# SYNTHESIS AND CHARACTERIZATION OF PHOSPHATE AND NITRATE GROUPS SUPPORTED ON PROTONATED FIBROUS SILICA BETA-ZEOLITE FOR *n*-HEXANE AND CYCLOHEXANE HYDROISOMERIZATION

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# ABSTRACT

Research octane number (RON) is used as a reference in petrochemical refining industries to indicate the quality of fuel. A higher RON can be achieved through hydroisomerization. In this study, protonated fibrous silica BEA (HSi@BEA) catalyst with unique bicontinuous concentric lamellar structure morphology was successfully prepared by microemulsion technique coupled with zeolite BEA seed. The HSi@BEA catalyst was compared with protonated commercial BEA zeolite (HBEA) on the hydroisomerization of *n*-hexane and cyclohexane. The catalysts were characterized using X-ray diffraction (XRD), surface area analysis, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Ultraviolet-Diffuse Reflectance Spectroscopy (UV-DRS), Fourier transform infrared spectroscopy (FTIR), pyridine adsorption FTIR, 2,6-lutidine adsorption FTIR, nuclear magnetic resonance (NMR), and electron spin resonance (ESR). The catalytic performance was conducted in a microcatalytic pulse reactor at 423-623 K under atmospheric pressure. The surface area analysis showed that HSi@BEA catalyst exhibited higher surface area and bigger average pore size compared to the commercial HBEA catalyst. $^{27}$Al Magic angle spinning NMR (MAS NMR) results displayed that the additional silica lamellar structure of the HSi@BEA catalyst increased the extra-framework aluminium (EFAl). During hydroisomerization, the additional Lewis acid sites in the HSi@BEA generated high amount of protonic acid sites by playing a role as electron acceptors after the dissociation of $H_2$ or C6 alkanes. The high amount of protonic acid sites in HSi@BEA catalyst enhanced catalytic activity at 523 K with isomers yield of 19.8% and 13.2% for *n*-hexane and cyclohexane respectively, compared to 2.50% and 6.64% over commercial HBEA catalyst. Further modification of HSi@BEA catalyst with phosphoric acid (P/HSi@BEA) and nitric acid (N/HSi@BEA) by wet impregnation further enhanced the catalytic activity which is attributed to the different behaviour of the fibrous silica BEA support. FTIR analysis showed that the phosphate group favoured to form P-OH species in the catalyst framework which resulted in a higher number of weak acid sites. Additionally, the nitrate group interacted with EFAl species on HSi@BEA catalyst and increased the formation of Brønsted acid sites of the catalyst. In *n*-hexane and cyclohexane hydroisomerization, the P/HSi@BEA catalyst favoured the production of the *n*-hexane isomers, while the N/HSi@BEA were selectively towards production of cyclohexane isomers, with isomers yield 50.3% and 48.4%, respectively. This fundamental study exhibits that significant interactions given by such phosphate and nitrate groups with the unique silica fibrous BEA support could enhanced hydroisomerization which contribute to the high RON of fuel.

# ABSTRAK

Nombor oktana penyelidikan (RON) digunakan sebagai rujukan dalam industri penapisan petrokimia untuk menunjukkan kualiti bahan api. RON yang lebih tinggi boleh dicapai melalui penghidroisomeran. Dalam kajian ini, mangkin BEA silika berserabut berproton (HSi@BEA) dengan struktur morfologi lamela sepusat dwiselanjar yang unik telah berjaya disediakan melalui teknik mikroemulsi yang digandingkan dengan benih zeolit BEA. Mangkin HSi@BEA telah dibandingkan dengan zeolit BEA berproton komersial (HBEA) untuk penghidroisomeran *n*-heksana dan sikloheksana. Mangkin telah dicirikan menggunakan pembelauan sinar-X (XRD), analisis luas permukaan, mikroskopi elektron pengimbas pancaran medan (FESEM), mikroskopi elektron penghantaran (TEM), spektroskopi pantulan serakan ultralembayung-cahaya nampak (UV-DRS), spektroskopi inframerah transformasi Fourier (FTIR), FTIR penjerapan piridina, FTIR penjerapan 2,6-lutidina, resonans magnet nucleus (NMR), dan resonans spin elektron (ESR). Prestasi pemangkin telah dijalankan di dalam reaktor denyut pemangkinan mikro pada 423-623 K di bawah tekanan atmosfera. Analisis luas permukaan menunjukkan bahawa mangkin HSi@BEA memperlihatkan luas permukaan yang lebih tinggi dan saiz liang purata yang lebih besar berbanding mangkin HBEA komersial. Keputusan NMR penspinan sudut ajaib $^{27}$Al (MAS NMR) menunjukkan peningkatan struktur lamela silika mangkin HSi@BEA telah meningkatkan aluminium di luar rangka (EFAl). Semasa penghidroisomeran, tapak asid Lewis tambahan di dalam HSi@BEA menghasilkan jumlah tapak asid proton yang tinggi dengan memainkan peranan sebagai penerima elektron selepas penceraian $H_2$ atau alkana C6. Tapak asid proton yang tinggi di dalam mangkin HSi@BEA meningkatkan aktiviti pemangkinan pada 523 K dengan hasil isomer 19.8% dan 13.2% masing-masing bagi *n*-heksana dan sikloheksana, berbanding 2.50% dan 6.64% bagi mangkin HBEA komersial. Pengubahsuaian lanjutan mangkin HSi@BEA dengan asid fosforik (P/HSi@BEA) dan asid nitrik (N/HSi@BEA) melalui pengisitepuan basah telah meningkatkan lagi aktiviti pemangkinan yang dikaitkan dengan tingkah laku berlainan penyokong BEA silika berserabut. Analisis FTIR menunjukkan bahawa kumpulan fosfat memihak untuk membentuk spesies P-OH di dalam rangka mangkin yang menyebabkan lebih banyak tapak asid lemah. Tambahan lagi, kumpulan nitrat telah berinteraksi dengan spesies EFAl pada mangkin HSi@BEA dan meningkatkan pembentukan tapak asid Brønsted mangkin. Dalam penghidroisomeran *n*-heksana dan sikloheksana, mangkin P/HSi@BEA memihak kepada pengeluaran isomer *n*-heksana, manakala N/HSi@BEA memilih ke arah pengeluaran isomer sikloheksana masing-masing dengan hasil 50.3% dan 48.4%. Kajian asas ini memperlihatkan bahawa interaksi penting yang diberikan oleh kumpulan fosfat dan nitrat dengan keunikan penyokong BEA silika berserabut dapat meningkatkan penghidroisomeran yang menyumbang kepada RON bahan bakar yang tinggi.

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# LIST OF ABBREVIATIONS

Al - Aluminium
BEA - Zeolite Beta
cus Coordination unsaturated
$C_{12}H_{25}N(CH_3)_3Br$ - Dodecyltrimethylammonium bromide
CTAB - Cetyl trimethylammonium bromide
2,6-$DMPH^+$ - 2,6-dimethylpyridine species
$E_a$ - Activation energy
EDX - Electron Dispersive X-ray
EFAl - Extra-framework aluminium
FAU - Faujasite framework
FESEM - Field Emission Scanning Electron Microscopy
FID - Flame Ion Detector
FTIR - Fourier Transform Infrared spectroscopy
FZSM-5 - Fibrous Zeolite Socony Mobil–5
GC - Gas chromatography
HSi@BEA - Protonated Bicontinuous concentric silica lamellar BEA
KBr - Potassium bromide
KCC - KAUST Catalytic Center
LTA - Linde Type A framework
MCP - methylcyclopentane
MFI - Mordenite Framework Inverted
MOR - Mordenite
2MP - 2-methylpentane
3MP - 3-methylpentane
MPa - Megapascal
MSN - Mesoporous Silica Nanoparticle
NMR - Nuclear Magnetic Resonance
$NH_4NO_3$ - Ammonium nitrate
NLDFT - Non-local density functional theory

| | | |
|---|---|---|
| N/HSi@BEA | - | Nitrate loaded on protonated bicontinuous concentric silica lamellar BEA |
| P/HSi@BEA | - | Phosphate loaded on protonated bicontinuous concentric silica lamellar BEA |
| Pt | - | Platinum |
| RON | - | Research Octane Number |
| SAPO | - | Silica Aluminium Phosphate |
| Si | - | Silicon |
| TEA+ | - | Tetraethylammonium ion |
| TEM | - | Transmission Emission Microscopy |
| TEOS | - | Tetraethyl orthosilicate |
| TGA | - | Thermogravimetric Analysis |
| TMS | - | tetramethylsilane |
| USY | - | Ultra Stable Y |
| UV-DRS | - | Ultraviolet-Diffuse Reflectance Spectroscopy |
| XRD | - | X-ray Diffraction |
| ZSM-5 | - | Zeolite Socony Mobil–5 |

