

*n*-PENTANE ORIGINATED PROTONIC ACID SITES  
OVER ZINC PROMOTED HZSM-5

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*Teristimewa untuk;  
ibunda Siti Mulyani, Bp. Zaed Nurul Hadi (alm) dan semua kakakku  
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## ABSTRACT

The formation of protonic acid sites from hydrogen and *n*-pentane over Zn/HZSM-5 was evidenced by pyridine adsorption IR spectroscopy. The results showed that protonic acid sites were formed by heat treatment of Zn/HZSM-5 in the presence of molecular hydrogen which started at room temperature with a concomitant elimination of Lewis acid sites. Removal of molecular hydrogen decreased the protonic acid sites and restored the Lewis acid sites to its original intensity at 573 K. These phenomena are consistent with the concept of 'molecular hydrogen-originated protonic acid sites' in which the process is initiated by dissociation of hydrogen molecules to hydrogen atoms, spilling over onto the HZSM-5 and followed by surface diffusion. Then hydrogen atom converts into a proton by releasing electron to Lewis acid site. The formation of protonic acid sites on Zn/HZSM-5 induced by molecular hydrogen is a reversible process. The protonic acid sites were also formed from *n*-pentane on Zn/HZSM-5. Lewis acid sites were converted to protonic acid sites when the sample was heated in *n*-pentane, and the formed protonic acid sites were subsequently eliminated by removal of *n*-pentane with a restoration of Lewis acid sites. These are essentially the same as a formation of protonic acid sites from molecular hydrogen. It is plausible that the formation of protonic acid site was initiated by dissociation of *n*-pentane to form hydrogen atom and certain molecule. Then, the hydrogen atom spills over onto the HZSM-5 followed by surface diffusion to form protonic acid sites by releasing electron to the Lewis acid sites. The formed protonic acid sites which act as active sites played significant role in the reactions of *n*-pentane.

## ABSTRAK

Pembentukan tapak asid protonik daripada hidrogen dan *n*-pentana atas Zn/HZSM-5 telah dibuktikan melalui penjerapan piridin menggunakan spektroskopi inframerah. Hasil kajian menunjukkan bahawa tapak asid protonik terbentuk manakala tapak asid Lewis tersingkir apabila Zn/HZSM-5 dipanaskan bermula pada suhu bilik dalam kehadiran molekul hidrogen. Penyingkiran molekul hidrogen ini mengurangkan tapak asid protonik dan mengembalikan tapak asid Lewis kepada kepekatan asalnya pada suhu 573 K. Fenomena ini didapati menepati konsep ‘molecular hydrogen-originated protonic acid sites’ di mana ia dimulakan dengan pemisahan molekul hidrogen kepada atom hidrogen yang melimpah ke atas HZSM-5 dan diikuti dengan penjerapan di permukaannya. Atom hidrogen ini seterusnya bertukar menjadi proton dengan memindahkan elektron kepada tapak asid Lewis. Pembentukan tapak asid protonik pada Zn/HZSM-5 yang dijana oleh molekul hidrogen ini merupakan proses berbalik. Tapak asid protonik juga didapati terbentuk daripada *n*-pentana pada Zn/HZSM-5. Pada mulanya, tapak asid Lewis akan ditukarkan kepada tapak asid protonik apabila sampel dipanaskan dalam *n*-pentana, seterusnya tapak asid protonik yang terbentuk itu dihapuskan dengan menyingkirkan *n*-pentana untuk menjanakan semula tapak asid Lewis. Ini bertepatan dengan pembentukan tapak asid protonik daripada molekul hidrogen. Dengan ini pembentukan tapak asid protonik berkemungkinan dimulakan dengan penguraian *n*-pentana bagi membentuk atom hidrogen dan molekul tertentu. Kemudian, atom hidrogen akan melimpah ke atas HZSM-5 diikuti dengan pembauran permukaan untuk membentuk tapak asid protonik dengan membebaskan elektron kepada tapak asid Lewis. Tapak asid protonik yang terbentuk bertindak sebagai tapak aktif yang berperanan penting dalam tindak balas *n*-pentana.

