

MOLECULAR HYDROGEN ORIGINATED PROTONIC ACID SITES OVER  
PROTONATED FIBROUS SILICA Y ZEOLITE FOR *N*-HEXANE  
ISOMERIZATION

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*Specially dedicated to my beloved father and mother*

*Jamari Salekan and Sahimah Arsad*

*&*

*My beloved ones*

*“ Thank you for the endless support and everything ”*

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## ABSTRACT

Nowadays, isomerization of linear alkanes to their branched isomers has become the most demanded process in increasing the octane rating of gasoline. Fibrous silica zeolite Y (FY) catalyst has been prepared via the microemulsion system with zeolite Y seed assisted crystallization. The platinum loaded on protonated FY (Pt/HFY) was prepared by protonation of FY followed by the impregnation of platinum on HFY. The catalysts were characterized by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), nitrogen physisorption (BET), Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) and Fourier Transform Infrared (FTIR) spectroscopies. The XRD results of the FY catalyst exhibited diffraction peaks in the range of  $4^\circ$  to  $40^\circ$   $2\theta$ , which has been attributed to the faujasite-type zeolite Y. FESEM images showed a spherical morphology with bicontinuous lamellar in the range of 500 - 700 nm in diameter, while the EDX result showed that silica was a dominant material in Pt/HFY. NMR spectra confirmed the presence of both tetrahedral and octahedral Al species with dominant  $Q^4$  sites in HFY. Nitrogen physisorption results showed that the presence of fibrous silica generated mesoporosity in the range of 3 - 6 nm and increased the BET surface area from 473 to 550  $m^2/g$ , while the addition of Pt slightly decreased the BET surface area to 483  $m^2/g$  which might be due to pore blockage by the Pt particles. At 573 K, *n*-hexane isomerization over Pt/HFY resulted in 72.3% *n*-hexane conversion with 91.4% selectivity of *mono*-branched, 7.7% selectivity of *di*-branched and 0.9% selectivity of cracking products ( $C_3$ - $C_5$ ). The result obtained for Pt/HFY is higher than that of Pt/HY with only 27.2% conversion of *n*-hexane and selectivity of 70.7% *mono*-branched and 1.0% *di*-branched isomers. In the absence of Pt, HY exhibited a very low activity with less than 5% of *n*-hexane conversion and 51.5% selectivity of *mono*-branched isomer without *di*-branched isomers, whereas HFY achieved higher conversion and isomers selectivity compared to HY. The acidity of the catalysts was determined by pyridine preadsorption IR spectroscopy which showed that the presence of fibrous silica increased the number of Lewis acid sites and generated more protonic acid sites. Hydrogen adsorbed IR study revealed that the protonic acid sites which acted as active sites in the isomerization were formed via the dissociative-adsorption of molecular hydrogen releasing electrons close to the Lewis acid sites. The presence of fibrous silica which possessed strong Lewis acid sites increased and stabilized the formation of protonic acid sites by trapping of electrons. Thus, it is suggested that the presence of Pt and fibrous silica improved the activity and stability of zeolite Y in the *n*-hexane isomerization via the hydrogen spillover mechanism.