# LIST OF SYMBOLS

µm - micrometer
kHz - kilo hertz
mA - miliampere
Å - Angstrom
$2\theta$ - Bragg angle
$\beta$ - Beta
$^{o}$C - Degree celcius
K - Kelvin
$\theta$ - angle
P - pressure
g - gram
mL - millilitre
min - minutes
h - hours
K$\alpha$ - K shell alpha
kV - kilo volt
$\lambda$ - wavelength
µs - microsecond
s - seconds

# LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Reducing emission from transportation is of great importance due to the challenges in climate change and the increasing demand for mobility. Spark ignited engines operating on gasoline fuels are primary technology for light duty passenger vehicles, and their efficiency is limited by knocking (Kalghatgi, 2014). As a result, restrictions are imposed on gasoline to reduce its benzene, heavy aromatics and olefins concentrations along with the removal of tetramethyl lead. However, the octane number of aromatics and olefins is relatively high, so reducing their concentration in gasoline causes a decrease in octane number and, consequently, fuel quality *(*Naqvi *et al.*, 2018). Therefore, numerous studies have been implemented to enhance the quality of gasoline by increasing the Research Octane Number (RON), which is used in the quality control of gasoline that provide information on the auto ignition (Splitter *et al.*, 2016). High octane component is a gasoline additive that is needed for the proper functioning of modern engines. High octane sources have taken many forms throughout the years, both renewable and petroleum-based. They include lead, methyl tertiary butyl ether (MTBE), benzene, toluene, ethyl-benzene and xylene, and ethanol (a biofuel). However, this method has been under scrutiny due to their deleterious environmental effects such as the increase in the nitrogen oxide emission and speeds up corrosion (Chambers, 2011). In addition, MTBE is an expensive component that can further increase the cost of gasoline from its application.

In this regard, high octane components can be obtained by the hydroisomerization of *n*-alkanes with low carbon numbers, relieving the increasing severe legal restrictions on the use of environmentally-unfriendly aromatics in high-octane gasoline (Zhang *et al.*, 2019). This process is able to convert the *n*-alkanes into corresponding branched isomers which possess a higher octane number compared to the linear alkanes. Therefore, hydroisomerization is an alternative technology to produce high quality gasoline to meet the needs of the automobile industry. However, the process mainly depends on the catalysts and how efficient they are in their activity and selectivity.

Hydroisomerization of *n*-alkanes generally occurs on bifunctional catalysts, which consist of the metal constituent providing the hydrogenation/dehydrogenation functions, and the acid constituent for skeletal transformations of alkene intermediates via carbenium ions rearrangement. Previously, chloride alumina-based catalysts have been extensively applied in industrial production, however, they have common drawbacks of high cost and tolerance to sulfur and water because the active components of them are generally noble metals such as Pt (Ono, 2003). Furthermore, hydroisomerization catalyst requires a solid support with acidic function where several supports have been reported such as SAPO-11 (Liu *et al.*, 2008), MOR (Konnov *et al.*, 2012), $ZrO_2$ (Ruslan *et al.*, 2012), alumina (Vandegehuchte *et al.*, 2014), ZSM-5 (Setiabudi *et al.*, 2013), HY(Aziz *et al.*, 2012) and HBEA (Kamarudin *et al.*, 2012). Currently, the catalysts used for hydroisomerization are facing problems such as low surface area, rapid deactivation, unstable structure, high temperature reaction and low selectivity of desired product and conversion of reactants.

