

**COMPOSITE MICRO-MESOPOROUS MATERIALS
AS CATALYSTS FOR THE PRODUCTION
OF LIQUID FUELS
FROM CATALYTIC CRACKING OF
FATTY ACIDS MIXTURE AND USED PALM OIL**

by

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ABBREVIATIONS

ANOVA	Analysis of variance
APS	Average pore size
BEA	Zeolite Beta
BET	Brunaur-Emmett-Teller
BJH	Barrett, Joyner and Halenda
BTX	Benzene, toluene and xylene
C ₁₂ TMA-Cl	Dodecyltrimethyl ammonium chloride
C ₁₆ TMA-Br/Cl	Cetyltrimethyl ammonium bromide/chloride
CMBAX	Composite aluminosilicate MCM-41 with zeolite Beta prepared via seeding method with X referred to the Si/Al ratio of MCM-41 in the composite (10,20 and 40).
CMBIX	Composite silica MCM-41 with zeolite Beta prepared via two-step crystalline method with X referred to the aging time (48, 96, 144 hr).
CMBX	Composite silica MCM-41 with zeolite Beta prepared via seeding method with X referred to the weight percent of MCM-41 in the composite (20, 30, 40).
cmc	Critical micelle concentration
CMZAX	Composite aluminosilicate MCM-41 with ZSM-5 prepared via seeding method with X referred to the Si/Al ratio of MCM-41 in the composite (10,20 and 40).
CMZIX	Composite aluminosilicate MCM-41 with ZSM-5 prepared via two-step crystalline method with X referred to the aging time (48, 96, 144 hr).
CMZX	Composite silica MCM-41 with ZSM-5 prepared via seeding method with X referred to the weight percent of MCM-41 in the composite (20, 30 and 40).
CSZAX	Composite aluminosilicate SBA-15 with ZSM-5 prepared via seeding method with X referred to the Si/Al ratio of SBA-15 in the composite (10 and 20).
CSZX	Composite silica SBA-15 with ZSM-5 prepared via seeding method with X referred to the weight percent of SBA-15 in the composite (20, 30, 60 and 90).
DOE	Design of experiments

EDX	Energy dispersive X-ray
EO	Ethylene oxide
FAM	Fatty acids mixture
FCC	Fluid catalytic cracking
FTIR	Fourier transformed infra red
HRTEM	High resolution transmission electron microscopy
I	Inorganic precursor
ICP	Inductive coupled plasma
IUPAC	International union of Pure and Applied Chemistry
IZA	International Zeolite Association
LCT	Liquid crystal templating
LPMM	Large pore mesoporous material
M	Metal ion
MCM	Mobil Crystalline Material
MFI	Mobil Five
MgCMZ(L)	Magnesium loaded CMZ20 by liquid ion exchange
MgCMZ(X)	Magnesium loaded CMZ20 by solid ion exchange with X referred to Mg/Al ratio
MTG	Methanol to gasoline
NiCMZ(L)	Nickel loaded CMZ20 by liquid ion exchange
NiCMZ(X)	Nickel loaded CMZ20 by solid ion exchange with X referred to Ni/Al ratio
OLP	Organic liquid product
PEO-PPO-PEO	Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)
PO	Propylene oxide
PONA	Paraffin, olefin, naphthalene and aromatic
RKF	Runge-Kutta-Fehlberg
RSM	Response surface methodology
S	Surfactant head group
SBA	Silica block assembly
SEM	Scanning electron microscopy
TEAOH	Tetra-ethyl ammonium hydroxide
TEM	Transmission electron microscopy
TEOS	Tetra-ethyl orthosilicate

TGA	Thermal gravimetric analysis
TMA	Tetra-methyl ammonium
TMOS	Tetra-methyl orthosilicate
TPABr	Tetra-propyl ammonium bromide
TPD	Temperature programmed desorption
UPO	Used palm oil
USY	Ultra stable Y
XRD	X-ray diffraction
ZnCMZ(L)	Zinc loaded CMZ20 by liquid ion exchange
ZnCMZ(X)	Zinc loaded CMZ20 by solid ion exchange with X referred to Zn/Al ratio
ZSM-5	Zeolite Socony Mobil Five

NOMENCLATURES

A	Temperature code (K)
a_0	Unit cell dimension (nm)
B	Feedstock to catalyst ratio code (g/g cat)
C	Weight hourly space velocity code (h^{-1})
C_p	Fatty acids mixture/ used palm oil weight fraction (wt%)
$C_{product}$	Product weight fraction (wt%)
Dv	Differential pore volume ($\text{cc}/\text{\AA}/\text{g}$)
E	Activation energy (kJ/mol)
F-value	Ratio of model mean square to the residuals mean square
k_d	Deactivation rate constant (h^{-1})
k_i	Reaction rate constant, $i = 1, 2, \dots, 7$ ($\text{kg}^{1-n} \text{kg}_{\text{feed}}^n \text{kg}_{\text{catalyst}}^{-1} \text{h}^{-1}$)
n	Order of reaction
n_d	Order of the deactivation rate
O/C	Oil (fatty acids) to catalyst ratio (g/g cat)
P_c	Conversion (wt%)
R	Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	Reaction temperature (K)
t	Time on stream (h)
WHSV **	Weight hourly space velocity ($\text{kg}_{\text{feed}} \text{kg}_{\text{catalyst}}^{-1} \text{h}^{-1}$)
x	Independent variable
Y	Response
$Y_{product}$	Yield of desired product (wt%)

