ROLE OF HYDROGEN ON THE FORMATION OF MOLYBDENUM OXYHYDRIDE FOR CUMENE HYDROCRACKING OVER PLATINUM LOADED MOLYBDENUM OXIDE

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To my beloved husband, Mohd. Zaid Hasani Ahmad Shazali and my twins, thank you for picking up all my missing pieces.

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To my family for the everlasting love and support throughout my study years.

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ABSTRACT

The acidic nature of platinum supported molybdenum oxide (Pt/MoO$_3$) catalyst has been found to have effects on cumene hydrocracking. The molybdenum oxide (MoO$_3$) sample was prepared by calcination of molybdic acid (H$_2$MoO$_4$) at 673 K for 3 h. The Pt/MoO$_3$ was prepared by impregnation of MoO$_3$ with an aqueous solution of chloroplatinic acid (H$_2$PtCl$_6$) followed by calcination at 673 K in air. The catalyst was characterized by x-ray diffraction (XRD), field emission scanning electron microscopy-energy dispersive x-ray (FESEM-EDX), fourier transformation infra red (FTIR) and electron spin resonance (ESR). The hydrogen influence on surface of Pt/MoO$_3$ was studied by *in-situ* XRD, 2,6-lutidine preadsorbed FTIR, ESR spectroscopy and hydrogen uptake capacity. 2,6-lutidine preadsorbed FTIR showed that both catalysts possess doublet adsorption bands ascribed to Lewis acid sites, and duo-doublet bands ascribed to hydroxyl groups; these indicate an -OH defect structure of MoO$_3$ and Mo-OH Brönsted acidic sites. The XRD result confirmed the formation of molybdenum oxyhydride (MoO$_x$)$^-$(H$_y$)$^+$ on the hydrogen treated Pt/MoO$_3$, whereas the hydrogen adsorption on 2,6-lutidine preadsorbed catalysts showed the formation of protonic acid sites over Pt/MoO$_3$. These results strongly suggested that the interaction of molecular hydrogen with Pt/MoO$_3$ formed acidic Brönsted (MoO$_x$)$^-$(H$_y$)$^+$ via a hydrogen spillover mechanism. In fact, no (MoO$_x$)$^-$(H$_y$)$^+$ and protonic acid sites were observed on Pt-free MoO$_3$. Hydrogen adsorption of Pt/MoO$_3$ was studied at the temperature range of 373 - 573 K and at the initial hydrogen pressure of 6.7 kPa. The hydrogen uptake exceeded the H/Pt ratio of unity for adsorption at and above 423 K, indicating that hydrogen adsorption processes involves dissociative adsorption of hydrogen on Pt sites, hydrogen atom spillover and surface diffusion of the spiltover hydrogen atom over the bulk surface of MoO$_3$ followed by formation of (MoO$_x$)$^-$(H$_y$)$^+$. The rate controlling step of the hydrogen adsorption on Pt/MoO$_3$ was the surface diffusion of the spiltover hydrogen with the activation energy of 83.1 kJ/ mol. The presence of hydrogen enhanced the activity of Pt/MoO$_3$ in the cumene hydrocracking in which the rate conversion of cumene increased by about 30%, while the apparent activation energy decreased by approximately 28 kJ/mol. From the Response Surface Methodology (RSM), the optimum conditions for cumene hydrocracking for Pt/MoO$_3$ were at treatment temperature of 673 K, treatment time of 4 h, reaction temperature of 573 K and flow of hydrogen over weight of catalyst (*F/W*) of 375 ml g^{-1} min^{-1}, which the predicted value of propylene yield was 16.7% while the experimental value gave 17.1%.

