SULFATED ZIRCONIA SUPPORTED ON SBA-15 FOR SELECTIVE GLYCEROL ESTERIFICATION WITH PALMITIC ACID TO MONOPALMITIN

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by

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CPO	Crude palm oil
CTAB	Cetyltrimethyl ammonium bromide
DAG	Diglyceride
EDX	Energy dispersive X-ray
FAME	Fatty acid methyl ester
FTIR	Fourier transformed infrared
G	Glycerol
GHG	Greenhouse gases
GMO	Glycerol monooeleate
GMP	Glycerol monopalmitate
HCl	Hydrochloric acid
HMF	5-hydroxymethyl-2-furfural
HPW	12-tungstophosporic acid
HRTEM	High resolution transmission electron microscopy
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
MAG	Monoglyceride
MCM-41	Mobile Composition of Matter No. 41
MPIC	Malaysia's Ministry of Plantation Industries and Commodities
NaOH	Sodium hydroxide
NH_3-TPD	Temperature-programmed desorption of ammonia
PA	Palmitic acid
PFAD	Palm fatty acid distillate
SBA-15	Santa Barbara Amorphous No. 15

SEM	Scanning electron microscopy
STP	Standard temperature and pressure
SZ	Sulfated zirconia
SZSBA-15	Sulfated zirconia supported SBA-15
TAG	Triglyceride
TBAB	Tetrabuthyl ammonium bromide
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
TPD	Temperature – programmed desorption
VIH	Vapor – induced hydrolysis
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbols	Description	Unit
A	Pre-exponential factor	$L\cdot mol^{-1}g_{cat}^{-1}h^{-1}$
A_i	Peak area of mono, di- or tripalmitin in the sample	Dimensionless
A_{IS}	Peak area of internal standard	Dimensionless
$A_{SD,i}$	Peak area of mono, di- or tripalmitin in the standard reference	Dimensionless
C_G	Concentration of glycerol	mol/L
C_i	Concentration of mono-, di- or tripalmitin	mol/L
C_{PA}	Concentration of palmitic acid	mol/L
C_{PAO}	Initial concentration of palmitic acid	mol/L
$C_{SD,i}$	Concentration of mono-, di- or tripalmitin for standard reference	mol/L
D_f	Dilution factor	Dimensionless
E_a	Activation energy	kJ/mol
H_o	Hammett acidity function	Dimensionless
k_s	Specific rate constant	$L\cdot mol^{-1}h^{-1}$
M	Molar ratio	Dimensionless
R	Universal gas constant	$cal\cdot K^{-1}\cdot mol^{-1}$
r_{PA}	Rate of reaction	$mol\cdot g_{cat\cdot}^{-1}\cdot h^{-1}\cdot L^{-1}$
R_{SD}	Ratio of peak area of mono-, di- or tripalmitin in the standard reference to peak area of the internal standard	Dimensionless
S_{Mono}	Selectivity of monopalmitin	Dimensionless
S_{Di}	Selectivity of dipalmitin	Dimensionless
S_{Tri}	Selectivity of tripalmitin	Dimensionless
t	Time	h

T	Temperature	K
W	Weight of catalyst	g
X_{G0}	Initial glycerol conversion	Dimensionless
X_{PA}	Conversion of palmitic acid	Dimensionless
X_{PA0}	Initial palmitic acid conversion	Dimensionless
Y_M	Monopalmitin yield	Dimensionless

ZIRKONIA TERSULFAT BERPENYOKONG SBA-15 UNTUK PENGESTERAN TERPILIH GLISEROL DENGAN ASID PALMITIK KEPADA MONOPALMITIN

ABSTRAK

Peningkatan pesat dalam pengeluaran biodiesel di Malaysia menjana lebihan gliserol mentah sebagai produk utama yang mempunyai aplikasi yang terhad dalam industri tempatan. Berdasarkan keadaan semasa, penukaran gliserol kepada produk bernilai tinggi seperti monogliserida adalah satu alternatif yang menarik. Dalam kajian ini, mangkin meso liang SZSBA-15 telah disintesis dengan muatan zirkonia (5 – 20 % berat) dan suhu pengkalsinan akhir (450 – 650 ^oC) yang berbeza. Mangkin-mangkin yang disintesis telah dicirikan melalui analisis permukaan, SEM, TEM, XRD, FTIR, EDX, TGA, NH_3-TPD dan penentuan keasidan melalui titratan. Ciri-ciri mangkin tersebut kemudiannya dikaitkan dengan aktiviti mangkin dalam pengesteran gliserol dengan asid palmitik dan prestasinya ditunjuk berdasarkan penukaran asid palmitik dan hasil monopalmitin. Kesan keadaan tindak balas seperti masa (1 – 6 jam), kadar aliran N_2 (5 – 40 cm^3/min), suhu tindak balas (160 – 180 ^oC), muatan mangkin (1 – 3 % berat), nisbah bilangan mol gliserol/asid palmitik (2:1 – 6:1) juga dijelaskan dan dikaitkan dengan ciri-ciri mangkin. Didapati bahawa mangkin SZSBA-15 yang disediakan menggunakan 10 % berat muatan zirkonia dan dikalsin pada 500 ^oC (10SZSBA-15(500)) menunjukkan aktiviti yang tinggi dalam penghasilan monopalmitin. Peningkatan masa tindakbalas, kadar aliran N_2, suhu tindakbalas dan muatan mangkin telah meningkatkan penukaran asid palmitik. Sebaliknya, perubahan dalam penukaran asid palmitik tidak ketara apabila nisbah bilangan mol melebihi 4:1.

Tambahan pula, keadaan tindak balas terbaik telah diperolehi pada masa tindak balas 3 jam, suhu tindak balas 170 °C, muatan mangkin 2 % berat dan nisbah gliserol/asid palmitik 4:1. Di bawah keadaan ini menggunakan mangkin 10SZSBA-15(500), sebanyak 86 % penukaran asid palmitik dan 43 % hasil monopalmitin telah diperolehi. Dari segi kebolehgunaan semula, mangkin ini boleh digunakan semula sehingga empat kali dalam tindak balas ini dengan sedikit penurunan dalam aktiviti pemangkin. Ini disebabkan oleh kehilangan kumpulan sulfur daripada mangkin. Walau bagaimanapun, struktur liang tidak terjejas setelah empat kitaran pemangkin. Pengesteran gliserol dengan asid palmitik didapati menepati model kinetik tertib kedua terhadap gliserol dan asid palmitik dengan tenaga pengaktifan yang rendah sebanyak 38.2 kJ/mol. Sebagai kesimpulan, mangkin 10SZSBA-15(500) yang menunjukkan aktiviti yang baik merupakan mangkin aktif dan sesuai digunakan dalam tindak balas melibatkan molekul-molekul besar.

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ABSTRACT

The rapid increase of biodiesel production in Malaysia generates an excess of crude glycerol as the primary co-product which has limited application in local industries. Based on the current situation, the conversion of glycerol to higher value products like monoglyceride is an attractive alternative. In the present work, mesoporous SZSBA-15 catalyst has been synthesized with different zirconia loadings (5 - 20 wt. %) and final calcination temperatures (450 – 650 ^{o}C). The synthesized catalysts were characterized by means of surface analysis, SEM, TEM, XRD, FTIR, EDX, TGA, NH_3-TPD and determination of acidity by titration. The characteristics of the catalyst were then correlated with the catalytic activity in glycerol esterification with palmitic acid and the performance was demonstrated based on the palmitic acid conversion and monopalmitin yield. Effects of reaction conditions such as time (1 – 6 h), N_2 flow rate (5 – 40 cm^3/min), reaction temperature (160 – 180 ^{o}C), catalyst loading (1 – 3 wt. %) and glycerol/palmitic acid molar ratio (2:1 – 6:1) were also elucidated and correlated with the characteristics of the catalysts. It was found that SZSBA-15 catalyst prepared using 10 wt. % of zirconia loading and calcined at 500 ^{o}C (10SZSBA-15(500)) demonstrated high activity in the production of monopalmitin. An increase in the reaction time, nitrogen flow rate, reaction temperature and catalyst loading increased the conversion of palmitic acid. On the contrary, changes in the palmitic acid conversion were insignificant when the molar ratio exceeded 4:1. On top of that, the best reaction conditions were obtained at a reaction time of 3 h, a reaction temperature of 170 ^{o}C, 2 wt. % of catalyst loading and 4:1 of glycerol/palmitic acid molar ratio. Under these conditions using 10SZSBA-15(500) catalyst, 86 % of palmitic acid conversion and 43 % monopalmitin yield were obtained. In terms of reusability, this catalyst was reusable for up to four times in this reaction with slight decrease in the catalytic activity. This was attributed to the loss of sulfur groups from the catalyst. Nevertheless, the pore structure remained unaffected after four catalytic cycles. The glycerol esterification with palmitic acid was found to follow a second order kinetic model with respect to glycerol and palmitic acid with a low activation energy of 38.2 kJ/mol. As a conclusion, 10SZSBA-15(500) catalyst which exhibited good activity was as an active catalyst and suitable to be used in the reaction involving bulky molecules.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Energy is one of the essential inputs for economic, social and industrial development of any nation. A sustainable and continuous supply of energy resources is essential to maintain and improve the socio-economic conditions. However, in the current era of energy shortage, conventional energy sources which are mainly derived from fossil fuels are depleting at very fast rate. They are also facing major challenges with respect to high price and environmental problems such as emission of greenhouse gasses (GHG). In the light of current and future status of energy demand coupled with the availability of fossil fuel resources and their environmental impacts, Malaysia along with international communities are in urgent search for alternative energy resources.

1.1.1 Surplus of glycerol from biodiesel overproduction

Biodiesel which comes from renewable resource has been gaining more attention as an alternative fuel option for future due to its enormous resources, environmental benefits and potential as a substitute for petroleum-based diesel fuels (Yusoff *et al.*, 2013). In Malaysia, as of October 2011, a total of 60 palm oil-based biodiesel manufacturing licenses had been approved by the Malaysia's Ministry of Plantation Industries and Commodities (MPIC) with a total annual capacity of 6.79 million tonnes. Until recently, there were 11 active biodiesel plants in the country with a total capacity of 1.65 million tonnes per year (Kheang and May, 2012).