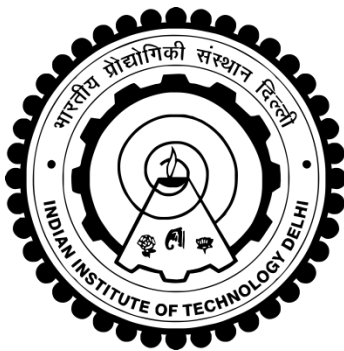


**PREPARATION AND CHARACTERIZATION OF MEDIUM
PORE MOLECULAR SIEVES FOR N-HEXADECANE
ISOMERIZATION**

SNEHALKUMAR PARMAR



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
SEPTEMBER 2015**

**PREPARATION AND CHARACTERIZATION OF MEDIUM
PORE MOLECULAR SIEVES FOR N-HEXADECANE
ISOMERIZATION**

by

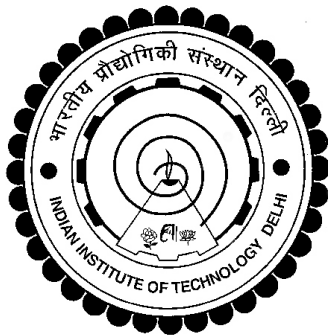
SNEHALKUMAR PARMAR

DEPARTMENT OF CHEMICAL ENGINEERING

*Submitted in fulfillment of
the requirements of the degree of*

DOCTOR OF PHILOSOPHY

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

SEPTEMBER 2015

Dedicated to

My Family

CERTIFICATE

This is to certify that the thesis entitled, “**PREPARATION AND CHARACTERIZATION OF MEDIUM PORE MOLECULAR SIEVES FOR N-HEXADECANE ISOMERIZATION**” being submitted by **Mr. Snehalkumar Parmar** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

Dr. K. K. Pant
Professor,
Department of Chemical Engineering,
Indian Institute of Technology Delhi,
New Delhi - 110016.

Dr. B. L. Newalkar
Chief Manager (R&D),
Corporate R&D Centre,
Bharat Petroleum Corporation Ltd.,
Greater Noida - 201306.

ACKNOWLEDGMENTS

First of all I would like to thank my supervisors, Dr. K. K. Pant, Professor, Department of Chemical Engineering and Dr. Bharat L. Newalkar, Chief Manager (R&D), Corporate R&D Centre, Bharat Petroleum Corporation Ltd., Greater Noida for their motivation, inspiration and keen interest throughout my research work. Since last four years, they have been my mentors and a huge source of inspiration. Despite of their busy schedules, they used to review my all the results, reports, journal papers and thesis progress, gave their valuable suggestions and made corrections. Without their unconditional support, the reported work wasn't so easy for me. It was a fortunate and unforgettable experience to work under their reflective and revered guidance. Their friendly natures and endless kindness can't be thanked adequately here.

I am highly thankful to R&D management of Bharat Petroleum Corporation Ltd. for the permission to carry out my Research work at Corporate R&D Centre, B.P.C.L., Greater Noida.

I am also thankful to Prof. S. Basu, Head, Chemical Engineering Department, for providing me permission to carry out my research work at Corporate R&D Centre, B.P.C.L., Greater Noida.

The encouragement, critical reviews and important suggestions given by Dr. Anupam Shukla, Dr. Sreedevi Upadhyayula and Prof. A. Ramanan throughout my research work are greatly acknowledged. I wish to convey my sincere thanks to Prof. Ratan Mohan, Prof. Shantanu Roy, Dr. Vivek Buwa, and Dr. V. M. Chariar (CRDT) for their encouragement and motivation towards the research work and helping me in many other works. I also wish to thank the other faculty members and office staff of the Department.

The acknowledgement is incomplete without recognition to Mr. Matthew John, Dr. Shivanand Pai, Mr. S. A. Kishore Kumar, Dr. Yogesh Niwate (presently at Reliance Industries Ltd., Mumbai), Mr. Sunil Mehla (presently at Hindustan Petroleum Corporation Ltd., Bangalore), Dr.

Mahesh Kasture, Ms. Sayanti Ghosh, Dr. Jitendra Satyarthi, Mr. Lalit Kumar, Mrs. Shalini Gupta, and last but not the least Dr. N. V. Choudary (presently at Hindustan Petroleum Corporation Ltd., Bangalore) as well as all the other Research Scientists and Management Staff of R&D Centre, Bharat Petroleum Corporation Ltd., Greater Noida.

My sincere thanks have highly extended for Mr. Ranjit Kumar Das and Mr. Chandan Jana for their unforgettable help in each and every aspect of my experimental work at R&D Centre, B.P.C.L., Greater Noida.

I am grateful to my friends and colleagues of IIT Delhi Dr. Pravakar Mohanty, Dr. Sachchit Majhi, Dr. Dinesh Kumar, Dr. Jay Pandey, Dr. Sushil Saraswat, Dr. Tarak Mondal, Dr. Jogender Singh, Dr. Garima Chauhan , Ms. Sonal, Mr. Rohit Kumar, Mr. Ritesh Mittal, Mr. Sonit Balayan, Mr. Kaushal R. Parmar, Mr. Abhijeet H. Thaker and Mr. Sourabh Mishra for their help and unconditional support during my research work. I am highly obliged to Mr. