SYNTHESIS AND CHARACTERIZATION OF IRIDIUM/PLATINUM-HZSM5 CATALYST FOR ISOMERIZATION OF *n*-PENTANE

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Specially dedicated to Abah and Mak,

Setiabudi Mohamed Khosni & Rustijah Jamin,

‘Thank you for always being here with me’

&

Beloved husband, Mohd Shamsul Riza Bashri, thank you for picking up all my missing pieces

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ABSTRACT

Catalytic isomerization of *n*-alkane has been one of the important processes in petrochemical refining industry to increase the octane number of gasoline. This study investigates the catalytic activity of Ir/Pt-HZSM5 for *n*-pentane isomerization. The potential of iridium (Ir) as a catalyst for *n*-pentane isomerization was preliminarily investigated by using Ir-HZSM5. The result showed that Ir has a great potential to be used as a promoter, hence as a co-promoter for Pt-HZSM5. Ir/Pt-HZSM5 was prepared by impregnation of Ir on 0.1wt% Pt-HZSM5. The catalyst was characterized with X-Ray Diffraction (XRD), Surface Area Analyzer, Fourier Transformation Infra Red (FTIR), Nuclear Magnetic Resonance (NMR), Electron Spin Resonance (ESR) and X-Ray Photoelectron Spectroscopy (XPS). The acidity was determined by 2,6-lutidine adsorbed FTIR spectroscopy, while the catalytic activity was carried out in a microcatalytic pulse reactor. The results showed that Ir in the form of IrO_2 was bonded to perturbed silanol groups. The presence of 0.1 wt% Ir slightly increased the acidity of Pt-HZSM5 and selectivity of isopentane. Ir enhanced the formation of protonic acid sites which participate in the isomerization, and inhibited the formation of hydroxyl groups which may participate in the enhancement of the cracking reaction. An increase in Ir loading (0-2.0 wt%) continuously decreased the acid sites. At low Ir loading, cracking process proceed through dimerization-cracking step, whereas high Ir loading reduces the contribution of dimerization-cracking step and promotes the contribution of hydrogenolysis. An increase in Si/Al ratio (23-280) decreased the number of strong acid sites which led to a decrease in the activity towards *n*-pentane isomerization. From the Response Surface Methodology (RSM) experiments, the optimum conditions for the *n*-pentane isomerization over Ir/Pt-HZSM5 were at treatment temperature of 723 K, treatment time of 6 h, reaction temperature of 548 K and flow of hydrogen over weight of catalyst, F/W of 500 ml g^{-1} min^{-1} in which the predicted value for the *n*-pentane conversion, isopentane selectivity and isopentane yield was 63.0%, 98.2% and 61.9%, respectively. The catalytic activity studies confirmed that *n*-pentane isomerization over Ir/Pt-HZSM5 strongly depending on the promotive effect of hydrogen. Ir/Pt-HZSM5 exhibited high stability during the coke removal process which was shown by the high activity of Ir/Pt-HZSM5 in the *n*-pentane isomerization after 90 pulses (30 h).

ABSTRAK

Pengisomeran bermangkin *n*-alkana telah menjadi salah satu proses penting dalam industri penapisan petrokimia untuk meningkatkan nombor oktana petrol. Kajian ini meneliti aktiviti pemangkin Ir/Pt-HZSM5 untuk pengisomeran *n*-pentana. Potensi iridium (Ir) sebagai pemangkin untuk pengisomeran *n*-pentana awalnya dikaji dengan Ir-HZSM5. Hasil menunjukkan bahawa Ir berpotensi besar untuk digunakan sebagai penggalak, justeru sebagai penggalak bersama untuk Pt-HZSM5. Ir/Pt-HZSM5 telah disediakan dengan pengisitepuan Ir ke atas 0.1wt% Pt-HZSM5. Pemangkin telah dicirikan dengan Pembelauan Sinar-X (XRD), Analisis Luas Permukaan, Transformasi Fourier Inframerah (FTIR), Magnet Nuklear Beresonans (NMR), Putaran Elektron Beresonans (ESR) dan Spektroskopi Fotoelektron Sinar-X (XPS). Keasidan telah ditentukan oleh spektroskopi FTIR jerap lutidina, manakala aktiviti pemangkin telah dijalankan dalam reaktor denyut microkatalitik. Keputusan menunjukkan bahawa Ir dalam bentuk IrO_2 terikat kepada kumpulan silanol terkacau. Kehadiran 0.1wt% Ir meningkatkan sedikit keasidan Pt-HZSM5 dan kepemilihan terhadap isopentana. Ir meningkatkan pembentukan tapak asid berproton yang mengambil bahagian dalam proses pengisomeran, dan menghalang pembentukan kumpulan hidroksil yang boleh mengambil bahagian dalam peningkatan tindak balas keretakan. Penambahan beban Ir (0-2.0 wt%) terus mengurangkan tapak asid. Pada pembebanan rendah Ir, proses keretakan berlaku melalui langkah pendimeran-keretakan, manakala pembebanan tinggi Ir mengurangkan sumbangan langkah pendimeran-keretakan dan menggalakkan sumbangan hidrogenolisis. Peningkatan nisbah Si/Al (23-280) mengurangkan bilangan tapak asid kuat yang membawa kepada penurunan dalam aktiviti pengisomeran *n*-pentana. Dari eksperimen Metodologi Respons Permukaan (RSM), keadaan optimum bagi pengisomeran *n*-pentana terhadap Ir/Pt-HZSM5 adalah suhu rawatan 723 K, masa rawatan 6 h, suhu tindakbalas 548 K dan aliran hidrogen bahagi berat pemangkin, *F/W* sebanyak 500 ml g^{-1} min^{-1} di mana nilai yang diramalkan untuk penukaran *n*-pentana, kepemilihan isopentana dan hasil isopentana adalah 63.0%, 98.2% dan 61.9%, masing-masing. Kajian aktiviti pemangkin mengesahkan bahawa pengisomeran *n*-pentana terhadap Ir/Pt-HZSM5 amat bergantung pada kesan penggalakan daripada hidrogen. Ir/Pt-HZSM5 menunjukan kestabilan yang tinggi semasa process penyingkiran kok yang dibuktikan melalui aktiviti yang tinggi untuk Ir/Pt-HZSM5 dalam pengisomeran *n*-pentana selepas 90 denyutan (30 j).

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LIST OF ABBREVIATIONS

Al	-	Aluminum
BET	-	Brunauer Emmett Teller
C_n	-	Carbon atom with *n* carbon number
cus	-	Coordinated Unsaturated
ESR	-	Electron Spin Resonance
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared Spectroscopy
HZSM5	-	Zeolite Socony Mobil-5
Ir	-	Iridium
Ir/Pt-HZSM5	-	Iridium/ Platinum-HZSM5
MCM-41	-	Mobil Composition Matter-41
MFI	-	Mordenite Framework Inverted
NMR	-	Nuclear Magnetic Resonance
Pt	-	Platinum
Pt-HZSM5	-	Platinum-HZSM5
RSM	-	Response Surface Methodology
RON	-	Research Octane Number
SAPO	-	Silica Aluminophosphate
Si	-	Silicon
USY	-	Ultra Stable Y
XRD	-	X-Ray Diffraction
XPS	-	X-ray Photoelectron Spectroscopy

LIST OF SYMBOLS

Å - Angstrom
cm - Centimeter
g - Gram
h - Hour
K - Kelvin
kJ - Kilojoule
m - Meter
µmol - Micromole
ml - Milliliter
min - Minutes
% - Percentage
θ - Theta
wt % - Weight Percentage

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Recently, the increasing awareness in improving environmental protection and promoting efficiency of automotive motors encourages the formulation of new catalysts and development of new processes for gasoline production. The widespread removal of lead antiknock additive from gasoline and the rising demands of high-performance internal-combustion engines are increasing the need for octane, or knock resistance, in the gasoline pool. Thus, the branched alkanes will play a major role as gasoline components due to the fact that they have higher octane number than linear alkanes. For example, research octane number (RON) of *n*-pentane is 62, while the isopentane is 92 (Ghosh *et al.*, 2006). For this reason, the use of gasoline with higher branched alkanes proportions is an alternative to obtain the required properties of fuel and it can be achieved by isomerizing *n*-pentane and *n*-hexane, which are the main component of light straight run (LSR) gasoline (Wang *et al.*, 2004).

