SYNTHESIS AND CHARACTERIZATION OF PLATINUM-ZIRCONIUM CATALYST SUPPORTED ON BICONTINOUS LAMELLAR SILICA MORDENITE FOR *n*-HEXANE HYDROISOMERIZATION

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ABSTRACT

Catalytic hydroisomerization of *n*-alkane has been one of the vital processes in the petroleum refining industry to improve the quality of gasoline. The existing catalysts have registered low isomerization performance due to the poor accessibility of active sites for the reactant molecules and the strong acid sites tend to be more selective towards cracking, thus affecting the overall efficiency of the process. This study investigated the catalytic performance of modified mordenite zeolite in *n*-hexane hydroisomerization. A novel protonated mordenite catalyst with bicontinuous lamellar morphology (HM@KCC-1) was successfully prepared via a microemulsion system with a mordenite seed-assisted crystallization technique. Platinum (Pt) was loaded by wet impregnation method and the catalytic performance was compared with Pt supported on commercial mordenite zeolite. The catalysts were characterized with X-ray diffraction, field emission scanning microscopy, transmission electron microscopy (TEM), surface area analyzer and electron spin resonance spectroscopy. The acidity was determined by pyridine and 2,6-lutidine adsorbed Fourier transformation infrared (FTIR) spectroscopy, while the catalytic performance was conducted in a microcatalytic pulse reactor at 150-350 °C under a hydrogen stream. The higher catalytic activity of Pt/HM@KCC-1 was achieved with 75% conversion, 98% isomer selectivity and 74% isomer yield compared to Pt/HM with 60% conversion, 40% isomer selectivity and 24% isomer yield at 300 °C. This was attributed to the well-dispersed Pt nanoparticles on the bicontinuous lamellar structure of HM@KCC-1 evidenced from the TEM images and the moderate acid sites on Pt/HM@KCC-1 as shown by FT-IR which favoured the dehydrogenation/hydrogenation function and the skeletal isomerization, respectively. Furthermore, the effect of zirconium (Zr) incorporation was investigated with different Zr loading (1, 5, 10wt %) on HM@KCC-1. The results showed formation of permanent Lewis acid sites which was selective towards the generation of mono-branched isomers. Hence, Zr has great potential as a promoter with 5Zr/HM@KCC-1 exhibiting the best catalytic performance. Zr as a promoter in Pt/5Zr-HM@KCC-1 was prepared by impregnation with 0.5wt % Pt. The isomer yield followed the order of Pt/5Zr-HM@KCC-1(86) > Pt/HM@KCC-1(74) > 5Zr-HM@KCC-1(60), best catalyst showed remarkable increased strength of Lewis acid sites and selectivity towards the di-branched isomer. Zr evidently enhanced the formation of molecular hydrogen-generated protonic acid sites which plays an important role in the hydroisomerization process. The optimum isomer yield for the *n*-hexane hydroisomerization obtained by response surface methodology was 85.7% at a reaction temperature of 293 °C, reduction temperature of 474 °C and flow of hydrogen over catalyst weight of 502 $ml.g^{-1}min^{-1}$. The experiment carried out at these optimum conditions yielded 84.1% isomer with 1.9% error. This study has highlighted the efficient design of Zr promoted Pt on HM@KCC-1 catalyst with appropriate metal/acid sites functions for hydroisomerization. In conclusion, the promising performance of PtZr/HM@KCC-1 catalyst demonstrated the potential to be used for the production of high-quality fuel, particularly for *n*-alkane hydroisomerization in the refining processes.

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ABSTRAK

Pengisomeran hidro n-alkana bermangkin telah menjadi salah satu proses penting dalam industri penapisan petroleum untuk meningkatkan kualiti petrol. Mangkin sedia ada telah mencatatkan prestasi isomerisasi yang rendah disebabkan oleh kebolehcapaian tapak aktif yang lemah untuk molekul reaktan dan tapak asid yang kuat lebih cenderung memilih terhadap keretakan, sekali gus menjejaskan kecekapan keseluruhan proses. Kajian ini dikendalikan untuk mengkaji prestasi pemangkin zeolit mordenit yang diubahsuai pada pengisomeran hidro n-heksana. Pemangkin mordenit berproton baharu dengan morfologi lamela dwiselanjar (HM@KCC-1) telah berjaya dihasilkan dengan menggunakan sistem mikroemulsi dengan dibantu oleh teknik penghabluran benih mordenit. Platinum (Pt) telah dimuatkan menerusi kaedah impregnasi basah dan prestasi pemangkinan telah dibandingkan dengan Pt yang disokong pada zeolit mordenit komersial. Mangkin-mangkin ini telah dicirikan dengan pembelauan sinar-X, mikroskopi elektron imbasan pancaran medan, mikroskopi penghantaran elektron (TEM), penganalisa luas permukaan dan spektroskopi resonans putaran elektron. Keasidan telah ditentukan menggunakan piridin dan 2,6-lutidin dijerap spektroskopi inframerah transformasi Fourier (FTIR), manakala prestasi pemangkinan dilakukan dalam reaktor denyut bermangkin mikro pada 150-350 °C dalam aliran hidrogen. Aktiviti pemangkinan yang lebih tinggi menggunakan Pt/HM@KCC-1 telah dicapai dengan 75% penukaran, 98% selektiviti isomer dan 74% hasil isomer berbanding Pt/HM dengan 60% penukaran, 40% selektiviti isomer dan 24% hasil isomer pada 300 °C. Ini adalah disebabkan oleh nanopartikel Pt yang tersebar dengan baik pada struktur lamela HM@KCC-1 yang dibuktikan daripada imej TEM dan tapak asid yang banyak di Pt/HM@KCC-1 seperti yang ditunjukkan oleh FTIR yang masing-masing cenderung terhadap fungsi nyah hidrogenasi /hidrogenasi dan isomerisasi rangka. Tambahan pula, kesan penggabungan zirkonium (Zr) telah diselidiki dengan kandungan muatan Zr yang berbeza (1,5,10% berat) pada HM@KCC-1. Keputusan menunjukkan pembentukan tapak asid Lewis kekal yang terpilih ke arah penghasilan isomer bercabang-satu. Oleh itu, Zr mempunyai potensi tinggi sebagai pengalak dengan 5Zr/HM@KCC-1 yang mempamerkan prestasi bermangkin terbaik. Zr sebagai pengalak dalam Pt/5Zr-HM@ KCC-1 telah disediakan menggunakan impregnasi dengan 0.5% berat Pt. Hasil isomer mengikut susunan adalah Pt/5Zr-HM@ KCC-1 (86)> Pt/HM@ KCC-1 (74)> 5Zr-HM@KCC-1 (60), mangkin terbaik menunjukkan peningkatan kekuatan tapak asid Lewis dan selektiviti yang luar biasa terhadap isomer bercabang-dua. Zr terbukti meningkatkan pembentukan tapak asid proton yang dihasilkan oleh molekul hidrogen yang memainkan peranan penting dalam proses pengisomeran hidro. Hasil isomer optimum untuk pengisomeran hidro n-heksana yang diperolehi melalui kaedah gerakbalas permukaan adalah 85.7% pada suhu tindak balas 293 °C, suhu penurunan 474 °C dan aliran hidrogen ke atas berat mangkin, 502 $ml.g^{-1}min^{-1}$. Eksperimen yang dijalankan pada keadaan optimum ini menghasilkan 84.1% isomer dengan ralat 1.9%. Kajian ini menyerlahkan pembuatan Zr yang efisien dibantu oleh Pt pada mangkin HM@KCC-1 dengan fungsi tapak logam/asid yang sesuai untuk pengisomeran hidro. Kesimpulannya, prestasi mangkin PtZr/HM@KCC-1 yang menggalakkan menunjukkan potensi untuk digunakan dalam pengeluaran bahan api berkualiti tinggi, terutamanya untuk pengisomeran hidro n-alkana dalam proses penapisan.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AKI	-	Anti-knock Index
ANOVA	-	Analysis of variance
AR	-	Analytical grade
BET	-	Brunauer-Emmett-Teller
CCD	-	Central Composite Design
CTAB	-	Cetyltrimethylamminium bromide
DF	-	Degree of freedom
DFT	-	Density functional theory
DOE	-	Design of experiment
Ea	-	Activation energy
EG	-	Ethylene glycol
ESR	-	Electron Spin Resonance
FD	-	Factorial design
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier-Transform Infrared
GC	-	Gas Chromatography
IUPAC	-	International Union of Pure and Applied Chemistry
JCPDS	-	Joint Committee on Powder Diffraction Standards
KBr	-	Potassium Bromide
KCC-1	-	KAUST Catalytic Centre one
NLDFT	-	Non-local density functional theory
NMR	-	Nuclear magnetic resonance
RSM	-	Response surface methodology
SS	-	Sum of Squares
SSR	-	Sum of Squares Regression
TEM	-	Transmission Emission Spectroscopy
TEOS	-	Tetraethyl Orthosilicate
TPR	-	Temperature Programmed Reduction
UV-VIS	-	Ultra Violet Visible Spectrophometer
XRD	-	X-ray diffraction

LIST OF SYMBOLS

nm	-	nanometer
wt %	-	weight percent
h	-	Hour
2θ	-	Bragg angle
s	-	Second
λ	-	wavelength
W	-	Watts
g	-	gram
°C	-	degree Celcius
min	-	minutes
K	-	Kelvin
mL	-	millilitre
P	-	pressure

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Recently, global concern on the environment and health has led to new stringent legislative policies regarding gasoline. Gasoline contains mainly C4-C10 hydrocarbons, with a significant portion composed of linear alkanes. Although several processes such as catalytic cracking, reforming and alkylation have been employed to improve the octane number, current gasoline specifications being implemented worldwide impose a strong restriction on limiting the amount of aromatic and olefin compounds in gasoline (Zhang *et al.*, 2018a). Decreasing the quantity of these compounds has resulted in negative effects on the anti-knocking properties of gasoline that have to be compensated with other environmentally clean technologies. The need for high-quality gasoline has prompted a search for new technologies to improve the existing process in oil refineries and industries.

In this regard, the hydroisomerization of linear alkanes to branched isomers has generated great interest in modern refining industries. The process has proved to be an effective strategy to transform linear alkanes with a low octane number to their corresponding branched-isomers with a high octane number sufficient to improve fuel quality (Chica and Corma, 1999; Galadima and Muraza, 2015; Pinto *et al.*, 2016). Hydroisomerization is a better option compared with other technologies proven to be perilous to the environment.

The hydroisomerization of *n*-alkanes proceeds by the classical bifunctional metal-acid mechanism. It involves the de/hydrogenation of the *n*-alkane on the metal sites and the skeletal rearrangement of the intermediate alkenes on the acid sites (Ono, 2003). Besides, hydrogen plays a vital role in *n*-alkane hydroisomerization in the generation of protonic acid sites by the hydrogen spill-over phenomena (Triwahyono

et al., 2007; Hattori, 2016). Hydrogen molecules split on the metal sites to form hydrogen atoms which then diffuse on the acid support and release their electrons to the Lewis acid sites, thereby forming protonic (Brønsted) acid sites. These acid sites participate in the reaction as the active sites, thus improving the catalytic performance (Hattori, 2016). Active protonic acid sites are involved in skeletal rearrangement to maintain high activity and stability of the catalysts (Li *et al.*, 2017). Besides, catalyst stability is also improved by the hydrogenation process to decrease coke deposition.

Several researchers have reported various types of acidic supports to include metal oxides and zeolites for the hydroisomerization process. Among which zeolites are the most promising due to their unique properties. Besides, different topologies of zeolite support such as SAPO-11, ZSM-22, ZSM-5, HY, HBEA and MOR have been widely applied for the hydroisomerization of *n*-alkanes. However, zeolites as support materials suffer several drawbacks which mainly include high diffusional limitation, easy catalyst deactivation and consequently low selectivity to bulky isomer products. Several strategies for the preparation of mesoporous zeolites have been reported, post-synthetic methods (top-down approach) such as demetallation which includes dealumination and desilication, hard-templating and soft-templating strategies (bottom-up approaches) (Schwieger *et al.*, 2016). Post-synthetic demetallation led to the loss of acidic sites by partial destruction of the zeolitic structure while the hard templating is expensive, often time-consuming and the constricted synthesis method is capable of not relinquishing any microporosity and acidity of parent zeolites during the formation of mesopores (Zhang and Ostraat, 2016). Soft-templating strategies represent the most attractive and efficient approach in the synthesis of mesoporous zeolites. It involves using surfactants which usually results in extensive mesoporosity with highly controllable structures. Thus, extensive efforts are being made to develop new catalysts with improved performance to achieve better mass transfer and a higher number of exposed active sites.

Typically, the mesoporous BEA (Musselwhite *et al.*, 2015), USY (Denayer *et al.*, 2000), ZSM-5 (Parsafard *et al.*, 2014), SAPO 11 (Zhang *et al.*, 2018a), ZSM-22 (Martens *et al.*, 2013) and even MOR (Monteiro *et al.*, 2014) were reported as good

hydroisomerization supports**.** However, these materials exhibited several drawbacks that include loss of acidity and low surface area.

Among the various zeolites with different topology which have been explored for hydroisomerization, mordenite zeolites with high thermal stability and tunable acidity has been very promising as supports in the hydroisomerization of *n*-alkanes (Monteiro *et al.*, 2014; Pastvova *et al.*, 2017; Pastvova, Pilar, Moravkova, Kaucky and Rathousky, 2018; Sazama *et al.*, 2018). Noble metals such as Pt, Pd and non-noble metals (Ni, Zn, Mo, Ga and Zr) have been utilized in *n*-alkane hydroisomerization. Particularly, Pt supported catalysts have been reported to be selective and stable in hydroisomerization. Accordingly, the isomerization of C6-C7 over Zr-Al-MCM-41 showed enhanced activity which was attributed to the appropriate proximity of Lewis acid sites that strengthened the strong Brønsted acid sites (Eswaramoorthi *et al.*, 2004). The isomerization selectivity to multibranched isomers for both *n*-hexane and *n*-heptane was higher for Zr containing Al-MCM-41 than Al-MCM-41 without zirconium.

Nonetheless, to date, there are no reports available regarding the modification of mordenite with bicontinuous concentric lamellar silica KCC-1 type material and incorporation of zirconium. In this thesis, bicontinuous lamella silica mordenite (HM@KCC-1) was used as the platinum support and *n*-hexane hydroisomerization was chosen as a model reaction. In addition, the physicochemical properties and catalyst activity of Pt/HM@KCCC-1 were compared with Pt/HM, since Pt is well known as an active noble metal for *n*-alkane hydroisomerization. The KCC-1 incorporation on mordenite modified the acidity to be moderate which facilitated the formation of isohexane in correlation with its catalytic activity. The presence of bicontinuous lamellar morphology and interparticle textural porosity contributing to a high surface area and large pore diameter of HM@KCC-1, which opens a new design possibility for a catalyst to with highly accessible active sites, which led to high selectivity towards isomerization suppressing the competing cracking reaction. Also, the influence of Zr as a promoter in *n*-hexane hydroisomerization was investigated by employing the bicontinuous concentric lamellar silica KCC-1 mordenite with zirconia. It was expected that the interaction of Zr with bicontinuous concentric lamellar silica

KCC-1 on mordenite would generate Lewis acid sites to improve the catalytic activity and selectivity. Further modification of Pt/HM@KCC-1 with zirconium to form PtZr/HM@KCC-1 was expected to enhance the hydroisomerization performance to obtain more di-branched isomers as it plays an important role in the generation of protonic acid sites via hydrogen spillover phenomena thus, enhancing the catalytic performance. The optimization of the *n*-hexane hydroisomerization process over PtZr/HM@KCC-1 was carried out using the response surface methodology (RSM).

1.2 Problem Statement and Hypothesis

In recent times, global energy demand has continued to increase due to the rapid growth in the world's population and the expansion of developing-world economies. Although fossil fuel will remain the major source of energy for the next few decades, environmental concerns have led to stringent policies to reformulate gasoline composition in order to improve fuel quality. The required quality of fuel can be achieved through progressive improvements in technology to increase product quality while minimizing undesirable effects on the environment. In an effort to address this problem, the hydroisomerization of linear alkanes has proved to be an effective industrial process to improve the octane number of gasoline. The product consists of branched alkanes with a considerably higher octane number than the corresponding linear alkanes. It is one of the key environmentally friendly processes employed to achieve high-quality clean gasoline, thereby meeting the required specifications of good fuel quality.

Industrial hydroisomerization catalysts are noble or transition metals supported on solid acids. These catalysts are bifunctional consisting of metallic and acidic functions. A suitable catalyst capable of high global conversion of *n*-alkanes and high selectivity to multi-branched isomers requires a proper choice of metal, as well as acidic functions for the hydroisomerization process. The current efficiency of refining and petrochemical industries is largely based on the use of highly active and durable catalysts, zeolites being the typical illustration of solid acids with large surface area as supports for developing environmentally benign processes. However, zeolite-based

catalysts suffer diffusional limitations and tend to be more selective towards the undesired cracking reaction because of their microporosity and strong acidity. Among the zeolite materials, mordenite is widely investigated in hydroisomerization due to its favourable properties such as high acidity, high thermal stability, shape selectivity, resistance to coke formation and high activity at moderate temperatures, but the hydroisomerization products are predominantly of mono-branched components, while the di-branched isomers are of essential importance for desired gasoline properties.

Recently considerable efforts have been made by researchers to improve the accessibility of active sites and molecular transport to and from active sites by introduction of micro-mesoporous materials. Although the development of hierarchical mordenite has been reported to enhance the diffusion of reacting species, the catalytic activity can still be improved by modifying the acidity to achieve a good balance in the metal/acid function. These are the two important parameters that can influence the extent of hydroisomerization reaction as well as the selectivity to the bulkier multi-branched products.

The main focus of this research is to design a new catalyst system to efficiently convert linear alkanes to high octane number branched alkanes. It was hypothesized that the incorporation of bicontinuous lamellar silica with mordenite could introduce mesoporosity to provide good accessibility of active sites and good metal dispersion as well as modify the acidity. This is due to the morphological changes, thus achieving suitable metal and acid functions in the dehydrogenation/hydrogenation and skeletal rearrangement in the hydroisomerization process. The addition of zirconium as a promoter would result in increased Lewis acidity which stabilizes the electron in the generation of protonic acid sites. These protonic acid sites could enhance the selectivity towards di-branched isomers.

1.3 Objectives of the Study

The objectives of this study are:

1. To prepare and characterize bicontinuous lamellar silica mordenite and compare its performance with commercial mordenite as a support for platinum in *n*-hexane hydroisomerization.

2. To investigate the influence of zirconium loading on HM@KCC-1 and Pt/HM@KCC-1 and study the reaction mechanism over PtZr/HM@KCC-1 in *n*-hexane hydroisomerization.

3. To optimize the *n*-hexane hydroisomerization process using response surface methodology (RSM).

1.4 Scope of the Study

This study is focused on designing hydroisomerization catalysts to solve the fundamental problems pertaining to low process efficiency. In this perspective, the effect of the incorporation of bicontinuous lamellar silica onto mordenite was compared with commercial mordenite as support for platinum, effect of zirconium loading on HM@KCC-1 and zirconium as a promoter on Pt/HM@KCC-1 in *n*-hexane hydroisomerization. Furthermore, the reaction mechanism and optimization of the *n*-hexane hydroisomerization process have been elucidated. The *n*-hexane hydroisomerization process efficiency is related to maximize the yield for multi-branched isomers thereby limiting the cracking selectivity. Therefore, the details of research scope are described as follows:

(a) The effect of the incorporation of KCC-1 on mordenite and the comparison of its performance with commercial mordenite both with and without platinum was investigated in the hydroisomerization of *n*-hexane. In this study,bicontinous lamellar silica mordenite was prepared as reported by previous protocols using water in oil microemulsion method with cetyltrimethylammonium bromide (CTAB) as a surfactant, butanol as a co-surfactant and toluene as the oil phase (Firminyansi *et al*., 2016). Incipient wetness impregnation method was chosen to load 0.5 wt% Pt based on literature reports (Musselwhite *et al*., 2016). The prepared catalysts were

characterized by X-Ray diffraction (XRD), N_2 physisorption, Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscope (TEM) in order to investigate the phase and crystal structure, surface area and pore size distribution and surface morphology and mesoporosity. Investigation of the nature and strength of acid sites was done by using Fourier Transform Infrared (FTIR) spectroscopy of preadsorbed pyridine, and 2,6-dimethylpyridine and the chemical environments was investigated by Electron Spin Resonance (ESR) Spectroscopy. Catalytic testing for *n*-hexane hydroisomerization was carried out at a temperature range of 150-350 °C under atmospheric pressure (Fatah *et al*., 2016). However, this application is limited to the operative pressure of the fixed bed reactor is 1 atm.

(b) The effect of zirconium loading on HM@KCC-1 and zirconium as a promoter on Pt/HM@KCC-1 in *n*-hexane hydroisomerization was investigated. A series of catalysts with different Zr loading (1, 5 and 10 wt %) were prepared using the incipient wetness impregnation method. The amount of zirconium was in the range stated based on literature (Triwahyono *et al.,* 2018) and preliminary studies on the catalytic activity evaluation using different zirconium loading. The prepared catalysts were characterized by XRD, N_2-physisorption, FESEM, TEM and 2,6-dimethylpyridine-FTIR. Catalytic testing on *n*-hexane hydroisomerization was carried out at temperature range of 150-350 °C and at atmospheric pressure. The mechanism of *n*-hexane hydroisomerization over different zirconium loaded PtZr/HM@KCC-1 was studied using in situ 2,6-dimethylpyrine + H_2 (Izan *et al.,* 2018) and *n*-hexane + H_2 FTIR spectroscopy (Kondo *et al*., 2007).

(c) The optimal conditions for the *n*-hexane hydroisomerization process were determined by RSM using a Central Composite Design (CCD) developed by Statistica 6.0 StatSoft. The independent variables selected in the study are reaction temperature (250-350 °C), treatment temperature (400-500 °C) and flow of hydrogen over the weight of catalyst (475-525 ml/gmin) while the response is the isomer yield obtained from the catalytic performance evaluated in *n*-hexane hydroisomerization. These variables were selected based on the previous results from the literature and the preliminary analysis conducted

prior to the main study (Ruslan *et al*., 2012, Fatah *et al.*, 2017, Setiabudi *et al.*, 2013).

1.5 Significance of the Study

In this study, a novel catalyst, bicontinuous lamellar silica mordenite was prepared for the *n*-hexane hydroisomerization. As compared to the commercial mordenite, HM@KCC-1 has a bicontinuous lamellar morphology. This unique morphology modified the properties of the catalyst to have high thermal stability, moderate acidity and allows diffusion of bulky hydroisomerization products. A detailed comparison study on the property-activity relationship of Pt supported on HM/KCC-1 and HM was carried out. In addition, the effect of zirconium loading was investigated. Furthermore, the catalytic activity of PtZr/HM@KCC-1 and mechanism for *n*-hexane hydroisomerization was studied. Optimization by response surface methodology highlighted the factors affecting the hydroisomerization process. This study will have a significant contribution to scientific research and innovation, especially in the development of a new catalyst for *n*-alkane hydroisomerization.

1.6 Thesis Outline

This thesis begins with Chapter one which described the research background, problem statement and hypothesis, objectives, scope and significance of the study. Chapter two reviewed the literature related to the catalysts and the recent progress on the hydroisomerization of *n*-alkanes. Chapter three described the step by step experimental procedure and characterization techniques for synthesized catalysts and *n*-hexane hydroisomerization. While chapter four presented data processing and discussion on physicochemical properties and catalytic performance of the catalysts. Finally, conclusions and recommendations for future research were highlighted in Chapter 5.

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APPENDIX A

Calculation of Percentage of Platinum (Pt) and Zirconium (Zr)

Taking the amount of catalyst HM@KCC-1 as 1g and 0.5 wt% of Pt as desired amount of Pt, the calculation was as follows,

Mass of Pt needed,

$$0.5\text{wt\% Pt} = \frac{\text{x g Pt}}{\text{1 g HM@KCC-1 + x g Pt}}$$

$$\text{x g Pt} = 5.025 \times 10^{-3} \text{ g Pt}$$

With MW Pt = 195.084 g $mole^{-1}$ and MW Pt solution = 517.9 g $mole^{-1}$

Mole of Pt needed,

$$\text{g Pt solution} = \frac{517.9 \text{ g mole}^{-1} \text{ Pt solution}}{195.084 \text{ g mole}^{-1} \text{ Pt}} \times 5.025 \times 10^{-3} \text{ g Pt}$$

$$= 1.3340 \times 10^{-2} \text{ g Pt solution}$$

With concentration of Pt solution = 9.6782 g/ 100 mL

Volume of Pt needed,

$$\text{mL Pt solution} = \frac{1.3340 \times 10^{-2} \text{ g Pt solution}}{9.6782 \text{ g/ 100 mL}}$$

$$= 0.1378 \text{ mL Pt solution}$$

Thus, 0.1378 mL of Pt solution is needed to prepare 0.5 wt% Pt on 1 g HM@KCC-1.

