

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

NOR AIZA BINTI ABDUL FATAH

UNIVERSITI TEKNOLOGI MALAYSIA

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

NOR AIZA BINTI ABDUL FATAH

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

MAY 2017

*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'

ACKNOWLEDGEMENTS

Alhamdulillah, all praise to Allah. Peace and blessing to Prophet Muhammad S.A.W. his families and all muslims. Special thanks to my supervisors, Prof. Dr. Aishah Abdul Jalil and Prof. Dr. Sugeng Triwahyono for the never ending advices and help during the study. Without their patience, criticisms, ideas and supports, this work could not have been accomplished.

A million thanks and appreciation goes to all the Green Technology and Advanced Materials (GTAM) research group members, for giving me a hand in the process of doing this research. A lot of appreciation also goes to the staffs of Ibnu Sina Institute for their valuable help and cooperation. My gratitude to the Ministry of Higher Education through financial support from MyPhD awards.

Last but not least, I wish to express my sincere appreciation to my beloved family for their continuous support, advices and motivation for me to complete my project. Thank you so much.

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 (MoO₃) to prepare Pt/MSN and MoO₃/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 microwave-assisted microemulsion, as MoO₃ support (MoO₃/KCC-1). In order to improve the catalytic activity, the effect of phosphorus (P) loading was carried out by impregnation of MoO₃/KCC-1 with phosphoric acid to form P/MoO₃/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 MoO₃/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 MoO₃/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 MoO₃/KCC-1 possessed low activation energy (28.1 kJ/mol), as well as gave higher yield of isomers (42.2%) compared to MoO₃/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/MoO₃/KCC-1 showed a decrease in the Brønsted acid while new Lewis acidic centers were formed at 1624 cm⁻¹ and 1587 cm⁻¹, as observed by 2,6-lutidine adsorbed infrared. High yield of isomers obtained by P/MoO₃/KCC-1 was related to the participation of the acidic centers at 1624 cm⁻¹ and 1587 cm⁻¹, 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_3) bagi menyediakan Pt/MSN dan MoO_3 /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_3 (MoO_3 /KCC-1). Untuk meningkatkan aktiviti pemangkin, penambahan fosforus (P) telah dijalankan melalui pengisitepuan MoO_3 /KCC-1 dengan asid fosforik untuk membentuk P/ MoO_3 /KCC-1. Pemangkin dicirikan menggunakan pembelauan sinar-x, analisis kawasan permukaan, mikroskop elektron pengimbas, penurunan berprogram suhu-hidrogen, resonans magnet nuklear, spektroskopi cahaya-nampak ultraungu, spektroskopi inframerah transformasi Fourier (FTIR) dan spektroskopi resonans putaran elektron (ESR). Aktiviti pengisomeran *n*-heptana yang tinggi diperhatikan pada MoO_3 /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_3 /MSN boleh dikaitkan dengan pemisahan-penjerapan molekul hidrogen untuk membentuk atom hidrogen, yang kemudiannya membentuk $(\text{MoO}_x)^-(\text{H}_y)^+$ aktif. Interaksi Pt/MSN dengan molekul hidrogen membentuk Pt-H, yang mana ia tidak aktif dalam pengisomeran *n*-heptana. Sebagai perbandingannya, MoO_3 /KCC-1 mempunyai tenaga pengaktifan yang rendah (28.1 kJ/mol), serta memberikan hasil isomer yang lebih tinggi (42.2%) berbanding dengan MoO_3 /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_3 /KCC-1 telah menunjukkan penurunan di dalam asid Brønsted manakala terdapat pusat berasid Lewis baharu terbentuk pada 1624 cm^{-1} dan 1587 cm^{-1} , seperti yang ditunjukkan oleh penjerapan inframerah 2,6-lutidina. Penghasilan isomer yang tinggi diperoleh dengan P/ MoO_3 /KCC-1 adalah berkaitan dengan penyertaan pusat berasid pada 1624 cm^{-1} dan 1587 cm^{-1} , dalam pembentukan proton melalui pemerangkapan elektron, serta akses yang tinggi kepada $(\text{MoO}_x)^-(\text{H}_y)^+$ 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 berubah suai di dalam kajian pemangkinan, terutamanya bagi pengisomeran alkana lurus.

TABLE OF CONTENTS

| CHAPTER | TITLE | PAGE |
|----------|--------------------------------------|-----------|
| | DECLARATION | ii |
| | DEDICATION | iii |
| | ACKNOWLEDGEMENTS | iv |
| | ABSTRACT | v |
| | ABSTRAK | vi |
| | TABLE OF CONTENTS | vii |
| | LIST OF TABLES | xi |
| | LIST OF FIGURES | xii |
| | LIST OF ABBREVIATIONS | xvi |
| | LIST OF SYMBOLS | xvii |
| | LIST OF APPENDICES | xviii |
| 1 | INTRODUCTION | 1 |
| | 1.1 Research Background | 1 |
| | 1.2 Problem Statement and Hypothesis | 5 |
| | 1.3 Objective of Study | 7 |
| | 1.4 Scope of Study | 7 |
| | 1.5 Significance of Study | 9 |
| | 1.6 Thesis Outline | 9 |
| 2 | LITERATURE REVIEW | 11 |

| | | |
|----------|---|-----------|
| 2.1 | Alkane Isomerization | 11 |
| 2.2 | Catalysts | 13 |
| 2.2.1 | Homogeneous Catalyst | 13 |
| 2.2.2 | Heterogeneous Catalyst | 14 |
| 2.3 | Catalysts for Alkane Isomerization | 15 |
| 2.3.1 | Sulphated zirconia and Pt-supported sulphated zirconia | 18 |
| 2.3.2 | Tungsten Oxide Supported on Zirconia ($\text{WO}_x\text{-ZrO}_2$) | 20 |
| 2.3.3 | Molybdenum Based Catalyst | 21 |
| 2.3.4 | Platinum as Catalyst Promoter | 22 |
| 2.3.5 | Effect of Phosphorus Loading | 23 |
| 2.4 | Mechanism of Isomerization | 25 |
| 2.4.1 | Bifunctional Mechanism | 25 |
| 2.5 | Determination of Acid Site using Probe Molecule by FTIR | 27 |
| 2.5.1 | 2,6-Lutidine Adsorption | 29 |
| 2.6 | Role of Hydrogen in Alkane Isomerization | 31 |
| 2.7 | Mesostructured Silica Nanoparticles | 33 |
| 2.8 | Bicontinuous Concentric Lamellar Silica KCC-1 | 34 |
| 2.9 | Response Surface Methodology (RSM) | 35 |
| 2.9.1 | Preliminary Work: Determination of Independent Variables and Their Level | 36 |
| 2.9.2 | Selection of the Experimental Design, Prediction and Verification of Model Equation | 37 |
| 2.9.3 | Selection of the Experimental Design, Prediction and Verification of Model Equation | 38 |
| 2.9.4 | Advantages of RSM | 38 |
| 3 | METHODOLOGY | 39 |
| 3.1 | Introduction | 39 |
| 3.2 | Chemical and Materials | 41 |

| | | |
|----------|---|-----------|
| 3.3 | Preparation of Catalysts | 41 |
| 3.3.1 | Synthesis of Mesoporous Silica Nanoparticles | 42 |
| 3.3.2 | Preparation of MoO ₃ /MSN and Pt/MSN | 43 |
| 3.3.3 | Synthesis of Bicontinuous Concentric Lamellar Silica KCC-1 | 44 |
| 3.3.5 | Preparation of Pt/KCC-1 and MoO ₃ /KCC-1 | 45 |
| 3.3.6 | Preparation of P/MoO ₃ /KCC-1 | 45 |
| 3.4 | Characterization of Catalysts | 45 |
| 3.4.1 | X-Ray Diffraction (XRD) Analysis | 45 |
| 3.4.2 | Nitrogen Physisorption Analysis | 46 |
| 3.4.3 | Nuclear Magnetic Resonance (NMR) | 46 |
| 3.4.4 | Ultraviolet Visible Spectroscopy (UV-Vis) | 46 |
| 3.4.5 | Fourier Transform Infrared (FTIR) Spectroscopy | 47 |
| 3.4.5.1 | KBr Method | 47 |
| 3.4.5.2 | 2,6-Lutidine Adsorbed IR | 47 |
| 3.4.5.3 | Generation of Protonic Acid Sites | 48 |
| 3.4.6 | In-situ Electron Spin Resonance (ESR) Spectroscopy | 48 |
| 3.4.7 | H ₂ Temperature Programmed Reduction (H ₂ -TPR) | 48 |
| 3.4.8 | Field Emission Scanning Electron Microscopy (FESEM) | 49 |
| 3.5 | Isomerization of <i>n</i> -heptane | 49 |
| 3.6 | Optimization by Response Surface Methodology (RSM) | 51 |
| 4 | RESULT AND DISCUSSION | 54 |
| 4.1 | Introduction | 54 |
| 4.2 | Effect of MoO ₃ and Pt Loading on MSN | 50 |
| 4.2.1 | Physicochemical Properties of the Catalysts | 50 |
| 4.2.2 | Dissociative Adsorption of Hydrogen Gas | 64 |
| 4.2.3 | Catalytic Performance | 69 |
| 4.3 | Effect of different support | 75 |
| 4.3.1 | Catalytic performance of KCC-1 based catalysts | 76 |

| | | |
|----------|--|------------|
| 4.3.2 | Physicochemical Properties of the Catalysts | 79 |
| 4.3.3 | Intrinsic acidity of catalysts | 83 |
| 4.3.3 | Interaction of catalysts with hydrogen | 85 |
| 4.4 | Effect of phosphorus on MoO ₃ /KCC-1 | 87 |
| 4.4.1 | Physicochemical Properties of the Catalysts | 87 |
| 4.4.2 | Intrinsic acidity | 90 |
| 4.4.3 | Catalytic performance of P/MoO ₃ /KCC- | 92 |
| 4.5 | Comparison of Catalytic Activity | 93 |
| 4.6 | Optimization of <i>n</i> -heptane Isomerization over P/MoO ₃ /KCC-1 by RSM | 95 |
| 5 | CONCLUSIONS AND RECOMMENDATIONS | 104 |
| 5.1 | Conclusion | 104 |
| 5.2 | Future Works | 106 |
| | REFERENCES | 107 |
| | Appendices A-D | 125-129 |