More recently, bifunctional metal catalysts supported on zeolites are widely used in a number of industrial processes such as catalysis, separation and adsorption (Rahimi and Karimzadeh, 2011; Wang *et al.*, 2016; Gao *et al.*, 2018). Various reactions used zeolite as active supports for reactions such as cracking, alkylation, aromatization and hydroisomerization of hydrocarbons. This is due to the presence of dual properties of acidic and basic sites which play an important role in many catalytic reactions. Besides, zeolites provide uniformity in micropore size and shape which makes zeolite a suitable catalyst in the oil refining. However, due to the constraints in pore diameter, the catalytic activity of zeolite dropped when bulkier molecule are used (Pérez-Ramírez *et al.*, 2008). Microporous structure and strong acidic properties of microporous zeolite such as ZSM-5, Y and β are important properties for catalysts in petrochemical industry. The improvement from microporosity to mesoporosity in zeolite was aimed to solve the problem of diffusion limitation and pore blockage incurred from the use of conventional zeolite (Firmansyah *et al.*, 2016). Thus, extensive effort has been made to develop new support material that can overcome the aforementioned limitations by considering the aspects of mesoporosity and balanced acidity properties.

Fibrous material was initially developed by Polshettiwar, *et al.* in 2010. Several studies showed the potential of fibrous material in photocatalysis (Seo *et al.*, 2017; Singh *et al.*, 2018), $CO_2$ methanation (Hamid *et al.*, 2017), alkane hydrogenolysis (Fihri *et al.*, 2012), cumene hydrocracking (Firmansyah *et al.*, 2016), and phenol hydrogenation (Karakhanov *et al.*, 2017). The unique bicontinuous silica lamellar morphology provides large surface area with more mesopores, high accessibility of bulky reactants to the active sites and tuneable acidity could improves their catalytic activity. Analogous to the structure of KCC-1, zeolite-based fibrous support using BEA as a seed was synthesized to cover some limitations from the use of silica-based fibrous for application in acid catalyzed reaction such as hydroisomerization.

In order to improve the performance of hydroisomerization using fibrous silica BEA (Si@BEA), the loading of oxoanions such as $SO_4^{2-}$, $PO_4^{3-}$ and $NO_3^-$ could be useful to improve the acidic property of supports. Sulfated catalyst was enormously studied in alkane hydroisomerization especially loaded on zirconia as a support (Triwahyono *et al.*, 2003a; Triwahyono *et al.*, 2010) or promoter (Tamizhdurai *et al.*, 2018). Tamizhdurai et al. reported that $SO_4$-$ZrO_2$ as solid-super acid created strong Brønsted acidity by attachment of $SO_4$ groups to $ZrO_2$-surface (Tamizhdurai *et al.*, 2018) . In addition, the conversion of *n*-butane hydroisomerization on $SO_4^{2-}/ZrO_2$ increased with increasing the sulfate ion loading due to existence of bidentate sulfate and/or polymeric sulfate species, which act as active sites for the hydroisomerization as revealed by Triwahyono *et al.* (2006). However, the use of sulfated-catalyst has some drawbacks such as higher cracking products due to high acidity and requires higher hydrogen to carbon ratio (Triwahyono *et al.*, 2003c; Valavarasu and Sairam, 2016).

Meanwhile, many works have been devoted related to phosphate group loaded catalysts (Yori *et al.*, 2000; Bij *et al.*, 2014; Van Der Bij and Weckhuysen, 2014; Lyu *et al.*, 2017). Literature reported that the strong Brønsted acid sites of ZSM-5 zeolite could be converted into weaker Brønsted acid sites when ZSM-5 zeolite was treated with phosphoric acid (Ghiaci *et al.*, 2007; Lyu *et al.*, 2017). Besides, the introduction of phosphorus passivated the external surface acid sites and narrowed the pore size, which in turn inhibited the hydroisomerization of xylene (Janardhan *et al.*, 2014). Fatah and co-workers reported the catalytic activity of *n*-heptane was enhanced due to the formation of $(MoO_x)^-(H_y)^+$ and the participation of acidic centers from the presence of phosphorus. This was also due to the creation of new Lewis and Brønsted acidic centers (Fatah *et al.*, 2017). Nevertheless, to date, there is no report available regarding the modification of bicontinuous concentric lamellar silica BEA type material using phosphate and nitrate group.

Previously, Ignesia *et al.* reported that the hydroisomerization of *n*-alkane to produce *iso*-alkene occurs in the absence of hydrogen on Fe/HZSM-5. They proposed that reaction via dehydrogenation of *n*-alkane to form hydrogen molecule and *n*-alkene and then molecular hydrogen reacts with *n*-alkene to produce *iso*-alkene (Li and Iglesia, 2008). Besides, Triwahyono *et al.* (2010) revealed that the generation of protonic acid sites from pentane molecules was observed by the adsorption of pyridine over the surfaces of $Pt/SO_4^{2-}$-$ZrO_2$ and Zn/H-ZSM5. Based on those reports, then we postulated that the active sites for hydroisomerization can be formed from the reactant with metal-free bicontinuous silica lamellar support. It is expected that the presence of additional Lewis acid sites on the HSi@BEA catalyst facilitates the formation of protonic acid sites by playing a role in trapping electrons. In addition, the unique morphology is expected to provide high surface area and better accessibility of active sites which leads to enhanced isomers products selectivity. Further modification on HSi@BEA catalyst with $PO_4^{3-}$ and $NO_3^-$ to form P/HSi@BEA and N/HSi@BEA catalyst, respectively, is expected to improve catalytic activity of hydroisomerization of *n*-hexane and cyclohexane.

## 1.2 Problem Statement

Current specifications for the production of cleaner fuels impose strong restrictions on the content of sulfur, aromatic compounds and olefins as well total interdiction of lead in the gasoline pool (Primo and Garcia, 2014). These restricted conditions led to the loss of the performance of internal combustion engine as these additives served as octane number enhancers (Primo and Garcia, 2014)(Singh *et al.*, 2017). In this regard, the skeletal hydroisomerization of linear alkanes represents a promising alternative since, with this process, low-octane straight chain paraffins are directly converted into high-octane branched molecules. Hydroisomerization of linear alkanes can, thus, be considered as an efficient and economically acceptable way of increasing the octane number of motor gasoline and, unlikely aromatics and/or other toxic additives, the isomers in gasoline is an ideal product that can satisfy the most stringent environmental legislation requirements. However, the production of branched alkanes is affected by the fierce competition between hydroisomerization and cracking reaction, including other problems such as fast deactivation of the catalyst due to coke deposition. In order to overcome these problems, the need to design new modified catalyst with better properties which could possibly give a higher yield of branched alkanes is an imperative task. Previously, platinum-supported on chlorinated alumina as bifunctional catalyst has been widely applied for alkane hydroisomerization but has several limitations due to its corrosion problems on the reactor (Jiménez *et al.*, 2003).

Zeolites such as ZSM-5, Y, and β have been utilized as catalysts in the hydroisomerization due to their tunable intrinsic acidity, surface area, and uniform pores. Zeolite consists of silica-alumina framework with a wide varieties of Si/Al ratio which results in good tunable acidity. Zeolite is a suitable material for facilitating acid-catalyzed reactions. Interestingly, ease of modification properties of zeolite-based catalyst would allow tuned surface area, acidity and porosity, rendering zeolite an attractive choice for catalyst support. Modhera *et al.*, (2011) studied *n*-hexane hydroisomerization over different support such as ZSM-5 and beta zeolite. Desilicated beta zeolite was found to be perform best due to high surface area, large pore diameter, moderate acidity and reduced coke formation.

Three-dimensional 12-membered-ring zeolite beta is usually chosen as a catalyst support in hydroisomerization of *n*-alkanes due to its high surface area, large pore diameter, moderate acidity and also ease to modify. However, the selectivity towards *iso*-alkanes over microporous zeolite beta is low cause of diffusion constraints of *n*-alkanes with six or more carbon atoms. This also will lead to poor accessibility of bulk reactant to the active sites located inside the pores, thus limits their applications. Development of hierarchically porous zeolite is one of the ways to overcome the diffusion limitation. Mesoporous material possesses highly ordered mesoporous structures which enabled the size-selectivity and extremely high surface area with large pore volume (Firmansyah *et al.*, 2016; Teh *et al.*, 2016).

Silica-based fibrous material provides high surface area due to the presence of the dendrimeric fiber. Furthermore, due to the high dispersion of active sites which are probably located in their dendrimeric fiber rather than inside the catalyst pore, it provides high accessibility of active sites (Firmansyah et al., 2016). However, it does not have adequate acid sites to promote acid-catalyzed reaction such as hydroisomerization because the fibrous material is fully composed of silica.

## 1.3 Hypothesis

To overcome the above-mentioned problems, zeolite with dendrimeric silica fibrous was developed which is expected to give better accessibility to the active sites, thus reduced the diffusion limitation of the reactants and/or products to pass through the catalyst pores. In addition, these new developed catalysts will provide higher Lewis acid sites in order to facilitate the generation of protonic acid sites.