The catalysts commercially used for the earlier industrial isomerization process are Friedel Crafts catalysts such as $AlCl_3$, $SbCl_3$ and $FeCl_3$. However, these catalysts do not exist anymore due to problems of corrosion of the reactor and the disposal of the used catalyst. Then, bifunctional catalysts containing metallic sites for hydrogenation-dehydrogenation and acid sites for skeletal isomerization via carbenium ions were used (Weitkamp, 1982). It is known that platinum supported on chlorinated alumina was effective for isomerization of *n*-alkanes and capable to perform the isomerization at lower temperature of 370-470 K. However, this catalyst causes corrosion and very sensitive to water and sulphur even in concentration as low as 10 ppm (Ono, 2003).

More recently, bifunctional catalyst of metal supported on zeolite was developed and a high conversion which was near to equilibrium value was obtained upon the catalyst was used at medium temperature of 533-588 K (Zhang *et al*., 1995). Zeolites have drawn much attention as support materials due to their high surface area, acidic nature and well-defined structure (Corma, 1997; Rahimi and Karimzadeh, 2011; Lima *et al*., 2011). In addition, some undesired side effects observed with other catalysts, such as corrosion, can be avoided. Among the available zeolites, a high-silica zeolite of the pentasil family, like HZSM5, has shown to be promising catalyst support for isomerization because of its acidity, shape selectivity, and thermal stability (Cañizares *et al*., 1997). The presence of promoters such as platinum (Fujimoto *et al*., 1992; Aboul-Gheit *et al*., 2011a; Chao *et al*., 2010; Aboul-Gheit *et al*., 2011b), gallium (Iglesia *et al*., 1992) and zinc (Biscardi *et al*., 1998; Biscardi and Iglesia, 1999; Triwahyono *et al*., 2011) in zeolite may favour the activity and selectivity for isomerization. In particular, platinum supported on HZSM5 was found to be active and stable for the isomerization of *n*-alkanes (Fujimoto *et al*., 1992).

It has been reported that the isomerization process over bifunctional heterogeneous catalysts was influenced by the hydrogen spillover phenomenon (Pajonk, 2000). The promotive effect of hydrogen has been interpreted by the generation of protonic acid sites, in which the hydrogen migrates or spills over from noble metal sites onto the acidic oxide support, during the reaction (Hattori, 1993). However, this hydrogen spillover effect has only been observed for a limited class of catalysts, including zeolite supported metal catalysts (Fujimoto *et al*., 1992; Triwahyono *et al*., 2011) and zirconia based acid catalysts (Ebitani *et al*., 1991; Hattori and Shishido, 1997; Triwahyono *et al*., 2003a; Triwahyono *et al*., 2006; Ruslan *et al*., 2011), with different mechanisms and rate formation of protonic acid sites (Conner and Falconer, 1995). Therefore, the development of new catalysts with a better hydrogen spillover phenomenon and higher activity is necessary for the isomerization process.

In certain cases, the introduction of a second metal is sometimes necessary to increase the activity and stability of the support and suppress the production of cracked products (Blomsma *et al*., 1997a; Mao *et al*., 2000). In addition to platinum, gallium and zinc, iridium has been used as a co-promoter to give these effects. In catalytic reforming, iridium species are well known co-promoters that are added to catalysts because of their stability during the coke removal process (Huang *et al*., 1989; Sinfelt, 1976; Dees and Ponec, 1989). Yang and Woo (1992) reported that Pt-Ir/NaY enhanced the activity and stability for the *n*-heptane reforming reaction than the Pt/NaY catalyst due to a decrease in the formation of coke. Additionally, Aboul-Gheit *et al.* (2008a) reported that iridium loaded on Pt-HZSM5 enhanced the catalytic activity for *n*-hexane hydroconversion, most probably due to the higher hydrogenation activity.

Although several studies have reported the isomerization of *n*-alkanes over iridium and platinum supported on zeolite catalysts, however, there is no detailed study on the interaction of iridium with the support and active sites that participate in the formation of active protonic acid sites from molecular hydrogen via hydrogen spillover phenomenon, as well as its relationship to the isomerization process over Ir/Pt-HZSM5 were reported.

1.2 Problem Statement and Hypothesis

Recently, parallel to the increasing awareness in improving environmental protection, the petrochemical refinery industry constantly reformulated their gasoline composition in order to improve their product quality while minimizing undesirable effects to human and environment. The extensive removal of lead antiknock additive from gasoline and the rising demands of high-performance internal-combustion engines are increasing the need for octane, or knock resistance, in the gasoline pool.