ABSTRAK

Sifat berasid platinum disokong pemangkin molibdenum oksida (Pt/MoO_3) telah didapati mempunyai kesan ke atas penghidropecahan kumena. Sampel molibdenum oksida (MoO_3) telah dihasilkan oleh pengkalsinan asid molibdik (H_2MoO_4) pada 673 K selama 3 jam. Pt/MoO_3 ini telah dihasilkan melalui proses pengisitepuan MoO_3 dengan asid kloroplatinik (H_2PtCl_6) diikuti pengkalsinan pada suhu 673 K. Pemangkin telah dicirikan dengan pembelauan sinar-x (XRD), mikroskop elektron pengimbas pancaran medan − tenaga serakan sinar-x (FESEM-EDX) , transformasi fourier inframerah (FTIR) dan putaran elektron beresonans (ESR). Kesan hidrogen pada permukaan Pt/MoO_3 telah dikaji menggunakan XRD, penjerapan 2,6-lutidin FTIR, ESR dan kapasiti penyerapan hidrogen. Penjerapan 2,6-lutidin FTIR menunjukkan bahawa kedua-dua pemangkin mempunyai penjerapan berkembar untuk tapak asid Lewis, dan duo-penjerapan berkembar untuk kumpulan hidroksil; ini menunjukkan -OH struktur cacat MoO_3 dan Mo-OH tapak asid Brönsted. Keputusan XRD mengesahkan pembentukan molibdenum oksihidrida $(MoO_x)^-(H_y)^+$ pada Pt/MoO_3 dirawat hidrogen, manakala penjerapan hidrogen pada pemangkin terjerap 2,6-lutidin menunjukkan pembentukan tapak asid protonik pada Pt/MoO_3. Keputusan ini mencadangkan bahawa interaksi molekul hidrogen dengan Pt/MoO_3 membentuk asid Brönsted $(MoO_x)^-(H_y)^+$ melalui mekanisma limpahan hidrogen. Malah, tidak ada $(MoO_x)^-(H_y)^+$ dan tapak asid protonik diperhatikan pada MoO_3 tanpa Pt. Hidrogen penjerapan Pt/MoO_3 dikaji pada julat suhu 373-573 K dan pada tekanan hidrogen awal 6.7 kPa. Pengambilan hidrogen melebihi nisbah perpaduan H/Pt bagi penjerapan pada dan lebih tinggi daripada 423 K, menunjukkan bahawa penjerapan hidrogen melibatkan proses pemisahan hidrogen pada tapak Pt, limpahan dan penyebaran atom hidrogen atas sebahagian besar permukaan MoO_3 diikuti dengan pembentukan $(MoO_x)^-(H_y)^+$. Langkah mengawal kadar adalah langkah penjerapan limpahan hidrogen oleh Pt/MoO_3 dengan tenaga pengaktifan 83.1 kJ/mol. Kehadiran hidrogen meningkatkan aktiviti Pt/MoO_3 dalam penghidropecahan kumena di mana meningkat sebanyak 30%, manakala tenaga pengaktifan menurun sebanyak 28 kJ/mol. Daripada Kaedah Gerakbalas Permukaan (RSM), keadaan optimum untuk penghidropecahan kumena oleh Pt/MoO_3 berada pada suhu 673 K, masa rawatan 4 jam, suhu tindak balas pada 573 K dan aliran hidrogen per jisim pemangkin (*F/W*) pada 375 ml $g^{-1}min^{-1}$, di mana hasil propilena yang diramalkan adalah 16.7%, manakala hasil propilena dalam eksperimen adalah 17.1 %.

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LIST OF ABBREVIATIONS

BET   -   Brunauer Emmet and Teller

Cus   -   Coordinated Unsaturated

FESEM-EDX   -   Field Emission Scanning Electron Microscopy-Energy Dispersive X-Ray