Greek symbols

α	Frequency factor ($\text{kg}^{1-n} \text{kg}_{\text{feed}}^n \text{kg}_{\text{catalyst}}^{-1} \text{h}^{-1}$)
β	Constant in statistical model
ε	Error of the response Y
φ	Deactivation function
τ	Residence time (h)

BAHAN KOMPOSIT BERLIANG MIKRO-MESO SEBAGAI MANGKIN UNTUK PENGHASILAN BAHAN API CECAIR DARIPADA PERETAKAN BERMANGKIN BAGI CAMPURAN ASID-ASID LEMAK DAN MINYAK KELAPA SAWIT TERPAKAI

ABSTRAK

Campuran asid-asid lemak daripada minyak kelapa sawit (FAM) serta minyak kelapa sawit terpakai (UPO), merupakan sumber yang murah dan boleh diperbaharui telah diterokai untuk penghasilan bahan api cecair daripada proses peretakan bermangkin. Proses peretakan bermangkin ini dikaji pada tekanan atmosfera dalam reaktor mikro, pada suhu tindakbalas 723 K dan halaju ruang (WHSV) pada 2.5 jam^{-1} . Mangkin ZSM-5 berliang mikro dengan nisbah Si/Al yang berbeza dan zeolit Beta, aluminosilikat berliang meso serta bahan komposit berliang mikro-meso telah digunakan sebagai mangkin peretakan.

Molekul ayak MCM-41 berliang meso disintesis dan dipascarawat dengan menggunakan pertukaran ion dan pembebanan untuk meningkatkan kestabilan hidrotermalnya. Mesitilena digunakan sebagai pengembang liang bagi sintesis bahan berliang meso yang besar (LPMM). SBA-15, bahan berliang meso dengan dinding liang yang lebih tebal dan kestabilan hidroterma yang lebih baik juga disintesis dalam keadaan berasid. Komposit MCM-41/zeolit (Beta/ZSM-5) telah disediakan dengan dua kaedah berbeza (a) kaedah berbenih (b) penghabluran dua-langkah. Kaedah berbenih juga digunakan untuk mensintesis SBA-15/ZSM-5. Bahan komposit berliang makro-meso disediakan dengan menyalut LPMM dengan alumina. Ion-ion logam dimuatkan dalam bahan komposit MCM-41/ZSM-5 dengan pertukaran ion secara cecair dan dalam keadaan pepejal masing-masing. Bahan-bahan tersebut dicirikan untuk luas permukaan BET dan taburan saiz liang menggunakan penyerapan nitrogen, pembelauan sinar-X

(XRD), mikroskopi elektron imbasan (SEM), mikroskopi elektron transmisi (TEM), plasma berganding aruhan (ICP), resonans magnet nuklear (NMR), inframerah transformasi Fourier (FTIR), analisis gravimetri terma (TGA), dan penyahjerapan pengaturcara suhu (TPD). MCM-41 dengan pascarawatan menunjukkan kestabilan hidroterma yang lebih baik berbanding dengan MCM-41 asal. Saiz liang bahan berliang meso LPMM bertambah daripada 2.9 kepada 4.2 nm dengan penggunaan mesitilena. SBA-15 mempunyai luas permukaan BET yang lebih besar dan saiz liangnya bertambah daripada 4.8 kepada 6.5 nm apabila aluminium diperkenalkan. Bahan komposit yang disediakan dengan kaedah berbenih membolehkan kawalan yang lebih baik terhadap nisbah berat fasa mikro/meso berbanding dengan kaedah penghabluran dua-langkah.

Mungkin HZSM-5 memaparkan penukaran lebih daripada 90 % berat dan 37–47 % berat hasil pecahan gasolin berbanding dengan zeolit Beta. MCM-41 dengan pascarawatan kurang memilih terhadap bahagian gasolin. Penambahan aluminium dalam SBA-15 meningkatkan penukaran dan kememilihan bahagian gasolin disebabkan peningkatan luas permukaan dan kebolehcapaian tapak-tapak aktif. Komposit MCM-41/ZSM-5 merupakan mungkin paling sesuai dalam peretakan FAM serta UPO dengan memberikan hasil bahagian gasolin dari 37 hingga 44 % berat.