LIST OF TABLES

| TABLE NO. | TITLE | PAGE |
|-----------|--|------|
| 2.1 | Research Octane Number (RON) of hydrocarbon (Nikolaou <i>et al.</i> , 2004) | 12 |
| 2.2 | Advantages and disadvantages of homogeneous catalysis (Cavani and Trifirb, 1997) | 14 |
| 2.3 | Advantages and disadvantages of heterogeneous catalysis (Cavani and Trifirb, 1997) | 15 |
| 2.4 | Existing catalysts that produced <i>di</i> -branched alkanes | 17 |
| 2.5 | Frequently used probe molecules (Jacobs <i>et al.</i> , 2001) | 28 |
| 3.1 | List of chemicals | 41 |
| 3.2 | Coded levels for parameters used in the experimental design | 52 |
| 3.3 | Experimental design of <i>n</i> -heptane isomerization | 53 |
| 4.1 | Product distributions of <i>n</i> -heptane isomerization over MSN based catalyst in the presence of hydrogen. | 71 |
| 4.2 | Catalytic activity of catalysts for <i>n</i> -heptane isomerization. | 74 |
| 4.3 | Product distributions of <i>n</i> -heptane isomerization over KCC-1 based catalyst in the presence of hydrogen | 77 |
| 4.4 | Product distributions of <i>n</i> -heptane isomerisation over P/MoO ₃ /KCC-1 in the presence of hydrogen | 93 |
| 4.5 | Experimental design and response value for different conditions | 96 |
| 4.6 | Analysis of variance (ANOVA) for 2 ³ center composite design (CCD) for the yield of isomer | 97 |
| 4.7 | Comparison between predicted and observed responses at the optimum condition obtained from RSM | 102 |

LIST OF FIGURES

| FIGURE NO. | TITLE | PAGE |
|-------------------|---|-------------|
| 2.1 | Diagrammatic representation of the mechanism of <i>n</i> -butane isomerization over sulphated zirconia (Matsushashi <i>et al.</i> , 1999) | 19 |
| 2.2 | A typical competition for isomerization and cracking in bimolecular pathways (Bloomsma <i>et al.</i> , 1996) | 26 |
| 2.3 | Lutidine and lutidinium species, and their ν_{8a} and ν_{8b} vibration modes (Leydier <i>et al.</i> , 2011). | 30 |
| 2.4 | Spectral location of mid-IR vibrational modes of free and adsorbed 2,6-lutidine (Morterra <i>et al.</i> , 2001) | 31 |
| 2.5 | General model for molecular hydrogen-originated protonic acid site | 32 |
| 3.1 | Research flow chart | 40 |
| 3.2 | Preparation of MSN | 42 |
| 3.3 | Preparation of MoO ₃ /MSN and Pt/MSN | 43 |
| 3.4 | Synthesis of Bicontinuous Concentric Lamellar Silica KCC-1 | 44 |
| 3.5 | Microcatalytic pulse reactor | 49 |
| 3.6 | Schematic diagram of microcatalytic pulse reactor | 50 |
| 4.1 | (A) Low angle XRD pattern of MSN and (B) Wide angle XRD patterns of MSN supported catalysts | 55 |
| 4.2 | H ₂ -TPR profiles of MSN based catalyst | 56 |

| | | |
|------|---|----|
| 4.3 | (A) and (B) IR KBr spectra and (C) activated OH region of (a) MSN, (b) Pt/MSN and (c) MoO ₃ /MSN. | 57 |
| 4.4 | UV-diffuse reflectance spectra of MoO ₃ and MSN based catalysts | 59 |
| 4.5 | N ₂ adsorption (white-circle symbol)-desorption (black-circle symbol) isotherms and NLDT pore size distribution (white-square symbol) of MSN, Pt/MSN and MoO ₃ /MSN catalysts. | 61 |
| 4.6 | IR spectra of 2,6-lutidine adsorbed on (a) MSN, (b) Pt/MSN and (c) MoO ₃ /MSN at room temperature, followed by outgassing at 100 °C. | 62 |
| 4.7 | Variations of peak intensity at 1604 + 1583 cm ⁻¹ for MSN (■), Pt/MSN (■) and MoO ₃ /MSN (●); and peak intensity at 1643 + 1628 cm ⁻¹ for MSN (□), Pt/MSN (Δ) and MoO ₃ /MSN (○) as a function of outgassing temperature after 2,6-lutidine adsorption | 63 |
| 4.8 | IR spectral changes when 2,6-lutidine pre-adsorbed catalyst (a) was heated in hydrogen at (b) room temperature, (c) 50, (d) 100, (e) 150 and (f) 200 °C. | 65 |
| 4.9 | ESR spectra of (A) MSN, (B) Pt/MSN and (C) MoO ₃ /MSN activated at (a) 400 °C for 1 h 100 Torr of hydrogen was adsorbed (b) room temperature, (c) 50, (d) 100, (e) 150 and (f) 200 °C. (D) Variations in the intensity of the ESR signal at g = 1.99 for MSN (□), Pt/MSN (●) and MoO ₃ /MSN (■) as a function of heating temperature. The dotted line represents the intensity of signals before the samples were heated in the presence of hydrogen. | 68 |
| 4.10 | Isomerization of <i>n</i> -heptane over MSN (◇), Pt/MSN (□) and MoO ₃ /MSN (○). The data were taken from the average of the sixth, seventh and eighth pulses. | 70 |

| | | |
|------|---|----|
| 4.11 | Rate conversion of <i>n</i> -heptane isomerization over KCC-1, Pt/KCC-1 and MoO ₃ /KCC-1 | 76 |
| 4.12 | Wide angle XRD patterns of KCC-1 and MoO ₃ /KCC-1 | 79 |
| 4.13 | FESEM images of (a) KCC-1 and (b) MoO ₃ /KCC-1 | 80 |
| 4.14 | (A) N ₂ adsorption (white circle symbol) – desorption (black circle symbol) isotherm and (B) NLDFT pore size distribution of bicontinuous concentric lamellar KCC-1 based catalysts | 82 |
| 4.15 | ²⁹ Si NMR spectra of bicontinuous concentric lamellar KCC-1 MoO ₃ /KCC-1 based catalysts | 83 |
| 4.16 | IR spectra of 2,6-lutidine adsorbed (a) KCC-1 and MoO ₃ /KCC-1. Brønsted acid site region at 1686-1632 cm ⁻¹ , and Lewis acid site region at 1630-1560 cm ⁻¹ when 2,6-lutidine is adsorbed at room temperature. Solid line: experimental spectra; dotted line: reconstituted spectra | 84 |
| 4.17 | ESR spectra of bicontinuous concentric lamellar KCC-1 and MoO ₃ /KCC-1 based catalysts activated at (a) 400 °C and heated in the presence of 100 Torr of H ₂ from (b) room temperature, (c) 50, (d) 100, (e) 150 and (f) 200 °C. The true line represents the spectrum before catalyst activation | 86 |
| 4.18 | (a) FESEM image and (b) Wide angle XRD pattern for P/MoO ₃ /KCC-1 | 87 |
| 4.19 | N ₂ adsorption (white circle symbol) – desorption (black circle symbol) isotherm and NLDFT pore size distribution of bicontinuous concentric lamellar KCC-1 based catalysts | 88 |
| 4.20 | ²⁹ Si NMR spectrum of P/MoO ₃ /KCC-1 | 89 |
| 4.21 | IR spectra of 2,6-lutidine adsorbed P/MoO ₃ /KCC-1. Brønsted acid site region at 1686-1632 cm ⁻¹ , and Lewis acid site region at 1630-1560 cm ⁻¹ when 2,6-lutidine is | 90 |

| | | |
|------|--|-----|
| | adsorbed at room temperature. Solid line: experimental spectra; dotted line: reconstituted spectra | |
| 4.22 | ESR spectra of P/MoO ₃ /KCC-1 activated at (a) 400 °C and heated in the presence of 100 Torr of H ₂ from (b) room temperature, (c) 50, (d) 100, (e) 150 and (f) 200 °C. The true line represents the spectrum before catalyst activation | 84 |
| 4.23 | Rate of <i>n</i> -heptane isomerization over P/MoO ₃ /KCC-1. | 92 |
| 4.24 | (A) Rate of <i>n</i> -heptane conversion and (B) yield of <i>di</i> -branched isomers | 94 |
| 4.25 | Pareto chart of the yield isomers. | 98 |
| 4.26 | Predicted vs observed value plot of the model | 99 |
| 4.27 | Response surface plot of the yield isomers showing interaction between treatment temperature and reaction temperature | 100 |
| 4.28 | Response surface plot of the yield isomers showing interaction between treatment time and reaction temperature | 101 |
| 4.29 | Response surface plot of the yield isomers showing interaction treatment time and treatment temperature | 102 |