Taking the amount of HM@KCC-1 as 1g and 5 wt % of Zr, the calculation is as follows,

Mass of Zr needed,

Mass of Pt needed,

$$5\ \text{wt\% Zr} = \frac{x\ \text{g Zr}}{1\ \text{g HM@KCC-1} + x\ \text{g Zr}}$$

$$x\ \text{g Zr} = 0.0526\ \text{g Zr}$$

With MW Zr = 91.224 g $mole^{-1}$ and MW $ZrOCl_2.H_2O$ = 322.252 g $mole^{-1}$

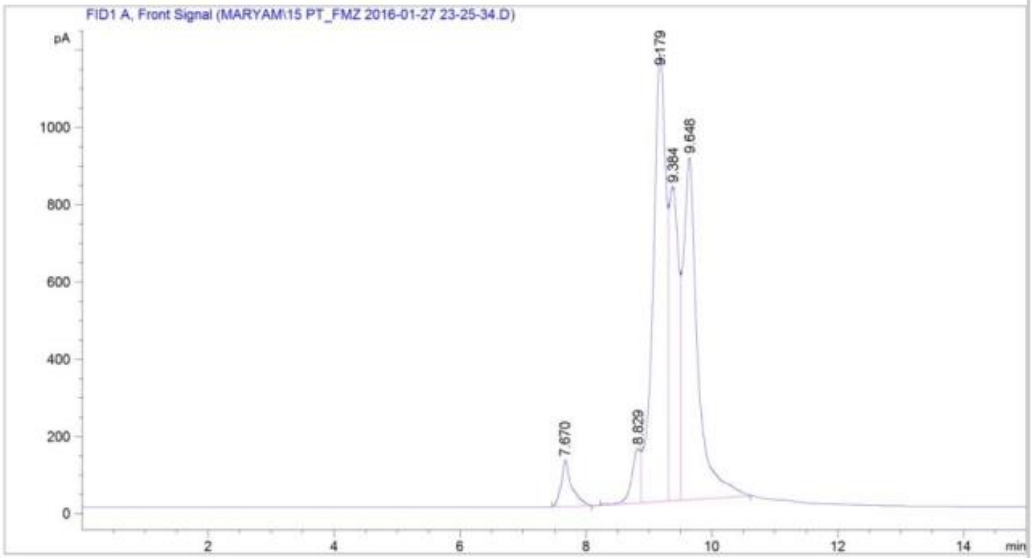
$$\text{g } ZrOCl_2.H_2O = \frac{322.252\ \text{g mole}^{-1}\ ZrOCl_2.H_2O}{91.224\ \text{g mole}^{-1}\ Zr} \times 0.0526\ \text{g Zr}$$

$$= 0.1858\ \text{g } ZrOCl_2.H_2O$$

Thus, mass of $ZrOCl_2.H_2O$ needed to prepare 5 wt% Zr on 1 g HM@KCC-1 is 0.1858 g $ZrOCl_2.H_2O$.

Appendix B

Raw Data For *n*-Hexane Hydroisomerization

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========================================================================
                        Area Percent Report
========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   7.670 BB    0.1603 1408.44055  119.16608  3.32507
   2   8.829 BV    0.1380 1390.48132  140.27710  3.28267
   3   9.179 VV    0.1895 1.65233e4  1159.17566 39.00850
   4   9.384 VV    0.1368 8534.38477  813.16589 20.14809
   5   9.648 VB    0.2134 1.45016e4   885.90479 34.23567

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Appendix C

Calculation for Catalytic Activity

Based on the raw data in Appendix B, the calculation of conversion, selectivity and yield of a particular product was calculated as below:

$X_{n\text{-hexane}}$

$$= \frac{1408.4+1390.5+16523.3+8534.4}{1408.4+1390.5+16523.3+8534.4+14501.6} \times 100$$

$$= 66\%$$

Selectivity of isomer was calculated as follows:

$$= \frac{1390.5+16523.3+8534.4}{1408.4+1390.5+16523.3+8534.4+14501.6} \times 100$$

$$= 95\%$$

And the yield,

$$= \frac{66 \times 95}{100}$$

$$= 63\%$$

Appendix D

Kinetic study

Calculation of Rate Constant, K

The rate constant, k was calculated according to the following equation:

$$k = \frac{\text{no. of mole } n\text{-hexane (mole)}}{\text{Weight of catalyst (g) x time of pulse } (s^{-1}) \text{x surface area}}$$