## ABSTRAK

Sekarang ini, pengisomeran alkana linear untuk menghasilkan isomer bercabang telah menjadi proses yang amat diperlukan bagi meningkatkan pengkadaratan oktana petrol. Mangkin silika bergentian zeolit Y (FY) telah disediakan melalui sistem mikroemulsi dengan penghabluran berbantuan benih zeolit Y. Platinum termuat ke dalam FY berproton (Pt/HFY) telah disediakan secara pemprotonan FY diikuti dengan pengisitepuan platinum ke dalam HFY. Mangkin dicirikan menggunakan pembelauan sinar-X (XRD), mikroskop pengimbasan elektron pancaran medan (FESEM), nitrogen fizijerapan (BET), spektroskopi resonans magnet nukleus-putaran sudut ajaib (MAS-NMR) dan spektroskopi inframerah transformasi Fourier (FTIR). Keputusan XRD untuk mangkin FY memperlihatkan puncak pembelauan dalam julat  $2\theta$  antara  $4^\circ$  hingga  $40^\circ$  yang dikaitkan dengan faujasit jenis zeolit Y. Imej FESEM menunjukkan morfologi sfera dengan lamela dwiberterusan yang mempunyai diameter dalam julat 500 - 700 nm, sementara keputusan EDX menunjukkan silika adalah bahan dominan dalam Pt/HFY. Spektrum NMR mengesahkan kehadiran kedua-dua spesies Al tetrahedral dan oktahedral dengan tapak  $Q^4$  yang dominan dalam HFY. Fizijerapan nitrogen menunjukkan bahawa kehadiran silika bergentian telah menjana keliangan meso dalam julat 3 - 6 nm dan meningkatkan luas permukaan BET dari 473 kepada  $550 \text{ m}^2/\text{g}$ , manakala penambahan Pt telah menurunkan luas permukaan BET kepada  $483 \text{ m}^2/\text{g}$  yang mungkin disebabkan oleh penyumbatan liang dengan adanya zarah Pt. Pada 573 K, keisomeran *n*-heksana yang menggunakan mangkin Pt/HFY telah menghasilkan penukaran *n*-heksana sebanyak 72.3% dengan kepilihan 91.4% untuk isomer ekacabang, 7.7% untuk dwicabang dan 0.9% untuk hasil peretakan ( $C_3$ - $C_5$ ). Keputusan yang diperoleh untuk Pt/HFY adalah lebih tinggi daripada Pt/HY dengan Pt/HY menghasilkan hanya 27.2% penukaran *n*-heksana dan kepilihan 70.7% untuk isomer ekacabang dan kepilihan 1.0% untuk isomer dwicabang. Tanpa Pt, HY mempamerkan aktiviti yang sangat rendah iaitu kurang daripada 5% penukaran *n*-heksana dan kepilihan 51.5% untuk isomer ekacabang tanpa sebarang isomer dwicabang, manakala HFY mencapai penukaran dan kepilihan isomer lebih tinggi berbanding dengan HY. Keasidan mangkin telah ditentukan menggunakan spektroskopi IR prapenjerapan piridina yang menunjukkan bahawa kehadiran silika bergentian telah meningkatkan bilangan tapak asid Lewis dan menghasilkan lebih banyak asid berproton. Kajian IR terjerap hidrogen mendedahkan bahawa tapak asid berproton yang bertindak sebagai tapak aktif dalam pengisomeran terbentuk melalui penceraian-penjerapan molekul hidrogen yang melepaskan elektron berhampiran tapak asid Lewis. Kehadiran silika bergentian yang mempunyai tapak asid Lewis kuat meningkatkan dan menstabilkan pembentukan tapak asid berproton dengan memerangkap elektron. Oleh itu, adalah dicadangkan bahawa kehadiran Pt dan silika bergentian meningkatkan aktiviti dan kestabilan zeolit Y dalam pengisomeran *n*-heksana melalui mekanisme hidrogen limpahan.

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**LIST OF SYMBOLS**

%	=	Percentage
K	=	Kelvin
Å	=	Angstrom
nm	=	Nanometer
w/o	=	Water in Oil
o/w	=	Oil in Water
$\Delta H$	=	Heat Enthalpy
J	=	Joule
G	=	Gram
cm	=	Centimeter
W	=	Watt
M	=	Molar
wt %	=	Weight Percentage
$\lambda$	=	Lambda
kV	=	Kilovolt
mA	=	Miliampere
Mbar	=	Milibar
MHz	=	Megahertz
$\mu s$	=	Microsecond
$\theta$	=	Theta
$^{\circ}C$	=	Degree Celcius
ppm	=	Part per million