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 | - | Miliampere |
| W | - | Watt |
| μmol | - | Micromole |
| kV | - | Kilovolt |

LIST OF APPENDICES

| APPENDIX NO. | TITLE | PAGES |
|---------------------|---|--------------|
| A | Calculation of percentage of molybdenum oxide (MoO ₃) and Platinum (Pt) | 125 |
| B | Raw data for <i>n</i> -heptane isomerisation | 126 |
| C | Calculation for catalytic activity | 127 |
| D | List of Publications and Proceeding | 129 |

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 C₅-C₈ paraffins possess a higher octane number compared to the corresponding linear paraffins (C₇) (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 -C₅ isomerisation due to its high acidity; however, it exhibited less selectivity when dealing with longer chain paraffins such as n -C₆ and n -C₇ (Chica *et al.*, 2001). Besides, different types of material such as SAPO-11 (Liu *et al.*, 2008), MOR (Lee and Rhee, 1997), ZrO₂ (Ruslan *et al.*, 2011; Triwahyono *et al.*, 2007), alumina (Vandegheuchte *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 CO₂ reforming of CH₄ (Sidik *et al.*, 2015), methanation of CO₂ (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 -C₅. 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 CO₂ 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 m²/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, MoO₃ has been extensively studied due to its potential in alkane isomerisation and environmentally friendly properties as compared to mineral acids such as HF and H₂SO₄ (Ono, 2003). Many works have been devoted to MoO₃-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/MoO₃ catalyst was greatly influenced by its surface area (Sakagami *et al.*, 2014). The improvement in the Pt/MoO₃ surface area due to the slow reduction rate of H₂ flow gave the MoO_x with the highest *n*-heptane isomerisation activity. Besides, previous study also has reported on the formation of acidic Brønsted (MoO_x)⁻(H_y)⁺ over Pt/MoO₃ 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_x)⁻(H_y)⁺ or protonic acid sites were observed on Pt-free MoO₃.

Although there are several reports published on MoO_x supported SiO₂ 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 MoO₃-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 MoO₃/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/MoO₃-SiO₂ can be controlled by the formation of MoO_xH_y, yielded from the reduction of MoO₃ along with its number of acid sites. The Pt/MoO₃-SiO₂ catalyst with 80 wt. % of MoO₃ 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 MoO₃ 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*-branched isomer products. In addition, the physico-chemical properties and catalytic activity of MoO₃/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 MoO₃. 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 MoO₃/KCC-1 with phosphorus to form P/MoO₃/KCC-1 was expected to enhance the catalytic activity. Then, the optimisation of *n*-heptane isomerization over P/MoO₃/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 (MoO₃) 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 SiO₂, Al₂O₃, ZrO₂ and TiO₂ 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^+) 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_3 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_3 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 MoO₃/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 MoO₃/MSN catalysts for *n*-heptane isomerisation;

The MSN was prepared using a co-condensation and sol-gel method. Then, the MoO₃/MSN was prepared by physically mixing of MoO₃ with MSN. In this study, physical mixing method was chosen for the preparation of MoO₃/MSN due to the property of MoO₃ 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 MoO₃ was adjusted to 40 wt%, based on literature study (Liu *et al.*, 2015; Matsuda *et al.*, 2009) and preliminary catalytic activity evaluation using different MoO₃ 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 (Timmiaati *et al.*, 2013). The prepared catalysts were characterised using X-Ray Diffraction (XRD), N₂ physisorption, H₂-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 MoO₃/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), N₂ physisorption, H₂-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 MoO₃/KCC-1 with H₃PO₄. The amount of H₃PO₄ concentration was adjusted to 0.5 N based on literature (Triwahyono *et al.*, 2006) and preliminary catalytic activity evaluation using different H₃PO₄ concentration.

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

The optimum condition for *n*-heptane isomerization over P/MoO₃/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 MoO₃ 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 MoO₃ 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.

REFERENCES

- Afanasiev, P., Geantet, C. and Breyse, M. (1995). Preparation of High Surface Area Mo/ZrO₂ Catalysts by a Molten Salt Method: Application to Hydrodesulfurization. *Journal of Catalysis*, 153(1), 17-24.
- Akhmedov, V. M., and Al-Khowaiter, S. H. (2007). Recent Advances and Future Aspects in the Selective Isomerization of High *n*-Alkanes. *Catalysis Reviews*, 49(1), 33–139.
- Al-Kandari, H., Al-Kharafi, F., and Katrib, A. (2009). Large Scale Hydroisomerization Reactions of *n*-heptane on Partially Reduced MoO₃/TiO₂. *Applied Catalysis A: General*, 361(1–2), 81–85.
- Al-Kandari, H., Mohamed, A. M., Al-Kharafi, F., Zaki, M. I., and Katrib, A. (2012). Modification of the Catalytic Properties of MoO_{2-x}(OH)_y Dispersed On TiO₂ by Pt and Cs Additives. *Applied Catalysis A: General*, 417–418, 298–305.
- Al-Kandari, H., Mohamed, A. M., Al-Kandari, S., Al-Kharafi, F., Mekhemer, G. a., Zaki, M. I., and Katrib, A. (2013). Spectroscopic Characterization–Catalytic Activity Correlation of Molybdena Based Catalysts. *Journal of Molecular Catalysis A: Chemical*, 368–369, 1–8.
- Al-Kandari, H., Mohamed, A. M., Al-Kharafi, F., and Katrib, A. (2011). Effect of Pt Addition on the Isomerization Properties of MoO_{2-x}(OH)_y Deposited on TiO₂. *Catalysis Communications*, 12(13), 1188–1192.
- Al-Kandari, S., Al-Kandari, H., Mohamed, A. M., Al-Kharafi, F., and Katrib, A. (2014). Tailoring Acid-metal Functions in Molybdenum Oxides: Catalytic and XPS-UPS, ISS Characterization Study. *Applied Catalysis A: General*, 475, 497–502.
- Alemán-Vázquez, L. O., Hernández-Pérez, F., Cano-Domínguez, J. L., Rodríguez-Hernández, A., and García-Gutiérrez, J. L. (2014). Binder Effect on the

- Catalytic Activity of MoO₃ Bulk Catalyst Reduced by H₂ for *n*-heptane Hydroisomerization. *Fuel*, 117, 463–469.
- Annur, N. H. R., Jalil, A. A., Triwahyono, S., Fatah, N. A. A., Teh, L. P., and Mamat, C. R. (2014). Cumene Cracking over Chromium Oxide Zirconia: Effect of Chromium(VI) Oxide Precursors. *Applied Catalysis A: General*, 475, 487–496.
- Annur, N. H. R., Jalil, A. A., Triwahyono, S., and Ramli, Z. (2013). Relating Cumene Hydrocracking Activity to the Acidic Center of CrO₃-ZrO₂. *Journal of Molecular Catalysis A: Chemical*, 377, 162–172.
- Arnoldy, P., De Jonge, J. C. M., and Moulijn, J. A. (1985). Temperature-programmed Reduction of MoO₃ and MoO₂. *Journal Physical Chemical*, 89(21), 4517-4526.
- Assis, J. C. R., Teixeira, J. S. R., Pontes, L. A. M., Guimarães, P. R. B., Vianna, R. F., Bezerra, M. A., and Teixeira, L. S. G. (2013). Using the Doehlert Matrix As A Tool for Studying the Influence of Gasoline Components on Octane Numbers, 113, 744–749.
- Avila-Flores, R., and Medellín, R. A. (2004). Ecological, Taxonomic, and Physiological Correlates of Cave Use by Mexican Bats. *Journal of Mammalogy*, 85(4), 675–687.
- Aziz, M. A. A., Jalil, A. A., Triwahyono, S., Mukti, R. R., Taufiq-Yap, Y. H., and Sazegar, M. R. (2014). Highly Active Ni-promoted Mesostructured Silica Nanoparticles For CO₂ Methanation. *Applied Catalysis B: Environmental*, 147, 359–368.
- Aziz, M. A. A., Kamarudin, N. H. N., Setiabudi, H. D., Hamdan, H., Jalil, A. A., and Triwahyono, S. (2012). Negative Effect of Ni on PtHY in *n*-pentane Isomerization Evidenced by IR and ESR Studies. *Journal of Natural Gas Chemistry*, 21(1), 29–36.
- Baran, R., Averseng, F., Millot, Y., Onfroy, T., Casale, S., and Dzwigaj, S. (2014). Incorporation of Mo into the Vacant T-atom Sites of the Framework of BEA Zeolite as Mononuclear Mo Evidenced by XRD and FTIR, NMR, EPR, and DR UV-vis Spectroscopies. *Journal of Physical Chemistry C*, 118(8), 4143–4150.
- Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., and Escalera, L. A. (2008). Response Surface Methodology (RSM) as A Tool for Optimization in Analytical Chemistry. *Talanta*, 76(5), 965–977.

- Biscardi, J. A., and Iglesia, E. (1996). Structure and Function of Metal Cations in Light Alkane Reactions Catalyzed by Modified H-ZSM5. *Catalysis Today*, 31(3–4), 207–231.
- Blasco, T., Corma, A., and Martínez-Triguero, J. (2006). Hydrothermal Stabilization of ZSM-5 Catalytic-cracking Additives by Phosphorus Addition. *Journal of Catalysis*, 237(2), 267–277.
- Blekkann, E. A., Cuong, P. H., Ledoux, M. J., and Guille, J. (1994). Isomerization of n-Heptane on an Oxygen-modified Molybdenum Carbide Catalyst. *Industrial & Engineering Chemistry Research*, 33(7), 1657–1664.
- Blomsma, E., Martens, J. A., and Jacobs, P. A. (1996). Mechanisms of Heptane Isomerization on Bifunctional Pd/H-Beta Zeolites. *Journal of Catalysis*, 159(2), 323–331.
- Brown, H. C., Gintis, D., and Domash, L. (1956). Steric Effects in Displacement Reactions. XII. Linear Strain Energy Relationships Involving Reactants of Large Steric Requirements. Steric Strains in the Transition State¹. *Journal of the American Chemical Society*, 78(20), 5387–5394.
- Busto, M., Dosso, L. A., Vera, C. R., and Grau, J. M. (2012). Composite Catalysts of Pt/SO₄²⁻-ZrO₂ and Pt/WO₃-ZrO₂ for Producing High Octane Isomerizate by Isomerization-cracking of Long Paraffins. *Fuel Processing Technology*, 104, 128–135.
- Brunner, E., Pfeifer, H., Auroux, A., Lercher, J., Jentys, A., Brait, A., Garrone, E. and Fajula, F., (2008). *Acidity and Basicity* (Vol. 6). Springer Science & Business Media.
- Caeiro, G., Magnoux, P., Lopes, J. M., Ribeiro, F. R., Menezes, S. M. C., Costa, A. F., and Cerqueira, H. S. (2006). Stabilization Effect of Phosphorus on Steamed H-MFI Zeolites. *Applied Catalysis A: General*, 314(2), 160–171.
- Calafat, A., Avilán, L., and Aldana, J. (2000). The Influence of Preparation Conditions on the Surface Area and Phase Formation of MoO₃/ZrO₂ Catalysts. *Applied Catalysis A: General*, 201(2), 215–223.
- Canizares, P., De Lucas, A., Dorado, F., and Aguirre, J. (2001). n-Butane Hydroisomerization over Pd/HZSM-5 Catalysts. Palladium Loaded by Ion Exchange. *Microporous and Mesoporous Materials*, 42(2), 245–254.
- Cardoso, M. J. B., Rosas, D. D. O., and Lau, L. Y. (2005). Surface P and Al Distribution in P-Modified ZSM-5 Zeolites. *Adsorption*, 11(5–6), 577–580.

- Caro, J., Bülow, M., Derewinski, M., Haber, J., Hunger, M., Kärger, J., Pfeifer, H., Storek, W., and Zibrowius, B. (1990). NMR and IR Studies of Zeolite H-ZSM-5 Modified with Orthophosphoric Acid. *Journal of Catalysis*, 124(2), 367–375.
- Cavani, F., and Trifirb, F. (1997). Classification of Industrial Catalysts and Catalysis for the Petrochemical Industry, 34, 269–279.
- Chao, K. J., Wu, H. C., and Leu, L. J. (1996). Hydroisomerization of Light Normal Paraffins over Series of Platinum-loaded Mordenite and Beta Catalysts. *Applied Catalysis A: General*, 143(2), 223–243.
- Chary, K. V. R., Reddy, K. R., Kishan, G., Niemantsverdriet, J. W., and Mestl, G. (2004). Structure and Catalytic Properties of Molybdenum Oxide Catalysts Supported on Zirconia. *Journal of Catalysis*, 226(2), 283–291.
- Chen, C.-Y., Burkett, S. L., Li, H.-X., and Davis, M. E. (1993). Studies on Mesoporous Materials I. Synthesis and Characterization of MCM-41. *Microporous Materials*, 2(1), 27–34.
- Chica, A., and Corma, A. (1999). Hydroisomerization of Pentane, Hexane, and Heptane for Improving the Octane Number Of Gasoline, 176, 167–176.
- Chica, A., Corma, A., and Miguel, P. J. (2001). Isomerization of C₅–C₇ n-alkanes on Unidirectional Large Pore Zeolites: Activity, Selectivity and Adsorption Features. *Catalysis Today*, 65(2), 101–110.
- Corma, A., Rodellas, C., and Fornes, V. (1984). Characterization of Acid Surfaces by Adsorption 2,6-dimethylpyridine. *Journal of Catalysis*, 88, 374–381.
- Corma, A., Fornes, V., Kolodziejcki, W., and Martinez-Triguero, L. J. (1994). Orthophosphoric Acid Interactions with Ultrastable Zeolite-Y: Infrared and NMR Studies. *Journal of Catalysis*, 145, 27–36.
- Debecker, D. P., Schimmoeller, B., Stoyanova, M., Poleunis, C., Bertrand, P., Rodemerck, U., and Gaigneaux, E. M. (2011). Flame-made MoO₃/SiO₂-Al₂O₃ Metathesis Catalysts with Highly Dispersed and Highly Active Molybdate Species. *Journal of Catalysis*, 277(2), 154–163.
- Del Gallo, P., Pham-Huu, C., Bouchy, C., Estournes, C., and Ledoux, M. J. (1997). Effect of the Total Activation Pressure on The Structural and Catalytic Performance of the SiC Supported MoO₃-Carbon-Modified Catalyst for the n-heptane Isomerization. *Applied Catalysis A: General*, 156(1), 131–149.
- Deldari, H. (2005). Suitable Catalysts for Hydroisomerization of Long-Chain Normal Paraffins. *Applied Catalysis A: General*, 293(1–2), 1–10.

- Devassy, B. M., Halligudi, S. B., Elangovan, S. P., Ernst, S., Hartmann, M., and Lefebvre, F. (2004). Zirconia Supported Phosphotungstic Acid as an Efficient Catalyst for Resorcinol Tert-butylation and *n*-heptane Hydroisomerization, 221, 113–119.
- Dhiman, M., Chalke, B., and Polshettiwar, V. (2015). Efficient Synthesis of Monodisperse Metal (Rh, Ru, Pd) Nanoparticles Supported on Fibrous Nanosilica (KCC-1) for Catalysis. *ACS Sustainable Chemistry and Engineering*, 3(12), 3224–3230.
- Di-Grégorio, F., Keller, V., Di-Costanzo, T., Vignes, J. L., Michel, D., and Maire, G. (2001). Cracking and Skeletal Isomerization of Hexenes on Acidic MoO₃-WO₃/α-Al₂O₃ Oxide. *Applied Catalysis A: General*, 218(1–2), 13–24.
- Dombrowski, D., Hoffmann, J., Fruwert, J., and Stock, T. (1985). Infrared Spectroscopic Investigation of Hydroxy-Group Siting in H Faujasites. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 81(10), 2257–2271.
- Dossi, C., Tsang, C. M., Sachtler, W. M. H., Psaro, R., and Ugo, R. (1989). Reforming-type Catalysis with Zeolite-Supported PtRe. *Energy & Fuels*, 3(4), 468–474.
- Du, X., and Zhang Qiao, S. (2015). Dendritic Silica Particles with Center-radial Pore Channels: Promising Platforms for Catalysis and Biomedical Applications. *Small*, 11(4), 392–413.
- Dyballa, M., Klemm, E., Weitkamp, J., and Hunger, M. (2013). Effect of Phosphate Modification on the Brønsted Acidity and Methanol-to-Olefin Conversion Activity of Zeolite ZSM-5. *Chemie Ingenieur Technik*, 85(11), 1719–1725.
- Ebitani, K., Konishi, J., and Hattori, H. (1991). Skeletal Isomerization of Hydrocarbons over Zirconium Oxide Promoted by Platinum and Sulfate Ion. *Journal of Catalysis*, 130(1), 257–267.
- Ebitani, K., Tsuji, J., Hattori, H., and Kita, H. (1992). Dynamic Modification of Surface Acid Properties with Hydrogen Molecule for Zirconium Oxide Promoted by Platinum and Sulfate Ions. *Journal of Catalysis*, 135(2), 609–617.
- F. Barath, M. Turki, V. Keller, and G. M. (1999). Catalytic Activity of Reduced MoO₃/α-Al₂O₃ for Hexanes Reforming I. Preparation, Characterization, and X-Ray Photoelectron Spectroscopy Studies. *Journal of Catalysis*, 185, 1–11.

- Fahim, M. A., Alsahhaf, T. A., and Elkilani, A. (2010). Hydroconversion. *Fundamentals of Petroleum Refining, Elsevier, Amsterdam*, 153–198.
- Febriyanti, E., Suendo, V., Mukti, R. R., Prasetyo, A., Arifin, A. F., Akbar, M. A., Triwahyono, S., Marsih, I. N., and Ismunandar. (2016). Further Insight into the Definite Morphology and Formation Mechanism of Mesoporous Silica KCC-1. *Langmuir*, 32(23), 5802–5811.
- Ferdous, D., Dalai, A. K., and Adjaye, J. (2004). A Series of NiMo/Al₂O₃ Catalysts Containing Boron and Phosphorus: Part I. Synthesis and Characterization. *Applied Catalysis A: General*, 260(2), 137–151.
- Fernandes, C. I., Capelli, S. C., Vaz, P. D., and Nunes, C. D. (2015). Highly Selective And Recyclable MoO₃ Nanoparticles in Epoxidation Catalysis. *Applied Catalysis A: General*, 504, 344–350.
- Fernandez, C., Stan, I., Gilson, J. P., Thomas, K., Vicente, A., Bonilla, A., and Pérez-Ramírez, J. (2010). Hierarchical ZSM-5 Zeolites in Shape-Selective Xylene Isomerization: Role of Mesoporosity and Acid Site Speciation. *Chemistry - A European Journal*, 16(21), 6224–6233.
- Fihri, A., Bouhrara, M., Patil, U., Cha, D., Saih, Y., and Polshettiwar, V. (2012). Fibrous Nano-silica Supported Ruthenium (KCC-1/Ru): A Sustainable Catalyst for the Hydrogenolysis of Alkanes with Good Catalytic Activity and Lifetime. *ACS Catalysis*, 2(7), 1425–1431.
- Fihri, A., Cha, D., Bouhrara, M., Almana, N., and Polshettiwar, V. (2012). Fibrous Nano-silica (KCC-1)-Supported Palladium Catalyst: Suzuki Coupling Reactions under Sustainable Conditions. *ChemSusChem*, 5(1), 85–89.
- Firmansyah, M. L., Jalil, a. a., Triwahyono, S., Hamdan, H., Salleh, M. M., Ahmad, W. F. W., and Kadja, G. T. M. (2016). Synthesis and Characterization of Fibrous Silica ZSM-5 for Cumene Hydrocracking. *Catalysis Science Technology*, 6, 5178–5182.
- Galperin, L. B., Bradley, S. A., and Mezza, T. M. (2001). Hydroisomerization of *n*-Decane in the Presence of Sulfur Effect of Metal–Acid Balance and Metal Location. *Applied Catalysis A: General*, 219, 79–88.
- Gao, Z., and Zharov, I. (2014). Large Pore Mesoporous Silica Nanoparticles by Templating with A Nonsurfactant Molecule, Tannic Acid. *Chemistry of Materials*, 26(6), 2030–2037.

- Geng, C., Zhang, F., Gao, Z., Zhao, L., and Zhou, J. (2004). Hydroisomerization of *n*-Tetradecane over Pt/SAPO-11 Catalyst, 95, 485–491.
- Ghedini, E., Menegazzo, F., Signoretto, M., Manzoli, M., Pinna, F., and Strukul, G. (2010). Mesoporous Silica as Supports for Pd-Catalyzed H₂O₂ Direct Synthesis: Effect of the Textural Properties of the Support on the Activity and Selectivity. *Journal of Catalysis*, 273(2), 266–273.
- Göhlich, M., Reschetilowski, W., and Paasch, S. (2011). Spectroscopic Study of Phosphorus Modified H-ZSM-5. *Microporous and Mesoporous Materials*, 142(1), 178–183.
- Gou, M. L., Wang, R., Qiao, Q., and Yang, X. (2015). Effect of Mesoporosity by Desilication on Acidity and Performance of HZSM-5 in the Isomerization of Styrene Oxide to Phenylacetaldehyde. *Microporous and Mesoporous Materials*, 206, 170–176.
- Guevara-Lara, A., Cruz-Perez, A. E., Contreras-Valdez, Z., Mogica-Betancourt, J., Alvarez-Hernandez, A., and Vrinat, M. (2010). Effect of Ni Promoter in the Oxide Precursors of MoS₂/MgO-Al₂O₃ Catalysts Tested in Dibenzothiophene Hydrodesulphurization. *Catalysis Today*, 149(3–4), 288–294.
- Haaland, P. D. (1989). *Experimental Design In Biotechnology* Marcel Dekker. *Inc, United State of America.*
- Hadjiivanov, K. I., and Vayssilov, G. N. (2002). Characterization of Oxide Surfaces and Zeolites by Carbon Monoxide as an IR Probe Molecule. *Advances in Catalysis*, 47, 307–511.
- Hattori, H. (1993). Molecular Hydrogen-originated Solid Acid Catalysts. *Studies in Surface Science and Catalysis*, 77, 69-76.
- Hattori, H. (2001). Molecular Hydrogen-Originated Protonic Acid Site. *Studies in Surface Science and Catalysis*, 138, 3–12.
- Hino, M., and Arata, K. (1988). Synthesis of Solid Superacid of Tungsten Oxide Supported on Zirconia and Its Catalytic Action for Reactions of Butane and Pentane. *Journal of the Chemical Society, Chemical Communications*, (18), 1259–1260.
- Hino, M., Kobayashi, S., and Arata, K. (1979). Solid Catalyst Treated With Anion. 2. Reactions Of Butane And Isobutane Catalyzed By Zirconium Oxide Treated With Sulfate Ion. Solid Superacid Catalyst. *Journal of the American Chemical Society*, 101(21), 6439–6441.

- Höchtel, M., Jentys, A., and Vinek, H. (2001). Alkane Conversion over Pd/SAPO Molecular Sieves: Influence of Acidity, Metal Concentration and Structure. *Catalysis Today*, 65(2–4), 171–177.
- Hua, W., and Sommer, J. (2002). Alumina-doped Pt/WO_x/ZrO₂ Catalysts for *n*-Heptane Isomerization. *Applied Catalysis A: General*, 232, 129–135.
- Huang, X., Tao, Z., Praskavich Jr, J. C., Goswami, A., Al-Sharab, J. F., Minko, T., Polshettiwar, V., and Asefa, T. (2014). Dendritic Silica Nanomaterials (KCC-1) With Fibrous Pore Structure Possess High DNA Adsorption Capacity and Effectively Deliver Genes In Vitro. *Langmuir*, 30(36), 10886–10898.
- Iglesia, E., Barton, D. G., Biscardi, J. A., Gines, M. J. L., and Soled, S. L. (1997). Bifunctional Pathways in Catalysis by Solid Acids and Bases. *Catalysis Today*, 38(3), 339–360.
- Ivanova, T., Surtchev, M., and Gesheva, K. (2002). Investigation of CVD Molybdenum Oxide Films. *Materials Letters*, 53(4–5), 250–257.
- Jacobs, P. A., Flanigen, E. M., Jansen, J. C., and van Bekkum, H. (2001). Introduction to Zeolite Science and Practice (Vol. 137). Elsevier.
- Jacobs, P. A., and Heylen, C. F. (1974). Active Sites In Zeolites: III. Selective Poisoning of Bronsted Sites on Synthetic Y Zeolites. *Journal of Catalysis*, 34(2), 267–274.
- Janardhan, H. L., Shanbhag, G. V., and Halgeri, A. B. (2014). Shape-selective Catalysis by Phosphate Modified ZSM-5: Generation of New Acid Sites with Pore Narrowing. *Applied Catalysis A: General*, 471, 12–18.
- Jentys, A., and Lercher, J. A. (2001). Techniques of Zeolite Characterization. *Studies in Surface Science and Catalysis*, 137, 345–386.
- Jiang, G., Zhang, L., Zhao, Z., Zhou, X., Duan, A., Xu, C., and Gao, J. (2008). Highly Effective P-modified HZSM-5 Catalyst for the Cracking Of C₄ Alkanes to Produce Light Olefins. *Applied Catalysis A: General*, 340(2), 176–182.
- Jusoh, N. W. C., Jalil, A. A., Triwahyono, S., Setiabudi, H. D., Sapawe, N., Satar, M. A. H., Karim, A. H., Kamarudin, N. H. N., Jusoh, R., Jaafar, N. F., Salamun, N., and Efendi, J. (2013). Sequential Desilication-Isomorphous Substitution Route to Prepare Mesoporous Silica Nanoparticles Loaded with ZnO and Their Photocatalytic Activity. *Applied Catalysis A: General*, 468, 276–287.
- Kamarudin, N. H. N., Jalil, A. A., Triwahyono, S., Mukti, R. R., Aziz, M. A. A., Setiabudi, H. D., Muhid, M. N. M., and Hamdan, H. (2012). Interaction of Zn²⁺