Although several studies have reported the generation of protonic acid sites from reactants over solid acid catalyst, no detail study on the mechanism of generation of protonic acid sites over metal-free protonated fibrous silica BEA catalyst (HSi@BEA) have been discussed. Therefore, it is desirable to study the generation of protonic acid sites from hydrogen molecules and reactants in the absence of metal sites for the hydroisomerization of n-hexane and cyclohexane. The oxoanions, phosphate and nitrate groups are loaded to enhance the production of isomers for n-hexane and cyclohexane. It is hypothesized that the loading of phosphate and nitrate group on the HSi@BEA catalyst, which possess high surface area and large pore diameter, will result in different catalytic activity towards n-hexane and cyclohexane isomers. The different interaction of phosphate and nitrate group towards HSi@BEA support is expected to alter the catalyst acidic property and catalytic performance.

## 1.4 Objectives of Study

The objective of this study is to synthesize phosphate and nitrate groups supported on fibrous silica beta zeolite for enhanced hydroisomerization of cyclohexane and *n*-hexane. The objective of this study could be specified as follows:

1. To synthesize and characterize the physicochemical properties of the protonated fibrous silica BEA (HSi@BEA) and protonated commercial BEA (HBEA).

2. To modify and characterize the physicochemical properties of the phosphate loaded HSi@BEA (P/HSi@BEA) and nitrate loaded HSi@BEA (N/HSi@BEA) catalysts.

3. To investigate the catalytic activity of HBEA, HSi@BEA, P/HSi@BEA and N/HSi@BEA catalysts towards *n*-hexane and cyclohexane hydroisomerization.

4. To elucidate the mechanism of hydroisomerization of *n*-hexane and cyclohexane using the synthesized catalysts (HBEA, HSi@BEA, P/HSi@BEA and N/HSi@BEA).

## 1.5 Scope of Study

To complete the objectives of this study, the four main scopes considered are listed below;

1. To synthesize and characterize the physicochemical properties of the protonated fibrous silica BEA (HSi@BEA) (Si/Al=38) and protonated commercial BEA (HBEA) (Si/Al=25);
   The fibrous silica BEA (Si@BEA) was synthesized using microwave assisted hydrothermal method. Commercial BEA was used for comparison purposes. Both of the catalysts were converted into ammonium form by ion-exchange and followed by calcination to convert the $NH_4^+$ species into $H^+$. The prepared catalysts were characterized using X-ray Diffraction (XRD), $N_2$ physisorption, Fourier Transform Infrared spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Transmission Emission Microscopy (TEM) and $^{27}$Al and $^{29}$Si MAS Nuclear Magnetic Resonance (NMR).

2. To synthesize and characterize the physicochemical properties of the phosphate loaded HSi@BEA (P/HSi@BEA) and nitrate loaded HSi@BEA (N/HSi@BEA) catalysts;
   In order to study the effect of phosphate and nitrate loading, the catalysts were prepared by impregnating HSi@BEA with $H_3PO_4$ and $HNO_3$, respectively. The amount of $H_3PO_4$ and $HNO_3$ concentration were adjusted to 0.5 N obtained from literature (Triwahyono *et al.*, 2006) and preliminary catalytic activity evaluation using different $H_3PO_4$ and $HNO_3$ concentrations. The prepared catalysts were characterized using X-ray Diffraction (XRD), $N_2$ physisorption, Fourier Transform Infrared spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Ultraviolet-Diffuse Reflectance Spectroscopy (UV-DRS), and $^{27}$Al MAS Nuclear Magnetic Resonance (NMR)

3. To investigate the catalytic activity of HBEA, HSi@BEA, P/HSi@BEA and N/HSi@BEA catalysts towards *n*-hexane, cyclohexane and methylcyclopentane (MCP) hydroisomerization;
   Hydroisomerization of *n*-hexane was performed under hydrogen and nitrogen stream in micro-catalytic pulse reactor with a reaction temperature range of 423-623 K at atmospheric pressure. The reaction was repeated using difference reactants which are cyclohexane and MCP while maintaining the other conditions. MCP was used as a bulkier reactant to investigate the diffusion limitation the catalysts.

4. To elucidate the mechanisms of hydroisomerization of *n*-hexane and cyclohexane using four synthesized catalysts (HBEA, HSi@BEA, P/HSi@BEA and N/HSi@BEA).
   2,6-lutidine adsorbed FTIR was used to determine the acid strength and structure of the catalyst. Adsorption of 2,6-lutidine coupled with FTIR has been accepted as a general practice to qualify the types of acids either a Lewis or Brønsted acid sites on the surface of the catalyst. Generation of protonic acid sites was elucidated using hydrogen or reactants adsorption Fourier Transform Infrared spectroscopy (FTIR) and ESR. The hydrogen adsorption on 2,6-lutidine pre-adsorbed FTIR and reactants adsorption on 2,6-lutidine pre-adsorbed FTIR were used to determine the active sites that participate in the formation of active protonic acid sites from hydrogen and reactants molecules, respectively. The ESR was used to investigate the correlation with the phase formation as well as the magnetic properties of the catalyst where it involves the treatment of hydrogen or reactants.

## 1.6 Significance of Study

The original contribution of this study is the utilization of new catalyst with unique morphology HSi@BEA in *n*-hexane and cyclohexane hydroisomerization. In this respect, the significance of the study includes explaining the behavior of

HSi@BEA catalyst especially on *n*-hexane and cyclohexane hydroisomerization. This study highlighted the potential of high surface area and higher accessibility HSi@BEA as a new support for *n*-hexane and cyclohexane hydroisomerization. Besides, a detail investigation on the effect of non-metal loadings involving phosphate and nitrate group on HSi@BEA catalyst toward the physicochemical properties and catalytic activity of the catalysts revealed the advantages of phosphate and nitrate group in improving the catalytic activity. This significantly to further elucidate the mechanism of *n*-hexane and cyclohexane hydroisomerization using loaded and non-loaded catalysts. Based on the present study, it could deliver the potential of utilizing non-metal like phosphate and nitrate group as promoters, which provide different catalytic activities towards *n*-hexane and cyclohexane isomers. In this respect, they contribute in hydroisomerization for gaining significant attention in the petroleum refineries to increase the fuel octane number.

## 1.7 Thesis Outline

This thesis begins with Chapter 1 describing the research background, problem statement and hypothesis, objectives, scopes and significance of this study. Chapter 2 reviewed the literatures related to the catalysts and current works about the hydroisomerization. Chapter 3 described the experimental and characterization of synthesized catalysts and Chapter 4 and Chapter 5 concerned with data processing and discussing of physicochemical properties and performance of the catalysts. The conclusions and recommendations for future studies were stated in Chapter 6.

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# APPENDIX F

## LIST OF PUBLICATIONS

1. S.M. Izan, S. Triwahyono, A.A. Jalil, Z.A. Majid, N.A.A. Fatah, M.Y.S. Hamid, M. Ibrahim (2019). Additional Lewis acid sites of protonated fibrous silica@ BEA zeolite (HSi@ BEA) improving the generation of protonic acid sites in the hydroisomerization of C6 alkane and cycloalkanes. *Applied Catalysis A: General*, *570*, 228-237.

2. Siti Maryam Izan**,** Aishah Abdul Jalil, CheKu Norliana CheKu Hitam, Walid Nabgan. (2020) Influence of Nitrate and Phosphate on silica fibrous beta zeolite framework for enhanced cyclic and non-cyclic alkane isomerization. Inorganic Chemistry, 59, 3, 1723-1735.

# LIST OF PROCEEDING

1. S. M. Izan, S. Triwahyono, A. A. Jalil, M. L. Firmansyah. “Preparation of Fibrous Silica Beta Zeolite for Cyclohexane Hydroisomerization”. 2nd International Seminar on Chemistry, ISoC 2016, Surabaya, Indonesia, 26-27 July 2016.

2. S. M. Izan, S. Triwahyono, A. A. Jalil, “Effect of Hydrogen Spillover to the cyclohexane Hydroisomerization over Different Supports”. 6th Conference on Emerging Energy & Process Technology, CONCEPT 2017, Johor Bahru, Malaysia, 27-28 November 2017.

3. S. M. Izan, S. Triwahyono, A. A. Jalil, “Effect of different metal loaded Fibrous Silica Beta Zeolite for *n*-hexane Hydroisomerization”. International Conference on Catalysis, iCAT 2016, Johor Bahru, Malaysia, 20-21 September 2016.