**LIST OF ABBREVIATIONS**

HY	=	Protonated Y zeolite
FY	=	Fibrous Y
HFY	=	Protonated Fibrous Y
Pt/HFY	=	Platinum Protonated Fibrous Y
Pt/HY	=	Platinum Protonated Y
XRD	=	X-Ray Diffraction
BET	=	Braunauer Emmett Teller
FTIR	=	Fourier Transform Infrared Spectroscopy
FESEM	=	Field Emission Scanning Electron Microscope
NMR	=	Nuclear Magnetic Resonance
MPAES	=	Microwave Plasma Atomic Emission Spectroscopy
EDX	=	Energy Dispersion X-Ray
RON	=	Research Octane Number
FCC	=	Fluid Catalytic Cracking
MTBE	=	Methyl Tert-Butyl Ether
KCC-1	=	KAUST Catalysis Center- 1
ZSM-5	=	Zeolite Socony Mobile – 5
CTAB	=	Cetyltrimethyl Ammonium Bromide
HMOR	=	Protonated Mordenite
HBEA	=	Protonated Beta
FAU	=	Faujasite
MCM-22	=	Mobil Crystalline Material – 22
MSN	=	Mesoporous Silica Nanosphere
CPB	=	Cetylpyridinium Bromide
TEOS	=	Tetraethyl Ortosilicate

OSDA	=	Structure Directing Agent
FID	=	Flame Ionization Detector
NLDFT	=	Non-Local Density Functional Theory
GC-MSD	=	Gas Chromatograph- Mass Selective Detector
NIST-14	=	National Institute of Standard and Technology -14
JCPDS	=	Joint Committee on Powder Diffraction Standards
MPAES	=	Microwave Plasma Atomic Emission Spectroscopy
USY	=	UltraStable Y
EFAL	=	Extra-framework Aluminium



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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Study

Nowadays, the demand for fossil fuels is increasing over the years because of the energy based on combustion of fossil fuels have become the main energy source. Based on the world energy consumption, fossil fuels contributed 80% of the total primary energies where the largest primary energy is petroleum. Based on this, 58% is consumed by the transportation sector. Petroleum liquid fuels produced from crude oil have through several refining processes such as naphtha isomerization, olefin alkylation, reforming, cracking, and hydrocracking. Over the years, the sources of fossil fuel are becoming exhausted and these have affected the global crude oil price. Therefore, people are moving toward the efficient and cost-effective refinery production (Nigam and Singh, 2011).

Over the decades, the modern global refinery process is becoming more complex to meet high demand for the cleaner fuel. Strict regulation on the earth's environment and health concern world-wide has been the greatest challenge for the oil refinery to find ways to manage the octane number in gasoline pool (Karthikeyan *et al.*, 2008). The characteristic of the gasoline quality is determined by the Research Octane Number (RON) in the gasoline pool. The higher the RON in the gasoline, will provide better engine performance, which enable greater thermal efficiency for future engines (Pasadakis, Gaganis and Foteinopoulos, 2006). Fluid Catalytic Cracking (FCC) and reforming processes have been introduced and still have limitations in blending which

contain high amount of aromatic hydrocarbons. The additives such as methyl *tert*-butyl ether (MTBE) which is one of the oxygenated material, also has been banned in gasoline because it will contaminate the ground water supplies. In addition, benzene as anti-knocking agent also has been banned in many countries due to health concerns (Bahadar, Mostafalou and Abdollahi, 2014).

In this regard, isomerization process offers an alternative way as the gasoline enhancer with branched-chain alkanes, which have a higher octane number than linear alkanes. Besides, the isomerization process has attracted much interest among researchers due to its facile and economical process compared with other octane-improving processes. Other than that, products from the isomerization process are low in sulfur and benzene contents which makes it an ideal process in refining industries (Valavarasu and Sairam, 2013).