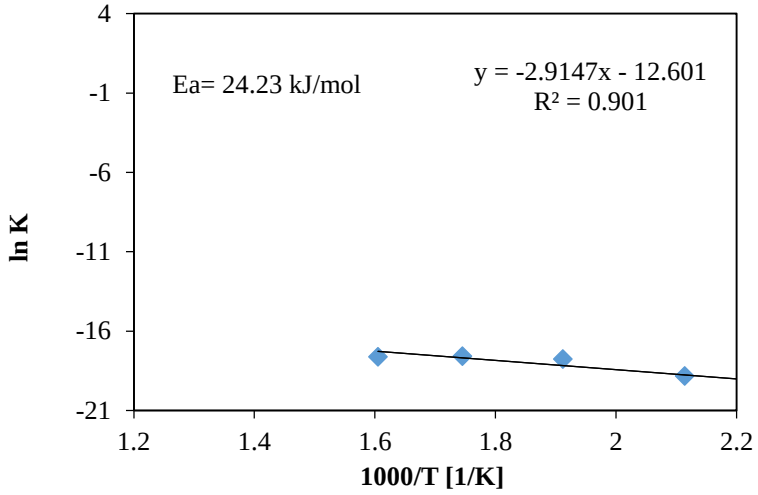
With the mole of *n*-hexane = 6.83×10^{-6}, the value of surface area is 679 m^2/g presented in Table 4.2, the weight of 5ZrHM@KCC-1 = 0.1 g, and by assuming the time of pulse per second is 1, the rate constant for 5ZrHM@KCC-1:

$$k = \frac{6.83 \times 10^{-6} \text{ (mole)}}{0.1 \text{ (g)} \times 1 \text{ } (s^{-1}) \times 679 m^2/g} = 3.638 \times 10^{-8} \text{ mole } g^{-1} \text{ s}$$

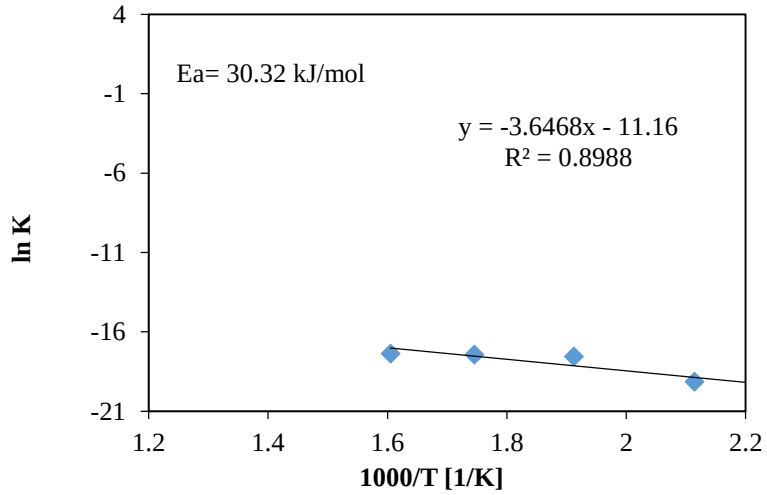
Thus, the rate constant of 5ZrHM@KCC-1 was 3.638×10^{-8} mole g^{-1} s

Arrhenius Plot

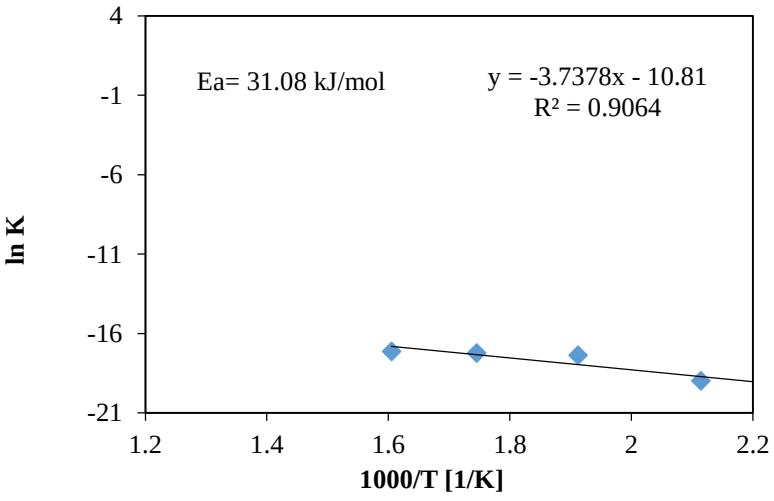
1Zr/HM@KCC-1(150-350 °C)



5Zr/HM@KCC-1 (150-350 C)



10Zr/HM@KCC-1 (150-350 C)



Appendix E

Calculation of Acid Sites Concentration

The amount of pyridine per gram of catalyst was calculated using integrated molar extinction coefficient (IMEC), 1.67 cm/μmole and 2.22 cm/μmole for for Brönsted acid sites and Lewis acid sites respectively.

$$Ø = [IA(B)/IMEC(B) + IA(L)/IMEC(L) = \frac{Cpy}{(3.14\ R^2)}$$

The amount of pyridine per gram catalyst (C) was obtained by dividing Ø by the weight per cm^2 disk

$$C_B \text{ (pyridine on Brönsted acid sites)} = \frac{1.88\ IA(B)\ R^2}{W}$$

$$C_L \text{ (pyridine on Lewis acid sites)} = \frac{1.42\ IA(L)\ R^2}{W}$$

With Brönsted integrated peak area at 1545 cm^{-1} of HM@KCC-1 = 0.15625 and Lewis acid sites integrated peak area at 1445 cm^{-1} of HM@KCC-1 = 0.48415. The calculation was made as follows,

$$C_B = \frac{1880\ \mu mole \times 0.15625 \times (2\ cm)^2}{25\ mg}$$

$$= 46.92\ \mu mole/g$$

$$C_L = \frac{1420\ \mu mole \times 0.48415 \times (2\ cm)^2}{25\ mg}$$

$$= 110.12\ \mu mole/g$$

Thus, the Brönsted and Lewis acid sites acid sites concentration for HM@KCC-1 are 47 μmole/g and 110 μmole/g, respectively.

