooi, Y.S., Zakaria, R., Mohamed, A. R. & Bhatia, S. (2004). Catalytic conversion of palm oil based fatty acid mixture to liquid fuel. *Biomass and Bioenergy* 27: 477-484.

Twaiq, F., Zabidi, N.A.M., & Bhatia, S. (1999). Catalytic conversion of palm oil to hydrocarbons: performance of various zeolites catalysts. *Ind. Eng. Chem. Res.* 38: 3230-3238.

Twaiq, F.A., Mohamed, A.R. & Bhatia, S. (2003). Liquid hydrocarbon fuels from palm oil by catalytic cracking over aluminosilicates mesoporous material with various Si/Al ratios. *Micropor. Mesopor. Mater.* 64: 95-107.