In petroleum refining, catalyst is the main key to the transformation process of crude oil into finished products. In the isomerization process, the requirement for catalysts with high selectivity to isomers and low side products are the most important and demanding in industries. Besides, the isomers products must be free from contaminations such as sulfur and nitro (Liu *et al.*, 2016). In order to meet high isomers-products, active catalysts of the isomerization process must have high acidic characteristics. Chlorinated alumina based catalysts are commonly used for this process. Although these catalysts are highly active, but they suffers from extreme sensitivity to all kinds of feed contaminants (Triwahyono, Abdullah and Jalil, 2006). Based on the previous study, zirconia-based catalyst such as Pt/SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub> (Busto *et al.*, 2012) and Pt/WO<sub>3</sub>-ZrO<sub>2</sub> (Triwahyono, Yamada and Hattori, 2003) have a great potential for isomerization due to its ability to produce high protonic acid sites.

Metal loaded-zeolite based catalysts such as mordenite, ZSM-5, Y and Beta (BEA) have been widely used as the acidic support for isomerization. Noble metals such as platinum (Pt) or palladium (Pd) are usually used for the dehydrogenation/hydrogenation function in isomerization reaction. Bifunctional catalysts

are expected to give high selectivity and activity for the isomerization due to the balance between the two catalytic functions, able to promote hydrogenation of hydrocarbon and to provide acidity (Soualah *et al.*, 2008). In addition, isomerization process over bifunctional heterogeneous catalyst is highly efficient in the hydrogen atmosphere due to hydrogen spillover phenomenon. It was suggested that the efficiency of the isomerization reaction was due to the generation of protonic acid sites from hydrogen molecules and became active sites for isomerization of *n*-alkanes (Hattori, 2010). However, this hydrogen spillover phenomenon has only been observed for certain types of catalysts. Previous literatures reported that zirconia based acid catalysts such as Pt/SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub> and Pt/WO<sub>3</sub>-ZrO<sub>2</sub> have a tendency to generate protonic acid sites via hydrogen spillover mechanism. Other than that, zeolite supported metal catalysts such as Zn/HZSM-5 form catalytically active protonic acid sites for isomerization of *n*-pentane in the hydrogen stream (Triwahyono *et al.*, 2011).

Zeolites is known as an outstanding catalyst used in oil refinery such as alkylation, isomerization, dewaxing and reforming. The wide applications of zeolite are commonly due to their unique properties such as high acidity, high surface area, high thermal stability, and shape selectivity provide them as a choice for various reactions (Weckhuysen and Yu, 2015). Nevertheless, zeolites possess diffusion limitation because of the sole presence of microporous which reduced the mass transfer within the active sites. To overcome such limitation, zeolites containing both microporous and mesoporous was designed to increase the rate of reaction in the catalytic process. The presence of micro - and mesoporous material in zeolite have been widely used as catalytic application and the catalytic activity of the catalyst still can be further enhanced by introducing more active sites on the catalyst (Liu *et al.*, 2016).

Fibrous silica nanosphere (KCC-1) with versatile properties have been reported by several researchers. This material was firstly introduced by Polshettiwar, *et al.* in 2010 in order to produce mesoporous and nanoscale silica materials with a wide range of morphologies. They reported that the silica nanosphere has high surface area due to the presence of dendrimeric silica fibers which allow active catalytic sites to disperse.

Recently, zeolite-based fibrous material which is fibrous silica ZSM-5 (FZSM-5) was reported to have a high surface area, wide pore diameter (2-20 nm), abundance strong acid sites and high catalytic activity towards cumene cracking (Firmansyah *et al.*, 2016).