- with Extraframework Aluminum in HBEA Zeolite and Its Role in Enhancing *n*-pentane Isomerization. *Applied Catalysis A: General*, 431–432, 104–112.
- Kamarudin, N. H. N., Jalil, A. A., Triwahyono, S., Salleh, N. F. M., Karim, A. H., Mukti, R. R., Hameed, B. H., and Ahmad, A. (2013). Role of 3-aminopropyltriethoxysilane in the Preparation of Mesoporous Silica Nanoparticles for Ibuprofen Delivery: Effect on Physicochemical Properties. *Microporous and Mesoporous Materials*, 180, 235–241.
- Karim, A. H., Jalil, A. A., Triwahyono, S., Sidik, S. M., Kamarudin, N. H. N., Jusoh, R., Jusoh, N. W. C., and Hameed, B. H. (2012). Amino Modified Mesostructured Silica Nanoparticles for Efficient Adsorption of Methylene Blue. *Journal of Colloid and Interface Science*, 386(1), 307–314.
- Katrib, A., Benadda, A., Sobczak, J. W., and Maire, G. (2003). XPS and Catalytic Properties of the Bifunctional Supported $\text{MoO}_2(\text{H}_x)\text{ac}$ on TiO_2 for the Hydroisomerization Reactions of Hexanes and 1-hexene, 242, 31–40.
- Kierys, A., Pasiczna-Patkowska, S., Ryczkowski, J., Borówka, A., and Goworek, J. (2008). Organic Deposits on MCM-41 Surface After Thermal Treatment of As-Synthesized Samples. *European Physical Journal: Special Topics*, 154(1), 335–338.
- Klinowski, J. (1984). Nuclear Magnetic Resonance Studies Of Zeolites. *Progress in Nuclear Magnetic Resonance Spectroscopy*, 16, 237–309.
- Klinowski, J. (1989). Solid-State NMR Studies of Zeolite Catalysts. *Colloids and Surfaces*, 36(2), 133–154.
- Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., and Beck, J. S. (1992). Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-crystal Template Mechanism. *Nature*, 359(6397), 710–712.
- Kuba, S. (2003). Structure and Properties of Tungstated Zirconia Catalysts for Alkane Conversion. *Journal of Catalysis*, 216(1–2), 353–361.
- Kuchar, P. J., Bricker, J. C., Reno, M. E., and Haizmann, R. S. (1993). Paraffin Isomerization Innovations. *Fuel Processing Technology*, 35(1–2), 183–200.
- Kumar, M.S., Chen, D., Holmen, A. and Walmsley, J.C., (2009). Dehydrogenation of Propane over Pt-SBA-15 and Pt-Sn-SBA-15: Effect of Sn on the Dispersion of Pt and Catalytic Behavior. *Catalysis Today*, 142(1), 17-23.

- Kuznetsov, P. N. (2003). Study of n-octane Hydrocracking and Hydroisomerization over Pt/HY Zeolites using the Reactors of Different Configurations. *Journal of Catalysis*, 218(1), 12–23.
- Le, X., Dong, Z., Li, X., Zhang, W., Le, M., and Ma, J. (2015). Fibrous Nano-silica Supported Palladium Nanoparticles: An Efficient Catalyst for the Reduction of 4-nitrophenol and Hydrodechlorination of 4-chlorophenol under Mild Conditions. *Catalysis Communications*, 59, 21–25.
- Lebarbier, V., Clet, G., and Houalla, M. (2006). Relations Between Structure, Acidity, and Activity of WO_x/TiO_2 : Influence of the Initial State of the Support, Titanium Oxyhydroxide, or Titanium Oxide. *Journal of Physical Chemistry B*, 110(45), 22608–22617.
- Lee, J.-K., and Rhee, H.-K. (1997). Characteristics of Pt/H-beta and Pt/H-mordenite Catalysts for the Isomerization of n-hexane. *Catalysis Today*, 38(2), 235–242.
- Lercher, J. A., and Rumpelmayr, G. (1986). Controlled Decrease of Acid Strength by Orthophosphoric Acid on ZSM5. *Applied Catalysis*, 25, 215–222.
- Leydier, F., Chizallet, C., Chaumonnot, A., Digne, M., Soyer, E., Quoineaud, A. A., Costa, D., and Raybaud, P. (2011). Brønsted Acidity of Amorphous Silica-alumina: The Molecular Rules of Proton Transfer. *Journal of Catalysis*, 284(2), 215–229.
- Li, Z., Gao, L., and Zheng, S. (2002). Investigation of the Dispersion of MoO_3 onto the Support of Mesoporous Silica MCM-41, 236, 163–171.
- Linares, N., Silvestre-Albero, A. M., Serrano, E., Silvestre-Albero, J., and Garcia-Martinez, J. (2014). Mesoporous Materials for Clean Energy Technologies. *Chemical Society Reviews*, 43(22), 7681–7717.
- Lischke, G., Eckelt, R., Jerschke, H. G., Parlitz, B., Schreier, E., Storek, W., Zibrowius, B., and Öhlmann, G. (1991). Spectroscopic and Physicochemical Characterization of P-Modified H-ZSM-5. *Journal of Catalysis*, 132(1), 229–243.
- Liu, J., Zhang, C., Shen, Z., Hua, W., Tang, Y., Shen, W., Yue, Y., and Xu, H. (2009). Methanol To Propylene: Effect of Phosphorus on A High Silica HZSM-5 Catalyst. *Catalysis Communications*, 10(11), 1506–1509.
- Liu, P., Ren, J., and Sun, Y. (2008). Influence of Template on Si Distribution of SAPO-11 and Their Performance For n-paraffin Isomerization. *Microporous and Mesoporous Materials*, 114(1), 365–372.

- Liu, P., Wu, M. Y., Wang, J., Zhang, W. H., and Li, Y. X. (2015). Hydroisomerization of *n*-heptane over MoP/H β Catalyst Doped with Metal Additive. *Fuel Processing Technology*, 131, 311–316.
- Liu, Y., Liu, C., Liu, C., Tian, Z., and Lin, L. (2004). Sn-Modified Pt/SAPO-11 Catalysts for Selective Hydroisomerization of *n*-Paraffins, 91(10), 1266–1271.
- López, C. M., Guillén, Y., García, L., Gómez, L., and Ramírez, Á. (2008). *n*-Pentane Hydroisomerization on Pt Containing HZSM-5, HBEA and SAPO-11. *Catalysis Letters*, 122(3–4), 267–273.
- Ma, D., Shu, Y., Han, X., Liu, X., Xu, Y., and Bao, X. (2001). Mo/HMCM-22 Catalysts for Methane Dehydroaromatization: A Multinuclear MAS NMR Study. *The Journal of Physical Chemistry B*, 105(9), 1786–1793.
- MacDonald, I. R., Howe, R. F., Zhang, X., and Zhou, W. (2010). In Situ EPR Studies of Electron Trapping in A Nanocrystalline Rutile. *Journal of Photochemistry and Photobiology A: Chemistry*, 216(2–3), 238–243.
- Martens, J. A., Tielen, M., and Jacobs, P. A. (1989). Relation Between Paraffin Isomerisation Capability and Pore Architecture of Large-pore Bifunctional Zeolites. *Studies in Surface Science and Catalysis*, 46, 49–60.
- Matsuda, T., Uchijima, F., Endo, S. and Takahashi, N., 1999. Effect of Pd Loading on the Catalytic Properties of Molybdenum Oxides for the Isomerization of Heptane. *Applied Catalysis A: General*, 176(1), 91-99.
- Matsuda, T., Hirata, Y., Suga, S., Sakagami, H., and Takahashi, N. (2000). Effect of H₂ Reduction on the Catalytic Properties Of Molybdenum Oxides for the Conversions of Heptane and 2-propanol. *Applied Catalysis A: General*, 193(1–2), 185–193.
- Matsuda, T., Ohno, T., Hiramatsu, Y., Li, Z., Sakagami, H., and Takahashi, N. (2009). Effects of the Amount of MoO₃ on the Catalytic Properties of H₂-reduced Pt/MoO₃-SiO₂ for Heptane Isomerization. *Applied Catalysis A: General*, 362(1–2), 40–46.
- Matsuda, T., Sakagami, H., and Takahashi, N. (2003). H₂-Reduced Pt/MoO₃ as A Selective Catalyst for Heptane Isomerization. *Catalysis Today*, 81(1), 31–42.
- Matsushashi, H., Shibata, H., Nakamura, H., and Arata, K. (1999). Skeletal Isomerization Mechanism of Alkanes over Solid Superacid of Sulfated Zirconia. *Applied Catalysis A: General*, 187(1), 99–106.

- Medina-Mendoza, A. K., Cortés-Jácome, M. A., Toledo-Antonio, J. A., Angeles-Chávez, C., López-Salinas, E., Cuauhtémoc-López, I., Barrera, M. C., Escobar, J., Navarrete, J., and Hernández, I. (2011). Highly Dispersed Uniformly Sized Pt Nanoparticles on Mesoporous Al-SBA-15 by Solid State Impregnation. *Applied Catalysis B: Environmental*, 106(1–2), 14–25.
- Mendes, G., Aleme, H. G., and Barbeira, P. J. S. (2012). Determination of Octane Numbers In Gasoline by Distillation Curves and Partial Least Squares Regression. *Fuel*, 97, 131–136.
- Miyaji, A., Ohnishi, R., and Okuhara, T. (2004). Skeletal Isomerization of *n*-heptane over Pd-H₄SiW₁₂O₄₀ Supported on SiO₂: Comparative Study with Typical Bifunctional Catalysts, 262, 143–148.
- Moon, D.-S., and Lee, J.-K. (2012). Tunable Synthesis of Hierarchical Mesoporous Silica Nanoparticles with Radial Wrinkle Structure. *Langmuir*, 28(33), 12341–12347.
- Morterra, C., and Cerrato, G. (1990). On the use of Pyridine Adsorption as an Analytical Tool In Surface Chemistry. *Langmuir*, 6(12), 1810–1812.
- Morterra, C., Cerrato, G., and Meligrana, G. (2001). Revisiting the Use of 2,6-Dimethylpyridine Adsorption as A Probe for the Acidic Properties of Metal Oxides. *Langmuir*, 17(22), 7053–7060.
- Newnham, R. E. (2012). Structure-property Relations (Vol. 2). Springer Science & Business Media.
- Nikolaou, N., Papadopoulos, C. E., Gaglias, I. A., and Pitarakis, K. G. (2004). A New Non-linear Calculation Method of Isomerisation Gasoline Research Octane Number Based on Gas Chromatographic Data, 83, 517–523.
- Ohno, T., Li, Z., Sakai, N., Sakagami, H., Takahashi, N., and Matsuda, T. (2010). Heptane Isomerization over Molybdenum Oxides Obtained by H₂ Reduction of H_xMoO₃ With Different Hydrogen Contents. *Applied Catalysis A: General*, 389(1–2), 52–59.
- Oliviero, L., Vimont, A., Lavalley, J.-C., Sarria, F. R., Gaillard, M., and Maugé, F. (2005). 2, 6-Dimethylpyridine as A Probe of the Strength of Brønsted Acid Sites: Study on Zeolites. Application to Alumina. *Physical Chemistry Chemical Physics*, 7(8), 1861–1869.