Thus, the isomerization of *n*-alkanes to branched alkanes is a useful industrial process due to the fact that branched alkanes have higher octane number than linear alkanes. However, the production of branched alkanes is affected by the fierce competition between isomerization and cracking reaction, including another problem 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. Among the metal present in nature, iridium was shown to be active for hydrogenolysis process and has been incorporated as a co-promoter in the naphtha reforming catalyst to minimize deactivation by coke deposition (Sinfelt, 1976; Dees and Ponec, 1989; Huang *et al.,* 1989). In addition, it has been reported that the combination of iridium to platinum based catalyst increased the yield of the catalyst towards *n*-alkanes isomerization (Yang and Woo, 1992; Ali *et al.,* 2001; Aboul-Gheit *et al.,* 2008a).

Although several studies have reported the isomerization of *n*-alkanes over iridium and platinum supported zeolite, no detail study on the hydrogen spillover phenomenon and its relationship to the isomerization process over this catalyst were discussed. Therefore it is desirable to study the hydrogen spillover phenomenon of Ir/Pt-HZSM5 for the *n*-pentane isomerization and its association to the enhancement in the isomerization process and inhibition in the formation of coke. It is expected that iridium species loaded on Pt-HZSM5 will form an interaction with Pt-HZSM5, simultaneously increase the number of strong Brönsted and Lewis acid sites and the number of protonic acid sites via hydrogen spillover phenomenon. According to the "hydrogen spillover phenomenon", hydrogen molecules are dissociatively adsorbed on the metal sites to form hydrogen atoms, followed by the release of electrons near to the cus metal cations forming protonic acid sites. Then, electrons will interact with second hydrogen to form hydride ions. The protonic acid sites originated from this phenomenon will promote the isomerization reaction via acid catalyzed mechanism and thus enhance the isomerization process. Whereas, the interaction between hydride ions on Lewis acid sites is expected to suppress the formation of coke on the surface of catalyst. Hydrogen adsorption FTIR and ESR spectroscopy will be used to determine the properties-activity relationship of Ir/Pt-HZSM5. Moreover, the optimum conditions of *n*-pentane isomerization over Ir/Pt-HZSM5 will be determined by Response Surface Methodology (RSM).

1.3 Objectives of the Study

The objectives of this study are:

1. To prepare Ir/Pt-HZSM5 catalyst by impregnation method.
2. To characterize the physical and chemical properties of Ir/Pt-HZSM5.
3. To study the interaction of iridium species with Pt-HZSM5 as well as its relationship to the *n*-pentane isomerization.
4. To study the effect of iridium loading on the properties and reaction mechanism of *n*-pentane isomerization over Ir/Pt-HZSM5.
5. To study the effect of Si/Al ratio on the properties and catalytic activity of Ir/Pt-HZSM5.
6. To study the optimum condition for *n*-pentane isomerization over Ir/Pt-HZSM5 by Response Surface Methodology (RSM).

1.4 Scope of Research

As the preliminary study, Ir-HZSM5 was used in order to investigate the potential of iridium metal for *n*-pentane isomerization. Ir-HZSM5 was prepared by wetness impregnation of HZSM5 with an aqueous solution of $IrCl_3{\cdot}3H_2O$, followed by drying at 383 K overnight and calcination at 823 K for 3 h in air. Then, the catalyst was characterized and subjected to *n*-pentane isomerization.

For the preparation of Ir/Pt-HZSM5, firstly, Pt-HZSM5 were prepared by incipient wetness impregnation of HZSM5 with an aqueous solution of $H_2PtCl_6{\cdot}H_2O$, followed by drying at 383 K overnight and calcination at 823 K for 3 h in air. The prepared catalyst was then impregnated with aqueous solution of $IrCl_3{\cdot}3H_2O$ to obtained Ir/Pt-HZSM5, followed by drying at 383 K overnight and calcination at 823 K for 3 h in air.

The physical and chemical properties of Ir/Pt-HZSM5 was characterized by using X-Ray Diffraction (XRD), Surface Area Analyzer, X-Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infra Red spectroscopy (FTIR) spectroscopy of adsorbed 2,6-lutidine.

The interaction of iridium species with Pt-HZSM5 was studied by Nuclear Magnetic Resonance (NMR), Fourier Transform Infra Red spectroscopy (FTIR) and hydrogen adsorption FTIR. The hydrogen adsorption on 2,6-lutidine preadsorbed FTIR and hydrogen adsorption ESR spectroscopy were used to determine the active sites that participate in the formation of active protonic acid sites and electron from molecular hydrogen, respectively. Then, Ir/Pt-HZSM5 was subjected to *n*-pentane isomerization under hydrogen atmosphere in order to study the role of hydrogen molecule-originated protonic acid sites on *n*-pentane isomerization. In this study, the amount of iridium was adjusted to 0.1 wt% and HZSM5 with Si/Al atomic ratio of 23 was used as a support material.

The effects of iridium loading on the properties and catalytic activity of Ir/Pt-HZSM5 were studied by varying the amount of iridium loading (0.1, 0.3, 0.5, 1.0, 2.0 wt%). HZSM5 with Si/Al atomic ratio of 23 was used as a support material. This study was conducted in order to elucidate the effects and limitation of iridium loading on the properties and catalytic activity of the catalyst towards *n*-pentane isomerization. In addition, the plausible reaction mechanisms of *n*-pentane isomerization over Ir/Pt-HZSM5 with different amounts of iridium loading were also studied. The optimum loading of iridium observed in this study was used in the subsequent study.

The effects of Si/Al ratio on the *n*-pentane isomerization over Ir/Pt-HZSM5 were studied by varying the Si/Al atomic ratio of commercial HZSM5 (23, 50, 80 and 280). This study was conducted in order to study the influence of Si/Al ratio on the properties of Ir/Pt-HZSM5, and consequently on the performance of Ir/Pt-HZSM5 in *n*-pentane isomerization. The most potential catalyst observed in this study was used in the optimization study by Response Surface Methodology (RSM) analysis.

Finally, the optimum conditions for *n*-pentane isomerization over Ir/Pt-HZSM5 was identified by RSM using Statsoft Statistica 8.0 software with face-centered central composite design (FCCD) method. The independent variables used in this study were treatment temperature, treatment time, reaction temperature and flow of hydrogen over weight of catalyst.

1.5 Significance of Study

This study was conducted to prepare the catalyst of Ir and Pt promoted on HZSM-5 (Ir/Pt-HZSM5). A detailed investigation of the properties of the catalyst, the active sites that participate in the formation of active protonic acid sites from molecular hydrogen, as well as its relationship to the catalytic activity is conducted. This catalyst is expected to give high conversion and selectivity for isopentane and consequently will be beneficial for knowledge transfer and also in oil and gas industries. In addition, the understanding of the properties-activity relationship of Ir/Pt-HZSM5 becomes an archetype in the development of new type of catalyst for isomerization of *n*-alkane.

1.6 Thesis Outline

This thesis is divided into five chapters. In Chapter 1, introduction is given about the fuel processing demand and the importance of high research octane number, which cleared the vision of catalytic isomerization process. The conventional preparation methods of catalyst were also mentioned and the potential of Iridium as second metal was highlighted. Problem statement of the current research was stated to give the clear objectives of the present study, and the scope of study covers the research work done to meet these objectives.

Chapter 2 or literature review covers the detailed reviews of all the previous studies that have been done in order to get clear view in the synthesis of Ir/Pt-HZSM5, the characterization of the catalyst, and the effect of hydrogen on the *n*-pentane isomerization.

Chapter 3 or experimental methodology describes the particulars of the materials and chemical reagents used in the present work, the procedure for catalyst preparation, characterization and *n*-alkane isomerization reaction which consists of experimental setup, and product analysis calculation.

In Chapter 4, results and discussion was divided into four parts, (i) effect of iridium loading on HZSM5 for isomerization of *n*-pentane, (ii) IR study of iridium bonded to perturbed silanol groups of Pt-HZSM5 for *n*-pentane isomerization, (iii) Ir/Pt-HZSM5 for *n*-pentane isomerization: Effect of iridium loading on the properties and catalytic activity, and (iv) Ir/Pt-HZSM5 for *n*-pentane isomerization: Effect of Si/Al ratio and reaction optimization by response surface methodology.

Finally, Chapter 5 covered the conclusions about the study. The recommendations for future studies were also given in this chapter.

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