Faktorial penuh 3^3 rekabentuk ujikaji telah digunakan untuk menyelidik kesan pelbagai keadaan operasi dalam peretakan FAM dan UPO masing-masing. Model kuadratik yang dicadangkan itu padan dengan data ujikaji dalam lingkungan 95% ketepatan. Model-model gabungan 3, 4 dan 6 telah digunakan untuk pengkajian kinetik bagi peretakan FAM dan UPO dengan HZSM-5 dan komposit MCM-41/ZSM-5. Nilai-nilai pemalar kadar peretakan FAM dengan mungkin komposit adalah lebih rendah berbanding dengan yang diperolehi dengan HZSM-5. Penukaran dan hasil produk-produk diperolehi daripada model gabungan 6 dan dibandingkan dengan data ujikaji.

ABSTRACT

Palm oil based fatty acids mixture (FAM) and used palm oil (UPO), low cost and renewable resources were explored for the production of liquid fuel using catalytic cracking process. The catalytic cracking reaction was studied at atmospheric pressure in a fixed bed micro-reactor at reaction temperature of 723 K and weight hourly space velocity (WHSV) of 2.5 h⁻¹. Microporous ZSM-5 catalyst with different Si/Al ratios and zeolite Beta, mesoporous aluminosilicates and composite micro-mesoporous materials were used as cracking catalysts.

Mesoporous molecular sieve MCM-41 was synthesized and post-treated using ion-exchange and impregnation method to improve its hydrothermal stability. Mesitylene was used as the pore expander for the synthesis of large pore mesoporous material (LPMM). SBA-15, another mesoporous material with thicker pore wall and better hydrothermal stability was synthesized under acidic condition. Composite MCM-41/zeolite (Beta/ZSM-5) was prepared using two different methods (a) seeding method (b) two-step crystallization. Seeding method was applied for the synthesis of SBA-15/ZSM-5. Macro-mesoporous composite material was prepared by coating LPMM with alumina. The metal ions were loaded in the composite MCM-41/ZSM-5 material by liquid and solid state ion exchange methods respectively. These materials were characterized for BET surface area and pore size distribution using nitrogen adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductive coupled plasma (ICP), nuclear magnetic resonance (NMR), Fourier transformed infra red (FTIR), thermal gravimetric analysis (TGA) and temperature programmed desorption (TPD). Post-treated MCM-41 showed improved

hydrothermal stability as compared to fresh MCM-41. The pore size of the mesophase in LPMM material increased from 2.9 to 4.2 nm with the addition of mesitylene. SBA-15 had large BET surface area and its pore size increased from 4.8 to 6.5 nm when aluminum was incorporated. The composite materials prepared via seeding method resulted in better control for the weight ratio of microphase/mesophase as compared to two-step crystallization.

HZSM-5 catalyst gave more than 90 wt% conversion and 37–47 wt% gasoline fraction yield as compared to zeolite Beta. The post-treated MCM-41 was less selective towards gasoline fraction. Incorporation of aluminum in SBA-15 enhanced both the conversion and selectivity of gasoline fraction due to the increase of surface area and improved accessibility to the active sites. Composite MCM-41/ZSM-5 was the most suitable catalyst in the cracking of FAM as well as UPO by giving gasoline fraction yield from 37 to 44 wt%.

3^3 full factorial design of experiments was used to study the effect of different operating conditions over FAM and UPO cracking respectively. The quadratic model proposed was in good agreement with the experimental data within 95% confidence. The 3-lump, 4-lump and 6-lump model were applied for the kinetic study of FAM and UPO cracking reaction over HZSM-5 and composite MCM-41/ZSM-5 respectively. The rate constant values for the cracking of FAM over composite catalyst were lower in magnitude compared to values obtained over HZSM-5. The simulated conversion and yield of products were obtained from 6-lump model and compared with the experimental data.

CHAPTER 1

INTRODUCTION

1.1 ALTERNATIVE RESOURCES

Transportation fuels are currently the main refinery products covering nearly 38% of world petroleum production (Anon, 1997). As crude oil resources eventually begin to deplete, there are large investments in developing alternative fuel engine (Kalam & Masjuki, 2002). The most common alternative fuels are compressed natural gas (CNG), liquefied natural gas (LNG), methanol, ethanol and hydrogen (fuel cell vehicle). However, instead of converting engine to run on alternative fuels in the future, the market is more willing to convert the alternative energy resources into synthetic liquid fuels that are similar to gasoline or diesel (Piel, 2001).

The conversion of hydrocarbon sources to produce fuels is one of the most significant developments. Yet, regulators, environmentalists and societies also demand for the environmentally sustainable development for the planet and at the same time looking for accelerating economic growth (Cusumano, 1995). As a consequence, several studies on the production of hydrocarbons from plant oils such as canola oil, tall oil and jojoba oil using cracking catalysts such as HZSM-5, silica alumina and their physical mixtures were reported (Sharma & Bakhshi, 1991; Katikaneni *et al.*, 1995; Adjaye *et al.*, 1996; Idem *et al.*, 1997). Most of these studies concentrated on developing alternative sources of hydrocarbons needed in a wide range of industrial applications.