- Onfroy, T., Clet, G., and Houalla, M. (2005). Quantitative IR Characterization of the Acidity of Various Oxide Catalysts. *Microporous and Mesoporous Materials*, 82(1–2), 99–104.
- Ono, Y. (2003). A Survey of The Mechanism in Catalytic Isomerization of Alkanes. *Catalysis Today*, 81(1), 3–16.
- Özer, A., Gürbüz, G., Çalimli, A., and Körbahti, B. K. (2009). Biosorption of Copper (II) Ions on *Enteromorpha Prolifera*: Application of Response Surface Methodology (RSM). *Chemical Engineering Journal*, 146(3), 377–387.
- Park, K., and Ihm, S. (2000). Comparison of Pt/Zeolite Catalysts for *n*-hexadecane Hydroisomerization, 203, 201–209.
- Patil, U., Fihri, A., Emwas, A.-H., and Polshettiwar, V. (2012). Silicon Oxynitrides of KCC-1, SBA-15 And MCM-41 for CO₂ Capture with Excellent Stability and Regenerability. *Chemical Science*, 3(7), 2224.
- Pawelec, B., Halachev, T., Olivas, A., and Zepeda, T. A. (2008). Impact of Preparation Method and Support Modification on the Activity of Mesoporous Hydrotreating CoMo Catalysts. *Applied Catalysis A: General*, 348(1), 30–41.
- Pérez-Romo, P., Potvin, C., Manoli, J.-M., and Djéga-Mariadassou, G. (2002). Phosphorus-Doped Tungsten Oxynitrides: Synthesis, Characterization, And Catalytic Behavior In Propene Hydrogenation and *n*-Heptane Isomerization. *Journal of Catalysis*, 205(1), 191–198.
- Pham-Huu, C., Gallo, P. Del, Peschiera, E., and Ledoux, M. J. (1995). *n*-Hexane And *n*-heptane Isomerization at Atmospheric and Medium Pressure on MoO₃-carbon-modified Supported on SiC And γ -Al₂O₃. *Applied Catalysis A, General*, 132(1), 77–96.
- Pinto, T., Arquilliere, P., Niccolai, G. P., Lefebvre, F., and Dufaud, V. (2015). The Comparison of Two Classes of Bifunctional SBA-15 Supported Platinum-heteropolyacid Catalysts for the Isomerization of *n*-hexane. *New Journal of Chemistry*, 39(7), 5300–5308.
- Polshettiwar, V., Cha, D., Zhang, X., and Basset, J. M. (2010). High-surface-area Silica Nanospheres (KCC-1) With A Fibrous Morphology. *Angewandte Chemie-International Edition*, 49(50), 9652–9656.
- Polshettiwar, V., Thivolle-Cazat, J., Taoufik, M., Stoffelbach, F., Norsic, S., and Basset, J. M. (2011). “Hydro-metathesis” of Olefins: A Catalytic Reaction Using a Bifunctional Single-site Tantalum Hydride Catalyst Supported on

- Fibrous Silica (KCC-1) Nanospheres. *Angewandte Chemie-International Edition*, 50(12), 2747–2751.
- Qureshi, Z. S., Sarawade, P. B., Albert, M., D'Elia, V., Hedhili, M. N., Köhler, K., and Basset, J. M. (2015). Palladium Nanoparticles Supported on Fibrous-Structured Silica Nanospheres (KCC-1): An Efficient and Selective Catalyst for the Transfer Hydrogenation of Alkenes. *ChemCatChem*, 7(4), 635–642.
- Regali, F., Liotta, L. F., Venezia, A. M., Boutonnet, M., and Järås, S. (2014). Hydroconversion of *n*-hexadecane on Pt/silica-alumina Catalysts: Effect of Metal Loading and Support Acidity on Bifunctional and Hydrogenolytic Activity. *Applied Catalysis A: General*, 469, 328–339.
- Ruslan, N. N., Fadzilillah, N. A., Karim, A. H., Jalil, A. A., and Triwahyono, S. (2011). IR Study of Active Sites for *n*-heptane Isomerization over MoO₃-ZrO₂. *Applied Catalysis A: General*, 406(1–2), 102–112.
- Ruslan, N. N., Triwahyono, S., Jalil, A. A., Timmiati, S. N., and Annuar, N. H. R. (2012). Study of the Interaction Between Hydrogen and The MoO₃-ZrO₂ Catalyst. *Applied Catalysis A: General*, 413–414, 176–182.
- Sakagami, H., Asano, Y., Takahashi, N., and Matsuda, T. (2005). H₂ Reduction of Hydrogen Molybdenum Bronze to Porous Molybdenum Oxide and Its Catalytic Properties for the Conversions of Pentane and Propan-2-ol. *Applied Catalysis A: General*, 284(1–2), 123–130.
- Sakagami, H., Ohno, T., Itoh, H., Li, Z., Takahashi, N., and Matsuda, T. (2014). Physical and Catalytic Properties of Pt/MoO₃ Reduced at Different H₂ Flow Rates. *Applied Catalysis A: General*, 470, 8–14.
- Sazegar, M. R., Jalil, A. A., Triwahyono, S., Mukti, R. R., Aziz, M., Aziz, M. A. A., Setiabudi, H. D., and Kamarudin, N. H. N. (2014). Protonation of Al-Grafted Mesoporous Silica Nanoparticles (MSN): Acidity and Catalytic Activity for Cumene Conversion. *Chemical Engineering Journal*, 240, 352–361.
- Scheithauer, M., Grasselli, R. K., and Knozinger, H. (1998). Genesis and Structure of WO_x/ZrO₂ Solid Acid Catalysts. *Langmuir*, 14(11), 3019–3029.
- Seo, G., and Ryoo, R. (1990). ³¹P, ²⁷Al, and ¹²⁹Xe NMR Study of Phosphorus-Impregnated HZSM-5 Zeolite Catalysts. *Journal of Catalysis*, 124(1), 224–230.
- Setiabudi, H. D., Jalil, A. A., Triwahyono, S., Kamarudin, N. H. N., and Jusoh, R. (2013). Ir/Pt-HZSM5 For *n*-pentane Isomerization: Effect of Si/Al Ratio and

- Reaction Optimization by Response Surface Methodology. *Chemical Engineering Journal*, 217, 300–309.
- Setiabudi, H. D., Jalil, A. A., Triwahyono, S., Kamarudin, N. H. N., and Mukti, R. R. (2012). IR Study of Iridium Bonded to Perturbed Silanol Groups of Pt-HZSM5 for *n*-Pentane Isomerization. *Applied Catalysis A: General*, 417–418, 190–199.
- Shen, S. C., and Kawi, S. (2003). Selective Catalytic Reduction of NO by Hydrocarbons in the Presence of Excess Oxygen using Pt/MCM-41 Catalysts. *Applied Catalysis B: Environmental*, 45(1), 63–76.
- Sidik, S. M., Jalil, A. A., Triwahyono, S., Abdullah, T. A. T., and Ripin, A. (2015). CO₂ Reforming of CH₄ over Ni/mesostructured Silica Nanoparticles (Ni/MSN). *RSC Advances*, 5(47), 37405–37414.
- Sigurdson, S., Sundaramurthy, V., Dalai, A. K., and Adjaye, J. (2008). Phosphorus Promoted Trimetallic NiMoW/ γ -Al₂O₃ Sulfide Catalysts in Gas Oil Hydrotreating. *Journal of Molecular Catalysis A: Chemical*, 291(1–2), 30–37.
- Sing, K. S. W., and Gregg, S. J. (1982). Adsorption, Surface area And Porosity. *Adsorption, Surface Area and Porosity*.
- Singh, A. K., Yadav, R., Sudarsan, V., Kishore, K., Upadhyayula, S., and Sakthivel, A. (2014). Mesoporous SAPO-5 (MESO-SAPO-5): A Potential Catalyst for Hydroisomerisation of 1-octene. *RSC Advances*, 4(17), 8727–8734.
- Singh, B., and Polshettiwar, V. (2016). Design of CO₂ Sorbents using Functionalized Fibrous Nanosilica (KCC-1): Insights Into the Effect of the Silica Morphology (KCC-1 vs. MCM-41). *Journal of Materials Chemistry A*, 4(18), 7005–7019.
- Singh, L. N., and Mishra, L. K. (2011). Study of BCS-BEC Crossover Physics and Evaluation of Energy Gap Parameters and Chemical Potential From BCS-Theory. *International Journal of Chemical Sciences*, 9(1).
- Stevens, R. W., Chuang, S. S. C., and Davis, B. H. (2003). In Situ Infrared Study of Pyridine Adsorption/desorption Dynamics over Sulfated Zirconia and Pt-promoted Sulfated Zirconia. *Applied Catalysis A: General*, 252(1), 57–74.
- Tanabe, K. (2012). *Solid Acids and Bases: Their Catalytic Properties*. Elsevier.
- Tanabe, K., and Yamaguchi, T. (1994). Acid-base Bifunctional Catalysis by ZrO₂ and Its Mixed Oxides. *Catalysis Today*, 20(2), 185–198.
- Taylor, R. J., and Petty, R. H. (1994). Selective Hydroisomerization of Long Chain Normal Paraffins. *Applied Catalysis A, General*, 119(1), 121–138.

