# *n*-HEPTANE ISOMERIZATION OVER PLATINUM AND PHOSPHORUS SUPPORTED ON MODIFIED MOLYBDENUM OXIDE-MESOPOROUS SILICA

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# Specially dedicated to Abah and Ma, (Abdul Fatah Che Omar & Halimah Yusof)

'Thank you for always being there; your endless love, faith, and encouragement never fail to strengthen me'

&

# To my beloved siblings, (Kak Na, Abe G, Kak Eni, Irah and Suha)

'Your continuous helps, cares, motivations and supports can never be repaid'

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#### ABSTRACT

Catalytic isomerization of *n*-alkanes into the corresponding branched isomers is an important reaction to produce clean fuel with high quality. Therefore, continuing studies on efficient catalysts for isomerization have been conducted in recent years. In this study, mesostructured silica nanoparticles (MSN) were mixed physically with platinum (Pt) and molybdenum oxide (MoO<sub>3</sub>) to prepare Pt/MSN and MoO<sub>3</sub>/MSN for *n*-heptane isomerization. Besides, the effect of support was studied by employing the bicontinuous concentric lamellar silica (KCC-1) which was prepared by microwaveassisted microemulsion, as MoO<sub>3</sub> support (MoO<sub>3</sub>/KCC-1). In order to improve the catalytic activity, the effect of phosphorus (P) loading was carried out by impregnation of MoO<sub>3</sub>/KCC-1 with phosphoric acid to form P/MoO<sub>3</sub>/KCC-1. The catalysts were characterized using x-ray diffraction, surface area analysis, scanning electron microscopy, hydrogen-temperature programmed reduction, nuclear magnetic resonance, ultraviolet-visible, Fourier transform infrared (FTIR) and electron spin resonance (ESR) spectroscopies. High activity of *n*-heptane isomerization was observed on MoO<sub>3</sub>/MSN compared to the Pt/MSN in the presence of hydrogen at 350 °C, with yield of mono- and di-branched iso-heptane reaching 36.6% and 6.8%, respectively. ESR and FTIR studies indicated that the high activity and stability of MoO<sub>3</sub>/MSN could be attributed to the dissociative-adsorption of molecular hydrogen to form atomic hydrogen, which subsequently formed active  $(MoO_x)^-(H_y)^+$ . The interaction of Pt/MSN and molecular hydrogen formed Pt-H, which was not active in *n*-heptane isomerization. In comparison, the MoO<sub>3</sub>/KCC-1 possessed low activation energy (28.1 kJ/mol), as well as gave higher yield of isomers (42.2%) compared to MoO<sub>3</sub>/MSN (35.8%). The result was related to the unique morphology of silica KCC-1, which allowed high accessibility of bulky mass reactant to the active sites. The P/MoO<sub>3</sub>/KCC-1 showed a decrease in the Brønsted acid while new Lewis acidic centers were formed at 1624 cm<sup>-1</sup> and 1587 cm<sup>-1</sup>, as observed by 2,6-lutidine adsorbed infrared. High yield of isomers obtained by P/MoO<sub>3</sub>/KCC-1 was related to the participation of the acidic centers at 1624 cm<sup>-1</sup> and 1587 cm<sup>-1</sup>, in the formation of protons by trapping electrons, as well as high accessibility to active  $(MoO_x)^-(H_y)^+$ . The ANOVA analysis indicated that the reaction temperature was the prominent significant variable in the production of isomers. Based on the optimization experiment, 44.9% yield of isomers was obtained at the optimum condition of 311 °C, treated at 464 °C for 6 h. This study highlighted the potential of modified mesoporous silica in the catalysis research, especially for linear alkane isomerization.

#### ABSTRAK

Pengisomeran bermangkin alkana kepada isomer bercabang merupakan tindak balas penting untuk menghasilkan bahan api bersih dengan kualiti yang tinggi. Oleh itu, kajian berterusan ke atas pemangkin yang cekap untuk pengisomeran telah dilakukan sejak kebelakangan ini. Dalam kajian ini, mesostruktur silika nanozarah (MSN) dicampur secara fizikal dengan platinum (Pt) dan molibdena oksida (MoO<sub>3</sub>) bagi menyediakan Pt/MSN dan MoO<sub>3</sub>/MSN untuk pengisomeran *n*-heptana. Selain itu, kesan penyokong telah dikaji dengan menggunakan silika lamela sepusat dwiselanjar (KCC-1), yang disediakan melalui kaedah mikroemulsi berbantu gelombang mikro, sebagai penyokong MoO<sub>3</sub> (MoO<sub>3</sub>/KCC-1). Untuk meningkatkan aktiviti pemangkin, penambahan fosforus (P) telah dijalankan melalui pengisitepuan MoO<sub>3</sub>/KCC-1 dengan asid fosforik untuk membentuk P/MoO<sub>3</sub>/KCC-1. Pemangkin dicirikan menggunakan pembelauan sinar-x, analisis kawasan permukaan, mikroskop elektron pengimbas, penurunan berprogram suhu-hidrogen, resonans magnet nuklear, spektroskopi cahayanampak ultraungu, spektroskopi inframerah transformasi Fourier (FTIR) dan spektroskopi resonans putaran elektron (ESR). Aktiviti pengisomeran *n*-heptana yang tinggi diperhatikan pada MoO<sub>3</sub>/MSN berbanding dengan Pt/MSN di dalam hidrogen pada 350 °C, dengan hasil iso-heptana mono- dan dwi-cabang masing-masing mencapai 36.6% dan 6.8%. Kajian ESR dan FTIR menunjukkan bahawa aktiviti yang tinggi dan kestabilan MoO<sub>3</sub>/MSN boleh dikaitkan dengan pemisahan-penjerapan molekul hidrogen untuk membentuk atom hidrogen, yang kemudiannya membentuk  $(MoO_x)^-(H_y)^+$  aktif. Interaksi Pt/MSN dengan molekul hidrogen membentuk Pt-H, yang mana ia tidak aktif dalam pengisomeran *n*-heptana. Sebagai perbandingannya, MoO<sub>3</sub>/KCC-1 mempunyai tenaga pengaktifan yang rendah (28.1 kJ/mol), serta memberikan hasil isomer yang lebih tinggi (42.2%) berbanding dengan MoO<sub>3</sub>/KCC-1 (35.8%). Keputusan ini adalah berkaitan dengan morfologi unik silika KCC-1, yang membenarkan akses bahan tindak balas berjisim besar yang tinggi terhadap tapak aktif. P/MoO<sub>3</sub>/KCC-1 telah menunjukkan penurunan di dalam asid Brønsted manakala terdapat pusat berasid Lewis baharu terbentuk pada 1624 cm<sup>-1</sup> dan 1587 cm<sup>-1</sup>, seperti yang ditunjukkan oleh penjerapan inframerah 2,6-lutidina. Penghasilan isomer yang tinggi diperoleh dengan P/MoO<sub>3</sub>/KCC-1 adalah berkaitan dengan penyertaan pusat berasid pada 1624 cm<sup>-1</sup> dan 1587 cm<sup>-1</sup>, dalam pembentukan proton melalui pemerangkapan elektron, serta akses yang tinggi kepada  $(MoO_x)^-(H_y)^+$  aktif. Analisa ANOVA menunjukkan bahawa suhu tindak balas adalah pemboleh ubah penting di dalam pengeluaran isomer. Berdasarkan uji kaji pengoptimuman, 44.9% hasil isomer telah diperoleh pada keadaan optimum 311 °C, dirawat pada 464 °C selama 6 jam. Kajian ini menyerlahkan potensi silika berliang meso terubah suai di dalam kajian pemangkinan, terutamanya bagi pengisomeran alkana lurus.

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### LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
APTES	-	3-aminopropyl triethoxysilane
BET	-	Brunauer Emmet Teller
CCD	-	Central Composite Design
CTAB	-	Cetyltrimethylammonium bromide
DOE	-	Design of experiment
EG	-	Ethylene glycol
FESEM	-	Field Emission Scanning Electron Field
FTIR	-	Fourier Transform Infra-Red
IUPAC	-	International Union of Pure and Applied Chemistry
MCM-41	-	Mobil composition of matter number 41
MSN	-	Mesostructured silica nanoparticles
NMR	-	Nuclear magnetic resonance
RSM	-	Response surface methodology
SBA-15	-	Santa Barbara Amorphous 15
TEM	-	Transmission Electron Field
TEOS	-	Tetraethylorthosilicate
XRD	-	X-Ray diffraction

### LIST OF SYMBOLS

nm	-	Nanometer
wt%	-	Weight percent
h	-	Hour
θ	-	Theta
S	-	Second
λ	-	X-ray wavelength
MHz	-	Mega hertz
mA	-	Miliamphere
W	-	Watt
μmol	-	Micromole
kV	-	Kilovolt

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#### **CHAPTER 1**

#### **INTRODUCTION**

### 1.1 Research Background

Worldwide concern over the destructive effect of oil usage on the environment has led several changes in regulation with the impact on gasoline, other jet fuels and lubricating oils. Therefore, numerous studies have been implemented to enhance the quality of gasoline by increasing the Research Octane, which is one of the main parameters used in the quality control of gasoline that provide information on the resistance to auto ignition (Mendes *et al.*, 2012). Previously, lead compound or aromatic known as methyl tertiary butyl ether (MTBE) was added into the gasoline mixture to improve the RON. 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 (Pinto *et al.*, 2015). In addition, MTBE is an expensive component that can further increase the cost of gasoline from its application.

In this regard, hydroisomerisation complements the catalytic reforming process in upgrading the octane number of refinery naphtha streams. It is well known that the branched isomers of  $C_5$ - $C_8$  paraffins possess a higher octane number compared to the corresponding linear paraffins ( $C_7$ ) (Singh *et al.*, 2014). Therefore, the production of paraffin based high octane gasoline blend stocks such as isomers from isomerisation of light and mid-cut naphtha might be a key technology for gasoline supply to cope with future gasoline regulations.

The isomerisation reaction proceeds through the consecutive branching reactions over bifunctional metal-acid catalysts. This process occurs at the acid sites of bifunctional catalyst, while the metal site provides hydrogenation-dehydrogenation capability. Previously, many studies have focused on various type of zeolite catalyst for isomerisation since conventional catalysts including chlorided Pt alumina led to corrosion and environmental problems. It has been reported that zeolite Pt/mordenite catalyst was catalytically active for *n*-C<sub>5</sub> isomerisation due to its high acidity; however, it exhibited less selectivity when dealing with longer chain paraffins such as  $n-C_6$  and  $n-C_6$ C<sub>7</sub> (Chica et al., 2001). Besides, different types of material such as SAPO-11 (Liu et al., 2008), MOR (Lee and Rhee, 1997), ZrO<sub>2</sub> (Ruslan et al., 2011; Triwahyono et al., 2007), alumina (Vandegehuchte et al., 2014), ZSM-5 (Fernandez et al., 2010), HY (Aziz et al., 2012), and HBEA (Kamarudin et al., 2012) were also commonly applied for the hydroisomerization process. However, these materials exhibited several limitations that include high acidity, which prone to form cracking products, low surface area, as well as small pore size. 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.

Previously, the development of mesostructured silica nanoparticles (MSN) with a highly ordered mesostructure, high surface area, large pore volume and well-defined pore size has attracted a lot of attention. MSN has been successfully applied in many different applications such as CO<sub>2</sub> reforming of CH<sub>4</sub> (Sidik *et al.*, 2015), methanation of CO<sub>2</sub> (Aziz *et al.*, 2014), drug delivery (Kamarudin *et al.*, 2013) and adsorption (Karim *et al.*, 2012). The tuneable pore size of MSN and high surface area offer an opportunity of designing an isomerisation catalyst for linear chain alkane longer than n-C<sub>5</sub>. However, the MSN requires modification to provide acidic property since it comprises of silica framework with no Brønsted acid sites (Sazegar *et al.*, 2014). Fortified by the discovery of new bicontinuous concentric lamellar silica KCC-1 (Febriyanti *et al.*, 2016; Polshettiwar *et al.*, 2010), this material had shown a great potential in several applications such as alkane hydrogenolysis (Fihri, Bouhrara, *et al.*, 2012), adsorbent for CO<sub>2</sub> capture (Patil *et al.*, 2012), propane methathesis (Polshettiwar *et al.*, 2011), cumene hydrocracking (Firmansyah *et al.*, 2016) and Suzuki coupling of aromatic halides (Fihri *et al.*, 2012). This is due to its high surface area (> 600 m<sup>2</sup>/g), large pore sizes, high thermal stability and unique bicontinuous concentric lamellar morphology of silica KCC-1 allowing high accessibility of bulky mass reactant to the active sites, which consequently improves the rate of reaction and products formation. Moreover, the presence of some large pores around its external surfaces with many small pores throughout its structure was also beneficial as carrier for drugs and genes (Du and Qiao, 2015). However, KCC-1 is made of neutral silica frameworks without active sites, thus limiting its application for acid catalytic reaction such as isomerization and cracking of hydrocarbon.

In order to improve the potential of MSN and bicontinuous concentric lamellar silica KCC-1 as catalyst for isomerisation, the loading of metal oxide could be useful to improve the support acidic property. Among the metal oxide catalysts, MoO<sub>3</sub> has been extensively studied due to its potential in alkane isomerisation and environmentally friendly properties as compared to mineral acids such as HF and H<sub>2</sub>SO<sub>4</sub> (Ono, 2003). Many works have been devoted to MoO<sub>3</sub>-related catalysts and discussed in several reviews (Akhmedov and Al-Khowaiter, 2007; Wehrer *et al.*, 2003). In recent studies, Sakagami and co-workers reported that the catalytic activity of Pt/MoO<sub>3</sub> catalyst was greatly influenced by its surface area (Sakagami *et al.*, 2014). The improvement in the Pt/MoO<sub>3</sub> surface area due to the slow reduction rate of H<sub>2</sub> flow gave the MoO<sub>x</sub> with the highest *n*-heptane isomerisation activity. Besides, previous study also has reported on the formation of acidic Brønsted (MoO<sub>x</sub>)<sup>-</sup>(H<sub>y</sub>)<sup>+</sup> over Pt/MoO<sub>3</sub> for cumene cracking (Timmiati *et al.*, 2013). It was evidenced by XRD and 2,6-lutidine IR spectroscopy that the presence of Pt was essential in the formation of the active site. In fact, no (MoO<sub>x</sub>)<sup>-</sup>(H<sub>y</sub>)<sup>+</sup> or protonic acid sites were observed on Pt-free MoO<sub>3</sub>.

Although there are several reports published on MoO<sub>x</sub> supported SiO<sub>2</sub> material for short alkane isomerisation, the presence of noble metal is still dispensable in these types of catalyst. Early study by Gallo *et al.*, (1997) reported that the *n*-heptane isomerisation activity of MoO<sub>3</sub>-carbon modified supported on silica carbide was influenced by its total activation pressure. A selectivity of 12.8 % *di*-branched isomers was obtained over the MoO<sub>3</sub>/SiC after 24 h activation at with 40 bar total activation pressure. On the other hands, Matsuda *et al.*, (2009) have reported that *n*-heptane isomerization over Pt/MoO<sub>3</sub>-SiO<sub>2</sub> can be controlled by the formation of MoO<sub>x</sub>H<sub>y</sub>, yielded from the reduction of MoO<sub>3</sub> along with its number of acid sites. The Pt/MoO<sub>3</sub>-SiO<sub>2</sub> catalyst with 80 wt. % of MoO<sub>3</sub> gave 17.3 % selectivity of di-branched isomers at 350 °C.

In recent years, the addition of second active sites in bifunctional catalyst has gained a lot of interests due to their positive effect in improving the catalytic activity, stability and selectivity towards isomers. In this area, noble metals such as Pt or Pd-supported bifunctional catalysts have been widely explored due to their role in hydrogen spillover which can enhanced the catalytic activity (Busto *et al.*, 2012; Park and Ihm, 2000; Triwahyono *et al.*, 2003). However, the high cost involving noble metal has led to alternative active sites including phosphorus. The positive effect of phosphorus on the activity and stability of has been widely reported especially for HZSM-5 type catalyst (Blasco *et al.*, 2006; Jiang *et al.*, 2008; Xue *et al.*, 2007; Zhao *et al.*, 2007). Nevertheless, to date, there is no report available regarding the modification of bicontinuous concentric lamellar silica KCC-1 type material using phosphorus.

In this thesis, MSN was used as  $MoO_3$  support and *n*-heptane isomerisation was chosen as a model reaction. The role of MSN as a silica framework with weak Lewis acid property in facilitating the formation of  $(MoO_x)-(H_y)^+$  by trapping electron was emphasised in correlation with its catalytic activity. The presence of interparticles textural porosity contributing to a high surface area and large pore diameter of MSN, promises a new design of catalyst with highly dispersed and accessible active sites, which leads to the selectivity towards *mono-* and *di*-branced isomer products. In addition, the physico-chemical properties and catalytic activity of MoO<sub>3</sub>/MSN were

compared with Pt/MSN, since Pt is well known as an active noble metal for alkane isomerisation. Additionally, the influence of support morphology in *n*-heptane isomerisation was investigated by employing the bicontinuous concentric lamellar silica KCC-1 as a support for MoO<sub>3</sub>. It was expected that the unique morphology of bicontinuous concentric lamellar silica KCC-1 would improve the accessibility of the active site. Further modification on MoO<sub>3</sub>/KCC-1 with phosphorus to form P/MoO<sub>3</sub>/KCC-1 was expected to enhance the catalytic activity. Then, the optimisation of *n*-heptane isomerization over P/MoO<sub>3</sub>/KCC-1 was carried out using the response surface methodology (RSM).

#### **1.2 Problem Statement and Hypothesis**

Recently, the increasing awareness towards environmental protection has urged the petrochemical refinery industry to reformulate their gasoline composition to improve the quality of their product. In an attempt to overcome this problem, the isomerisation of alkanes has been utilised as a useful industrial process to improve the gasoline octane number. In particular, the *di*-branched alkanes have drawn much attention as a useful component in gasoline due to their higher octane number compared to the linear alkane. Previously, platinum-supported on chlorinated alumina as bifunctional catalyst has been widely applied for alkane isomerisation but owns several limitations due to its corrosion problems. Therefore, many types of catalysts have been proposed for the isomerisation reaction and the molybdenum oxide (MoO<sub>3</sub>) based catalyst is considered as one of the potential catalyst due to its stability and regenerative properties (Matsuda *et al.*, 2003). Based on previous studies, molybdenum oxide catalyst supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> have been extensively studied due to their possible ability to catalyse the isomerization of linear alkanes (Al-Kandari *et al.*, 2009; Di-Grégorio *et al.*, 2001; Matsuda *et al.*, 2009).

However, despite the high conversion of alkane from the previously reported catalysts, the yield of the valuable *di*-branched alkane is still low. In addition, previous

studies claimed that the production of di-branched alkane isomers is mainly influenced by the catalyst acidity and metal dispersion (Park and Ihm, 2000). The balance between the two catalytic functions, such as density and strength of the Brønsted acid sites (H<sup>+</sup>) and the amount and the dispersion of the metal is what determines the desired selectivity (Chao *et al.*, 1996; Chica and Corma, 1999; Höchtl *et al.*, 2001). When the hydrogenating function is highly active, the activity and selectivity of the bifunctional catalyst will depend only on the acidic function, which is the rate-limiting step in the absence of diffusion limitations.

It was reported that the acidic function of molybdenum based catalyst can be altered by the addition of phosphorus (Ferdous *et al.*, 2004). Besides, previous studies demonstrated that the effect of phosphorus addition was related with changes in the molybdenum oxide dispersion, structure and morphology, as well as prevention of coke formation (Pawelec *et al.*, 2008; Sigurdson *et al.*, 2008; Xue *et al.*, 2010). In addition, phosphorus has been reported as hydrogen spillover promoter in molybdenum based catalyst for hydrodeoxygenation (HDO) reaction (Yang *et al.*, 2009). Nonetheless, the effects and roles of phosphorus in molybdenum based catalyst for alkane isomerisation were very limited. Therefore, it was significance to investigate the possible effects of phosphorus addition in alkane isomerisation with respect to the changes of catalyst physicochemical property. Considering all the factors mentioned above, an ideal isomerisation catalyst for producing *di*-branched alkane isomers should provide suitable compositional and structural characteristics, mainly the proper balance between metal and acid sites, suitable pore size, high dispersion of metal on the catalyst surface and mild acidity strength of acid sites.

In that case, an attempt were done to synthesise and characterise isomerization catalyst with desired properties to enhance the catalytic activity and efficiency. It was hypothesised that the loading of Pt and MoO<sub>3</sub> on high surface area of MSN which possess interparticles textural porosity and large pore diameter, will give different effect on the catalyst physicochemical properties, and hence reflects their catalytic activity in *n*-heptane isomerization. Besides, further development on new isomerisation catalyst by using the bicontinuous concentric lamellar silica KCC-1 as MoO<sub>3</sub> support was

expected to enhance the catalytic activity due to the unique morphology of the KCC-1. Lastly, the effect of phosphorus loading on the Mo supported catalyst was expected to alter the catalyst acidic property and enhanced the catalytic activity, respectively.

#### **1.3** Objective of Study

The objectives of this study are:

- 1. To prepare and characterise the MSN, Pt/MSN and MoO<sub>3</sub>/MSN catalysts for *n*-heptane isomerisation;
- 2. To study the effect of MSN and KCC-1 as catalyst support for *n*-heptane isomerisation;
- 3. To study the effect of phosphorus loading for improvement in the catalytic activity of *n*-heptane isomerisation;
- 4. To optimise the *n*-heptane isomerisation by response surface methodology (RSM).

#### 1.4 Scope of Study

To complete the objectives of this study, four main scopes are covered as below:

1. To prepare and characterise the MSN, Pt/MSN and MoO<sub>3</sub>/MSN catalysts for *n*-heptane isomerisation;

The MSN was prepared using a co-condensation and sol-gel method. Then, the MoO<sub>3</sub>/MSN was prepared by physically mixing of MoO<sub>3</sub> with MSN. In this study, physical mixing method was chosen for the preparation of MoO<sub>3</sub>/MSN due to the property of MoO<sub>3</sub> which can form solid-molten after calcination (Afanasiev, 1997). Besides, the molybdenum based catalyst prepared by physical mixing method showed high performance in isomerisation of *n*-heptane (Matsuda et al., 1999). Thus, physical mixing method was used in this study. The amount of MoO<sub>3</sub> was adjusted to 40 wt%, based on literature study (Liu et al., 2015; Matsuda et al., 2009) and preliminary catalytic activity evaluation using different MoO<sub>3</sub> loading. Besides, Pt/MSN was also prepared using similar method to compare the influence of noble metal in the catalytic activity. The amount of Pt was adjusted to 0.5 wt%, based on literature study (Timmiati et al., 2013). The prepared catalysts were characterised using X-Ray Diffraction (XRD), N<sub>2</sub> physisorption, H<sub>2</sub>-TPR, Ultraviolet visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), Electron Spin Resonance (ESR) spectroscopy and tested for *n*-heptane isomerisation with a reaction temperature range of 100-350 °C (Ruslan et al., 2012) under atmospheric pressure.

2. To study the effect of support morphology towards *n*-heptane isomerisation;

The of bicontinuous concentric lamellar silica KCC-1 was prepared using microwave assisted hydrothermal method. Then, Pt/KCC-1 and MoO<sub>3</sub>/KCC-1 was prepared by physically mixing the metal with KCC-1 to compare the catalytic activity with the MSN based catalysts. The catalyst was characterised using X-Ray Diffraction (XRD), N<sub>2</sub> physisorption, H<sub>2</sub>-TPR, field emission scanning electron spectroscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), Electron Spin Resonance (ESR) spectroscopy and tested for *n*-heptane isomerisation with a reaction temperature range of 100-350 °C under atmospheric pressure.

3. To study the effect of phosphorus loading for improving the catalytic activity of *n*-heptane isomerisation;

In order to study the effect of phosphorus loading, the catalyst was prepared by impregnating  $MoO_3/KCC-1$  with  $H_3PO_4$ . The amount of  $H_3PO_4$  concentration was adjusted to 0.5 N based on literature (Triwahyono *et al.*, 2006) and preliminary catalytic activity evaluation using different  $H_3PO_4$  concentration.

4. To optimise the *n*-heptane isomerisation by response surface methodology (RSM).

The optimum condition for *n*-heptane isomerization over P/MoO<sub>3</sub>/KCC-1 was identified by RSM using central composite design (CCD). In this study, the range of variables were chosen based on the literature studies on previous reported alkane isomerisation. The variables selected in the study are reaction temperature (250-350 °C) (Ruslan *et al.*, 2012), treatment temperature (400-450 °C) (Matsuda *et al.*, 2000) and treatment time (3-9 h) (Sakagami *et al.*, 2005). The performance of the catalyst was evaluated by analysing the yield of isomer as response.

#### 1.5 Significance of Study

In this study, new catalyst of MoO<sub>3</sub> supported on MSN was prepared for *n*-heptane isomerisation. A detail investigation on the interaction of catalyst with hydrogen was studied, in comparison with Pt/MSN. Besides, the potential of bicontinuous concentric lamellar silica KCC-1 as catalyst support for *n*-heptane isomerisation was investigated. In addition, the influence of phosphorus in creating new active site in catalyst, despite of noble metal, was also studied. The optimization study by RSM analysis showed the influenced of process variables such as reaction temperature, treatment time and treatment temperature. In summary, this study provides new information of *n*-heptane isomerisation over the MSN and bicontinuous concentric lamellar silica KCC-1 supported MoO<sub>3</sub> catalysts. This study will be a significant contribution to the research and science community, especially in the isomerization of alkane into products with high research octane number.

### 1.6 Thesis Outline

This thesis begins with Chapter 1 described 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 isomerization reaction. Chapter 3 described the experimental and characterization of the catalysts and chapter 4 concerned with data processing and discussing of physicochemical properties and catalytic activities of the catalysts. The conclusions and recommendation for future studies were stated in chapter 5.

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