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**LIST OF SYMBOLS**

|               |   |                        |
|---------------|---|------------------------|
| $\theta$      | - | Angle                  |
| $\varepsilon$ | - | Extinction coefficient |
| K             | - | Kelvin                 |
| $e^-$         | - | Electron               |

**LIST OF ABBREVIATIONS**

|       |   |                                   |
|-------|---|-----------------------------------|
| RON   | - | Research Octane Number            |
| ZSM-5 | - | Zeolite Socony Mobil-Five         |
| XRD   | - | X-Ray Diffraction                 |
| FTIR  | - | Fourier Transform Infra Red       |
| TPD   | - | Temperature-Programmed Desorption |
| CFR   | - | Continuous Flow Reactor           |
| L     | - | Lewis                             |
| B     | - | Brønsted                          |
| Py    | - | Pyridine                          |
| BET   | - | Brunauer, Emmet and Teller        |
| n     | - | Normal                            |
| i     | - | Iso                               |

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

The considerable need for high quality fuel in an era of pressing environmental concern demands the resurgence in chemical processes and catalysis science. It has given challenges and opportunities in these research areas to obtain a sustainable process and catalysts with high activity and selectivity as well as acceptable poison resistance.

A lot of research projects on the chemical processes and catalysis science have been done in order to enhance the quality of gasoline. The skeletal isomerization of hydrocarbon was recommended as the important processes to produce high quality gasoline by improving its research octane number (RON) [1-3]. The effective catalysts for this process such as solid acid catalysts based on metal oxide and zeolitic materials therefore were extensively observed as well. These solid acid catalysts were more favourable as compared to the liquid catalysts which cause significant corrosion and environment problems [3-5]. Moreover these types of solid acid catalyst have been widely applied in the petroleum industries.

Solid acid catalysts such as ZSM5 and/or Beta zeolite-based catalysts and chloride alumina-based catalysts are conventionally available for the skeletal isomerization of alkanes. Although zeolite-based catalysts have an outstanding tolerance of feedstock poisons, high temperature is still required. The chlorinated

alumina-based catalysts suffer from extreme sensitivity to all kinds of feed contaminants [2, 3]. Recently, zirconia-based 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> were reported as efficient catalysts for the skeletal isomerization of alkanes. Moreover, Pt/SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub> has been used as catalyst for industrial processes and Pt/WO<sub>3</sub>-ZrO<sub>2</sub> has been proposed as alternative catalyst for isomerization of alkanes [1, 4-5]. However, Pt/SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub> and Pt/WO<sub>3</sub>-ZrO<sub>2</sub> were less selective for production of clean gasoline by the skeletal isomerization of *n*-heptane. Okuhara [3] reported that metal loaded-zeolite based catalysts such as Pt/HZSM-5, Pd-H $\beta$ , and Pt/H- $\beta$  have great potential for production of clean gasoline by the skeletal isomerization of *n*-heptane. These solid acid catalysts were more active and selective for isomerization of *n*-heptane due to the effect of pore structure.

Pt/SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub> and Pt/WO<sub>3</sub>-ZrO<sub>2</sub> possess a high and stable activity for the isomerization of alkanes when the reaction is conducted in the presence of hydrogen. Hattori and co-workers [6-7] suggested that these catalytic performances were due to the generation of protonic acid sites from hydrogen molecule and became active sites for isomerization of alkanes. Moreover, hydrogen stream is required in the isomerization of heptane by Pt/HZSM-5, Pd-H $\beta$ , and Pt/H- $\beta$  to enhance and stabilize the activity of catalysts [3].

However, recently Iglesia *et al.* [8] reported that the isomerization 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. Based on that report, then we postulated that the active sites for isomerization can be formed from the reactant *i.e.* alkanes. However, the direct evidences and detail mechanism of the formation of active sites from reactant in the acid catalyzed reaction are not observed yet.

Therefore, we intended to study the formation of protonic acid sites from reactant *i.e.* alkanes over solid acid catalyst.



## 1.1 Objective of Research

The objective of this research is to elucidate the generation of protonic acid sites from *n*-pentane over Zn/HZSM-5 solid acid catalyst.

## 1.3 Scope of Research

This research enclosed the synthesis and characterization of catalysts as well FTIR study of pyridine adsorption for the generation of protonic acid sites. Zn/HZSM-5 solid acid catalyst was prepared by ion exchange method. The structure of catalysts was determined by X-ray Diffraction (XRD) technique, while the specific surface area of catalyst was measured with BET surface area analyzer. The functional group of catalysts was considered by Fourier Transform Infra Red (FTIR) spectroscopy. Ammonia Temperature-Programmed Desorption (TPD) was used to determine the distribution of acid sites on the catalyst. The activity of catalysts was tested on a Continuous Flow Reactor (CFR) in the presence and absence of hydrogen. The generation of protonic acid sites over solid acid catalysts was studied by pyridine pre-adsorbed FTIR spectroscopy.