- Thankamony, L., Sofia, A., Lion, C., Pourpoint, F., Singh, B., Perez Linde, A. J., Carnevale, D., Bodenhausen, G., Vezin, H., and Lafon, O. (2015). Insights Into the Catalytic Activity of Nitridated Fibrous Silica (KCC-1) Nanocatalysts from ^{15}N And ^{29}Si NMR Spectroscopy Enhanced by Dynamic Nuclear Polarization. *Angewandte Chemie International Edition*, 54(7), 2190–2193.
- Timmiati, S. N., Jalil, A. A., Triwahyono, S., Setiabudi, H. D., and Annuar, N. H. R. (2013). Formation of Acidic Brønsted $(\text{MoO}_x)^-(\text{H}_y)^+$ Evidenced by XRD and 2,6-lutidine FTIR Spectroscopy for Cumene Cracking. *Applied Catalysis A: General*, 459, 8–16.
- Tomishige, K., Okabe, A., and Fujimoto, K. (2000). Effect of Hydrogen on n-Butane Isomerization over $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ and $\text{Pt}/\text{SiO}_2 + \text{SO}_4^{2-}\text{-ZrO}_2$. *Applied Catalysis A-General*, 194, 383–393.
- Triwahyono, S., Jalil, A. A., and Hamdan, H. (2006). Isomerisation of Cyclohexane to Methylcyclopentane over $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ Catalyst. *Journal - The Institute of Engineers, Malaysia*, 67(1), 30–35.
- Triwahyono, S., Jalil, A. A., and Hattori, H. (2007). Study of Hydrogen Adsorption on $\text{Pt}/\text{WO}_3\text{-ZrO}_2$ Through Pt Sites, 16, 252–257.
- Triwahyono, S., Jalil, A. A., and Musthofa, M. (2010). Generation of Protonic Acid Sites from Pentane on the Surfaces of $\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$ and $\text{Zn}/\text{H-ZSM5}$ Evidenced by IR Study of Adsorbed Pyridine. *Applied Catalysis A: General*, 372(1), 90–93.
- Triwahyono, S., Jalil, A. A., Ruslan, N. N., Setiabudi, H. D., and Kamarudin, N. H. N. (2013). $\text{C}_5\text{-C}_7$ Linear Alkane Hydroisomerization over $\text{MoO}_3\text{-ZrO}_2$ and $\text{Pt}/\text{MoO}_3\text{-ZrO}_2$ Catalysts. *Journal of Catalysis*, 303, 50–59.
- Triwahyono, S., Yamada, T., and Hattori, H. (2003). Kinetic Study of Hydrogen Adsorption on $\text{Pt}/\text{WO}_3\text{-ZrO}_2$ and $\text{WO}_3\text{-ZrO}_2$. *Applied Catalysis A: General*, 250(1), 65–73.
- Valavarasu, G., and Sairam, B. (2013). Light Naphtha Isomerization Process: A Review. *Petroleum Science and Technology*, 31(6), 580–595.
- Vandegehuchte, B. D., Thybaut, J. W., Detavernier, C., Deduytsche, D., Dendooven, J., Martens, J. A., Sree, S. P., Korányi, T. I., and Marin, G. B. (2014). A Single-Event MicroKinetic Assessment of n-Alkane Hydroconversion on Ultrastable Y Zeolites After Atomic Layer Deposition of Alumina. *Journal of Catalysis*, 311, 433–446.

- Wang, B., Ding, G., Shang, Y., Lv, J., Wang, H., Wang, E., Li, Z., Ma, X., Qin, S., and Sun, Q. (2012). Effects of MoO₃ Loading and Calcination Temperature on The Activity of the Sulphur-Resistant Methanation Catalyst MoO₃/γ-Al₂O₃. *Applied Catalysis A: General*, 431–432, 144–150.
- Wang, Y. M., Wu, Z. Y., Wang, H. J., and Zhu, J. H. (2006). Fabrication of Metal Oxides Occluded in Ordered Mesoporous Hosts Via A Solid-state Grinding Route: The Influence of Host-guest Interactions. *Advanced Functional Materials*, 16(18), 2374–2386.
- Wehrer, P., Hilaire, L., and Petit, E. (2004). Influence of the Reduction Conditions of MoO₃ on Its Isomerizing Properties. *Applied Catalysis A: General*, 273(1–2), 249–258.
- Wehrer, P., Libs, S., and Hilaire, L. (2003). Isomerization of Alkanes and Alkenes on Molybdenum Oxides, 238, 69–84.
- Xu, R. R., Gao, Z., and Xu, Y. (1995). Progress in Zeolites Science-A China Perspective. World Scientific.
- Xue, N., Chen, X., Nie, L., Guo, X., Ding, W., Chen, Y., Gu, M., and Xie, Z. (2007). Understanding the Enhancement of Catalytic Performance for Olefin Cracking: Hydrothermally Stable Acids in P/HZSM-5. *Journal of Catalysis*, 248(1), 20–28.
- Xue, N., Olindo, R., and Lercher, J. A. (2010). Impact of Forming and Modification with Phosphoric Acid on the Acid Sites of HZSM-5. *Journal of Physical Chemistry C*, 114(37), 15763–15770.
- Yadav, G. D., and Nair, J. J. (1999). Sulfated Zirconia and Its Modified Versions as Promising Catalysts for Industrial Processes. *Microporous and Mesoporous Materials*, 33(1), 1–48.
- Yamaguchi, A., Jin, D., Ikeda, T., Sato, K., Hiyoshi, N., Hanaoka, T., Mizukami, F., and Shirai, M. (2014). P-ZSM-5 Pretreated by High-temperature Calcination as Durable Catalysts for Steam Cracking of *n*-Hexane. *Catalysis Letters*, 144(1), 44–49.
- Yang, P., Gai, S., and Lin, J. (2012). Functionalized Mesoporous Silica Materials for Controlled Drug Delivery. *Chemical Society Reviews*, 41(9), 3679–3698.
- Yang, Y., Gilbert, A., and Xu, C. (Charles). (2009). Hydrodeoxygenation of Bio-crude in Supercritical Hexane With Sulfided CoMo and CoMoP Catalysts Supported

- on MgO: A Model Compound Study using Phenol. *Applied Catalysis A: General*, 360(2), 242–249.
- Yori, J. C., and Parera, J. M. (1996). *n*-Butane Isomerization on Metal-Promoted Sulfated Zirconia. *Applied Catalysis A: General*, 147(1), 145–157.
- Yori, J. C., Pieck, C. L., and Parera, J. M. (2000). Alkane Isomerization on MoO₃/ZrO₂ Catalysts. *Catalysis Letters*, 64(2), 141–146.
- Yoshioka, C. M. N., Jordão, M. H., Zanchet, D., Garetto, T. F., and Cardoso, D. (2009). A New Activation Process of Bimetallic Catalysts and Application to the *n*-Hexane Isomerization. *Applied Catalysis A: General*, 355(1), 20–26.
- Zakharova, G. S., Täschner, C., Volkov, V. L., Hellmann, I., Klingeler, R., Leonhardt, A., and Büchner, B. (2007). MoO₃ Nanorods: Synthesis, Characterization and Magnetic Properties. *Solid State Sciences*, 9(11), 1028–1032.
- Zhang, C., Miranda, R., and Davis, B. H. (1994). Platinum-Sulfated-Zirconia. Infrared Study of Adsorbed Pyridine. *Catalysis Letters*, 29(3), 349–359.
- Zhao, B. Y., Xu, X. P., Ma, H. R., Sun, D. H., and Gao, J. M. (1997). Monolayer Dispersion of Oxides and Salts on Surface of ZrO₂ and Its Application in Preparation of ZrO₂-supported Catalysts with High Surface Areas. *Catalysis Letters*, 45(3), 237–244.
- Zhao, G., Teng, J., Xie, Z., Jin, W., Yang, W., Chen, Q., and Tang, Y. (2007). Effect of Phosphorus on HZSM-5 Catalyst for C₄-Olefin Cracking Reactions to Produce Propylene. *Journal of Catalysis*, 248(1), 29–37.
- Zhu, J., Wang, T., Xu, X., Xiao, P. and Li, J., 2013. Pt Nanoparticles Supported on SBA-15: Synthesis, Characterization and Applications in Heterogeneous Catalysis. *Applied Catalysis B: Environmental*, 130, 197-217.
- Zhuang, J., Ma, D., Yang, G., Yan, Z., Liu, X., Liu, X., Han, X., Bao, X., Xie, P., and Liu, Z. (2004). Solid-State MAS NMR Studies on the Hydrothermal Stability of the Zeolite Catalysts for Residual Oil Selective Catalytic Cracking. *Journal of Catalysis*, 228(1), 234–242.