## 1.2 Problem Statement and Hypothesis

The increasing world demand for the clean gasoline are currently a big challenge for the petroleum refining companies to produce light crude oil with low level of impurities due to many restrictions and regulations by European legislation. The concentration of aromatic hydrocarbons and benzene in gasoline must be reduced according to Euro-4 and Euro-5 standards specified by United States and Europe (Dao and Luu, 2015). World concern related to the environmental and health problems restricted the limit for the addition of aromatics, benzene, sulfur, NO<sub>x</sub> and other dangerous compounds. Some octane number enhancer such as MTBE and an oxygenated compound has been banned because of alleged leaking from storage tanks and contaminate the water supplies. Benzene, also has been eliminated from the gasoline content due to its carcinogenic nature (Busto *et al.*, 2012). The restrictions of these compounds on gasoline have affected the gasoline quality and reduced the octane number, thus, contributed to the poorer engine performance. In this regard, isomerization process has been seen to be an alternative way to improve quality of gasoline, which converts linear alkanes to a higher octane number branched-chain alkanes.

The isomerization reaction is generally carried out over bifunctional metal/acidic catalyst consisting both metallic and acidic functions. In this process, an efficient catalyst is required to achieve high selectivity to various isomers and reduce undesired cracking products. Current industrial catalysts such as platinum supported on halogenated alumina and zirconia showed good potential for isomerization reaction. This kind of catalysts have high activity, high selectivity toward *n*-alkane isomers and can perform at low reaction temperature. However, these catalysts suffered from serious environmental pollution and their complicated operation (Hidalgo *et al.*, 2013). Among all the supports, zeolites are

the most promising solid acid catalyst, known as microporous crystalline aluminosilicates. They have been widely used in many industrial processes due to their shape selectivity, good thermal stability, hydrophobicity and strong electron transfer to their enormous acid sites (Triwahyono *et al.*, 2011). A three-dimensional network with well-defined channels and pore system of zeolite provide high activity and selectivity for the catalytic reactions. Other than that, the acidity of the zeolite can be controlled via the Si/Al ratio by using several treatment methods. The amazing properties of zeolite offers new advanced catalytic technologies to produce high-quality products with maximum selectivity and energy efficiency (Akhmedov and Al-Khowaiter, 2007). Unfortunately, zeolites have some diffusion limitations when dealing with bulky compounds owing to its small and merely micropores, which led to high diffusion limitation for catalytic reaction processes.

Silica-based fibrous material has been extensively studied by researchers after the discovery of fibrous silica nanosphere (KCC-1) by Polshettiwar *et al.*, 2010. The KCC-1 was first prepared using the microwave-assisted hydrothermal technique which exhibited excellent properties, including a high surface area, a fibrous surface morphology, good thermal and hydrothermal stabilities and mechanical stability. Moon, *et al.*, (2012) reported that the mesoporous silica with fibrous morphology has high surface area compared with a typical hexagonal or cubic pore structure which is suitable for good catalytic support. Previous studies have many discoveries related to the acid-catalyzed for isomerization reaction. They discovered that the isomerization supports must have appropriated acidity for the good catalytic activity. However, the KCC-1 which fully is composed with silica does not provide an adequate acid sites to promote acid-catalyzed isomerization reaction (Moon and Lee, 2012).

In the present work, newly combined zeolite-based with fibrous silica was prepared via self-assembly process in the microemulsion system. This new catalyst has a potential to overcome the diffusion limitation possessed by zeolite and inadequate acidity provided by KCC-1. Zeolite with dendrimeric silica fiber will provide better accesses to active sites. The presence of dendrimeric silica fiber gives high surface area and leads to

widely disperse of active sites in the dendrimeric silica fibers. Other than that, implementation of combined silica based material with zeolite has enhanced the acidity of the catalyst to overcome the unadequate acidity provided by solely silica of KCC-1. The high acidity will enhance the isomerization reaction towards producing high octane number gasoline.

### 1.3 Objectives

The objectives of this study are:

1. To synthesize fibrous silica Y (FY), protonated Y (HY), FY (HFY), platinum loaded on HY (Pt/HY), and platinum loaded on HFY (Pt/HFY).
2. To characterize the physicochemical properties of HY, HFY, Pt/HY, and Pt/HFY catalysts.
3. To study the catalytic activity of HY, HFY, Pt/HY, and Pt/HFY catalysts in the isomerization of *n*-hexane.
4. To study the acidity and the generation of protonic acid sites for all the catalyst in the presence of hydrogen.

### 1.4 Scope of Study

There are 4 scopes discussed in this study. The first scope was discussed in the preparation of the catalysts. The crucial preparation is on the synthesis of fibrous silica Y zeolite (FY). The synthesis involved microemulsion system from cetyltrimethyl ammonium bromide (CTAB), toluene, and *n*-butanol. CTAB is used as a surfactant, toluene as an oil phase and *n*-butanol as a co-surfactant. The preparation also involved protonation, in which all the catalysts were converted into ammonium form by ion-exchange and followed by calcination to convert the  $\text{NH}_4^+$  species into  $\text{H}^+$ . Additionally,

incipient wetness impregnation method was used in loading of platinum metal onto the support catalyst.

The physical properties of the catalysts were investigated using various characterization methods. The structural of the catalysts was detected by X-ray diffraction (XRD). The morphologies features were examined by a Field Emission Scanning Electron Microscope (FESEM). The elemental analysis was carried out with energy dispersion X-ray (EDX). The isotherm and pore size distribution were analyzed by N<sub>2</sub> physisorption (BET method). Molecular vibration was detected by FTIR spectroscopy. The composition of silica and alumina of the catalysts were determined by Nuclear Magnetic Resonance (NMR).

Catalytic activity of *n*-hexane isomerization for all the catalysts were studied in a continuous pulse reactor at the reaction temperature range of 423-623 K. The activity and stability of the catalysts in the presence and absence of hydrogen were studied. The isomerization reaction was first performed in the hydrogen stream then switched to the nitrogen stream and lastly switched back to hydrogen.

The acidity of all the catalyst was studied using IR pyridine preadsorbed. The pyridine was adsorbed at 423 K followed by outgassing from 423 K to 573 K. The generation of protonic acid sites from molecular hydrogen on the catalysts was elucidated using IR pyridine preadsorbed followed by adsorption of hydrogen at room temperature. The hydrogen was heated and removed stepwise and the spectra was recorded using Agilent Carry 640 FTIR spectrometer.

## 1.5 Significance of Study

HY, HFY, Pt/HY and Pt/HFY were prepared in this study as an efficient catalysts for isomerization of *n*-hexane by generation abundance of protonic acid sites. A detailed



study on the properties of the catalysts were conducted using the X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), energy dispersion X-ray (EDX), N<sub>2</sub> physisorption, FTIR-spectroscopy, IR pyridine preadsorbed FTIR, and Magic Angle Spinning-Nuclear Magnetic Resonance (MAS-NMR). The new catalyst based on fibrous silica Y zeolite increased Lewis acid sites due to the presence of dendrimeric silica for trapping the electrons produced from molecular hydrogen spillover.

## **1.6 Research Outline**

This study is divided into five chapters. Chapter 1 discussed the introduction of isomerization process, catalytic progress to enhance isomers yield and the potential of new catalyst to generate protonic acid sites. The problem statement discussed about main problem faced by previous isomerization catalysts and hypothesis provided solution to the limitation. The scope of study covers the overall research work to meet the objectives of the study.

Chapter 2 covered the literature review related to this study. The finding of the previous studies are discussed in detail to obtain a clearer view about the preparation of fibrous silica Y zeolite and the catalytic performance in the isomerization reaction.

Chapter 3 includes the research methodology describes the materials, chemicals and instrumentations used for the experimental purposes. This chapter also included the flow of the research from the preparation of the catalysts until the catalytic testing study.

Chapter 4 consists of the results and discussion of the overall study. All the results obtained are analyzed and discussed in detail in order to solve the problems facing by current technology.

Chapter 5 consists of the conclusion about the study and the recommendation for future studies.

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