Appendix F

Microcatalytic pulse reactor experimental set-up

Appendix G

Calculation of g-value

The g-value was calculated based on the energy absorbed in terms of Bohr magneton as given in the equation below:

$E = hv = g\ B_N\ H$

$g = hv/B_NH$

Where

B_N = Bohr magneton = $9.27 \times 10^{-24}\ JT^{-1} = 9.27 \times 10^{-27}$ J/mT

H = Magnetic field strength = 336.977 mT

h = Planck's constant = 6.626×10^{-34} Js

v = frequency of radiation = 9.015 GHz × 1000 = 9015 MHz = $9015 \times 10^6\ s^{-1}$

g = g value

$g = 6.626 \times 10^{-34}$ Js x $9015 \times 10^6\ s^{-1} / 9.27 \times 10^{-27}$ J/ mT x 336.977 mT

g = 1.91

Appendix H

Calculation for mass transfer parameter

The mass transfer parameters were evaluated based on the following equations:

Porosity, ε

$$\varepsilon = \frac{(Vp)}{Vcat} \quad (1)$$

Where Vp is catalyst pore volume (m^3) and Vcat is catalyst volume (m^3)

Tortuosity, τ

$$T = 1 - 0.5\ln(1 - \varepsilon) \quad (2)$$

Molecular diffusivity, $D_{AB(673\ K)}$

$$D_{AB(673\ K)} = D_{AB(298\ K)}\left(\frac{673}{298}\right)^{1.75} \quad (3)$$

Thiele modulus

$$\phi_1 = R_P\sqrt{\frac{K_1\rho_c S_a}{D_{eff}}} \quad (4)$$

Where R_p is the catalyst radius (m), k_1 is the specific reaction rate (m/s), ρ_c is the catalyst density (g/m^3), S_a is the catalyst surface area (m^2/g) and D_{eff} is the effective diffusivity.

Effective diffusivity:

$$D_{eff} = \frac{\varepsilon}{\tau}D_{AB} \quad (5)$$

Internal effectiveness factor:

$$\eta = \frac{3}{{\phi_1}^2}\left(\phi_1\left(\frac{\left(e^{\phi_1} + e^{-\phi_1}\right)}{\left(e^{\phi_1} - e^{-\phi_1}\right)}\right) - 1\right) \quad (6)$$

Weiz-Prater Criterion:

$$C_{WP} = \eta\phi_1^2 = 3(\phi_1\coth\phi_1 - 1) \quad (7)$$

For $C_{WP} < 1$ implies internal diffusion limitation is negligible and vice-versa

LIST OF PUBLICATIONS

Journal with Impact Factor

1. **Ibrahim, M**., Jalil, A.A., Triwahyono, S., Khusnun, N.F., Fatah, N.A.A., Hamid, M. Y. S., Gambo, Y., Abdulrasheed, A. A., Hassan N.S., and Mohamed, M. (2019). Enhanced *n*-Hexane Hydroisomerization Over Bicontinuous Lamellar Silica Mordenite Supported Platinum (Pt/HM@KCC-1) Catalyst. *International Journal of Hydrogen Energy*, doi.org/10.1016/j.ijhydene.2019.04.067.**(Q2, IF: 4.084)**

Non-Indexed Conference Proceedings

1. **Ibrahim, M**., Jalil, A.A., Triwahyono, S., Khusnun, N.F., Tuned acidic properties of fibrous mordenite zeolite for *n*-hexane isomerization. *4th International Conference of Chemical Engineering & Industrial Biotechnology*, Kuala lumpur, Malaysia, 1-2 August 2018.
2. **Ibrahim, M**., Jalil, A.A., Triwahyono, S., Fatah, N.A.A., Izan S.M., and Teh, L.P. Preparation of fibrous mordenite based catalyst for *n*-hexane isomerization. *5th Conference on Emerging Energy and Process Technology (CONCEPT)*, Negeri Sembilan, Malaysia, 7-8 December 2016.
3. **Ibrahim, M**., Jalil, A.A., Triwahyono, S., Khusnun, N.F. Silica modified mordenite zeolite for *n*-pentane isomerization: synthesis and catalytic reaction. *International Conference on Catalysis (ICAT)*, Johor Bahru, Malaysia, 20-21 September 2016.
4. **Ibrahim, M**., Jalil A.A., and Triwahyono, S. A review on catalytic CO_2 methanation for high calorie hydrocarbon. *4th Conference Emerging Energy & Process Technology (CONCEPT)*, Melaka, Malaysia, 15-16 December 2015.