ESR   -   Electron Spin Resonance

FID   -   Flame Ionization Detector

FTIR   -   Fourier Transformer Infra-Red

HZSM-5   -   Zeolite Socony Mobil-5

HPA   -   Heteropolyanion

HNaX   -   Faujasite

ISS   -   Ion Scattering Spectroscopy

MW   -   Molecular Weight

Pt/H-β -   Pt/H-Beta Zeolite

Pt-H-MOR   -   Pt- Mordenite Zeolite

Pt/MCM-22   -   Pt/Mobile Composition of Matter No. 22

RSM   -   Response Surface Methodology

SA   -   Surface Area

UPS   -   Ultraviolet Photoelectron Spectroscopy

XRD   -   X-Ray Diffraction

XPS   -   X-Ray Photoelectron Spectroscopy

2,6-DMP   -   2,6-dimethylpyridine

LIST OF SYMBOLS

°C	-	Degree celcius
mm	-	Millimeter
m	-	Meter
K	-	Kelvin
g	-	Gram
Å	-	Angstrom
mA	-	Miliampere
kV	-	Kilo Volt
θ	-	Theta
h	-	Hour
mL	-	Mililiter
min	-	Minute
nm	-	Nanometer
kPa	-	Kilopascal
μmol	-	Micromole
kJ	-	Kilojoule

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CHAPTER 1

INTRODUCTION

1.1   General Introduction

In petroleum refining, environmental clean technologies are always been sought due to the stringent environmental regulations (Okamoto *et al*., 2003). There are many industrially important acid catalyzed processes such as alkylation (Feller *et al*., 2004) isomerization (Olah *et al*., 1985) and cracking (Al-Khattaf and de Lasa, 2001) processes which are presently unavoidable drawback due to corrosive nature and environmental problems. Solid acid catalyst seems to be preferred alternatives to the present liquid acid based technologies and significant efforts have already been made to develop solid acid catalyst for this application (Platon and Thomson, 2005).

Heterogeneous solid acid catalysts provide a surface for the chemical reaction to take place. In heterogeneous catalysis, the modification of the essential surface acid-base properties was explored widely in order to obtain the desired solid catalyst by changing factors during preparation such as activation temperature, surface composition and additives. The acidic nature of this solid catalyst has been found to have profound effect on catalytic properties. In the case of cracking or isomerization catalysts, the acid strength is crucial. For oxide supports, the surface

acidity can often be an important factor in modifying catalytic performance. In addition, metal oxide-based catalysts are active over a wide range of temperatures and show good heat resistant properties.

Recently, solid acid catalysts such as Al_2O_3, zeolite, ZrO_2, and MoO_3 based have been explored widely due to stability and regenerable properties and are highly active at a wide range of reaction temperature (Larsen *et al*., 1996; Barton *et al*., 1999; Matsuda *et al*., 2003). Bifunctional catalysts consisting of acidic oxide and noble metal such as Pt and Pd metal showed high efficiency in the acid catalytic reaction such as alkylation, isomerization and cracking. Acid catalytic reaction is normally carried out in the presence of hydrogen due to the role of hydrogen in the formation of protonic acid sites and removal of coke deposits on the surface catalysts (Ebitani *et al*., 1991: Ebitani *et al*., 1992; Guesnet *et al*., 1997). For certain classes of catalyst, the presence of noble metal is indispensible in the interaction with molecular hydrogen which led to the formation of protonic acid sites (Shishido *et al*., 1996a; Triwahyono *et al*., 2003b).

MoO_3 type catalyst has been extensively focused for acid catalytic reaction. Some researchers have proposed that the isomerization reaction occurs on the MoO_x and MoO_xH_y phase, since MoO_3 became active for alkane isomerization after reduction with pure H_2. Blekham *et al.* (1994) and Pham Huu *et al.* (1995) reported that molybdenum compound containing carbon as an oxycarbide (MoO_xC_y) act as an active phase for alkane isomerization which concluded based on the XRD, XPS and HRTEM. In addition, Pham Huu and co-worker (Pham Huu *et al*., 1995; York *et al*., 1996) showed that oxygen-modified Mo_2C and carbon-modified MoO_3 were active and selective for heptanes isomerization. Whereas, Katrib *et al*. (2003) suggested that MoO_2 phase was responsible for hexane isomerization in which the isomerization on MoO_2 proceeds via a bifunctional mechanism. In contrast, Wehrer *et al.* (2003a; 2003b; 2004) pointed out that MoO have been proposed to act as the active phase for alkane isomerisation after incomplete reduction with pure H_2. Matsuda *et al*. (2002) suggested that the generation of the isomerization activity can

be related to reduction of H_xMoO_3 to MoO_xH_y and showed that more acidic MoO_xH_y can be formed from H_xMoO_3 with the larger hydrogen content.

The formation of active MoO_xH_y for isomerization was also reported over SiO_2 (Al-Kandari *et al*., 2009) and TiO_2 (Al-Kandari *et al*., 2008; 2009; 2010; 2013) supports. Based on XPS-UPS, ISS, FTIR and XRD techniques, they reported that the H_2-reduction of MoO_3/TiO_2 showed the formation of bifunctional (metal-acid) $MoO_{2-x}(OH)_y$ phase structure on the surface of TiO_2 which promoted high catalytic activity towards the isomerization of *n*-hexane and *n*-pentane.

In addition, the dynamic modifications of the surface acid-base properties by interaction between the surface and gas molecule have been observed. It has reported the role of hydrogen in the dynamic modification of active sites by molecular hydrogen (Hattori and Shishido, 1997; Triwahyono *et al.,* 2003b) and the quantitative analysis of hydrogen adsorption (Satoh *et al.,* 2000; Triwahyono *et al.,* 2003d; Ruslan *et al*., 2011) for the SO_4^{2-}- ZrO_2, and WO_3-ZrO_2 and MoO_3–ZrO_2 catalysts, respectively. The catalysts follow the concept of "Molecular hydrogen-originated protonic acid sites" in which the hydrogen is dissociatively adsorbed on specific active sites to form hydrogen atoms that spill over onto the supports and undergo surface diffusion to form protonic acid sites near Lewis acid sites.

Although several reports have been published on the MoO_3 type catalysts, there is lack of reports regarding to the study on the acidic properties, effect of hydrogen in the acidity that participate in the formation of active sites from hydrogen molecules via spillover phenomenon and the hydrogen uptake capacity, apparent activation energy, heat of adsorption and rate controlling step involved in the hydrogen adsorption uptake capacity. The promotive effect of hydrogen in cumene hydrocracking activity over Pt/MoO_3 also was reported.

1.2   Problem Statement and Hypotesis

The catalytic performance of MoO_3 is greatly improved in terms of the selectivity and catalyst life by loading a Pt metal operating at hydrogen pressure. Hydrogen has been played an important role in enhancing the acid catalytic process; hydrogen spillover phenomena become crucial in explaining the mechanism of various reactions, such as isomerization and cracking via the formation of hydride.

Catalytic activities of MoO_3 have been studied by several research groups. Matsuda *et al*. reported that reduction of Pt/MoO_3 involved the formation of H_xMoO_3 which accompanied by increases in the surface area (Matsuda *et al*., 2003). Furthermore, they observed the acidic sites based on NH_3-TPD technique. The result showed that reduction of H_xMoO_3 formed MoO_xH_y, which was active in the *n*-heptane isomerization (Matsuda *et al*., 2002). In addition, Al-Kandari and co-workers (Al-Kandari *et al*., 2008; 2009; 2010; 2013) reported the formation of active MoO_xH_y over MoO_3/TiO_2. They studied that the metallic-acidic property of $MoO_{2-x}(OH)_y$ phase promoted high catalytic in *n*-hexane alkane isomerization, which characterized by XPS-UPS, ISS, FTIR and XRD techniques. Despite of its catalytic activity, the effect of hydrogen in the acidic properties of MoO_3 type catalysts, and the hydrogen uptake and kinetics of hydrogen adsorption has not been classified yet.

Therefore, it is desirable to study the acidity properties of MoO_3 type catalyst and its catalytic activity in response to the interaction of molecular hydrogen with the surface catalyst. It is expected that the interaction of molecular hydrogen with catalyst may develop active sites for the acid catalyzed reaction. Cumene catalytic cracking was chosen as model reaction as cumene cracking is known to be probe reaction on Brönsted acid site (Shishido and hattori, 1996b). In this study, XRD, ESR, IR spectroscopy and acid-catalytic cumene hydrocracking will be tested on MoO_3 and Pt/MoO_3 catalysts in order to determine properties-activity relationship. Moreover, the optimum conditions of acid-catalytic cumene hydrocracking over Pt/MoO_3 will be determined by Response Surface Methodology (RSM).

1.3   Objective of Research

The detailed scopes of this research are as follows:

1. To prepare and characterize the MoO_3 and Pt/MoO_3.
2. To study the effect of molecular hydrogen on MoO_3 and Pt/MoO_3 related to;
   a) The acidic properties of the catalyst.
   b) Hydrogen uptake over the catalysts.
   c) Catalytic activity of cumene hydrocracking.
3. To identify the optimum condition of catalytic activity of Pt/MoO_3 catalyst on acid-catalytic cumene hydrocracking by Response Surface Methodology (RSM).

1.4   Scope of Research

In order to complete the objectives of this study, firstly, the molybdenum oxide (MoO_3) was obtained by calcination of molybdic acid, H_2MoO_4 at 673 K for 3 hours. the Pt loaded molybdenum oxide (Pt/MoO_3) was prepared by impregnation of MoO_3 powder with an aqueous solution of chloroplatinic acid, H_2PtCl_6 followed by calcination at 673 K in air, with the content of Pt was 0.5 wt%.

Secondly, MoO_3 and Pt/MoO_3 were characterized using X-ray diffraction analysis (XRD), nitrogen adsorption (BET), Thermogravimetry analysis (TGA), Field Emission Scanning Electron Microscopy-Energy Dispersive X-Ray (FESEM-EDX), IR/Raman spectroscopy, Electron Spin Resonance (ESR) spectroscopy and 2,6-lutidine adsorption IR in order to determine the properties of the catalyst.

The interaction of hydrogen with the catalysts was assessed based on *in-situ* XRD, *in-situ* ESR measurement and 2,6-lutidine preadsorbed IR spectroscopy to confirm the formation and role of the acidic Brönsted $(MoO_x)^-(H_y)^+$ phase on the surface of MoO_3 and MoO_3 catalysts. This study also intended to study the hydrogen adsorption on Pt/MoO_3 and to evaluate the interaction of hydrogen with the surface of Pt/MoO_3 in relation to the quantitative measurement hydrogen uptake, apparent activation energy, heat of adsorption and rate controlling step involved in the hydrogen adsorption on Pt/MoO_3.

Finally, the optimum conditions for acid-catalytic cumene cracking over Pt/MoO_3 was identified by Response Surface Methology (RSM) using Statsoft Statistica 8.0 software with face-centered central composite design (FCCD) method. The independent variables used in this study were treatment time (t), treatment temperature (K), reaction temperature (K) and flow of hydrogen over weight of catalyst (*F/W*). The reaction was carried out in a microcatalytic pulse reactor equipped with an online sampling valve for gas chromatography analysis.

1.5   Significance of Study

This study was conducted to prepare MoO_3 and Pt/MoO_3 and to characterize with XRD, BET surface area analyser, TGA spectrometer, FESEM-EDX, IR/Raman and ESR spectrometer, in order to understand the properties of the catalyst. A detailed investigation on the role of hydrogen in the formation of acidic Brönsted $(MoO_x)^-(H_y)^+$, quantitative measurement hydrogen uptake on the catalyst and acid-catalytic cumene hydrocracking. The optimization condition of acid-catalytic cumene hydrocracking over Pt/MoO_3 is conducted.

The understanding of the properties-activity relationship of MoO_3 and Pt/MoO_3 catalysts became a new finding and consequently beneficial in knowledge transfer in the solid acid catalyst types for acid-catalyzed reaction such as cumene hydrocracking and *n*-alkane isomerization.

1.6   Thesis Outline

This thesis begins with Chapter 1 describes the research background which is about the important of solid acid catalyst in acid catalyzed reaction in petroleum refining field. 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 reviews the details that have been previously studied related to the acid properties of MoO_3 type catalyst and the effect of hydrogen molecule on the acidity and acid catalytic reaction. Chapter 3 describes the experimental, characterization and catalytic testing of catalyst. Chapter 4 concerns with data processing and discussing of characterizations related to acidity, kinetic study and catalytic activities of the catalysts. Finally, the general conclusions and recommendation for future studies were stated in Chapter 5.

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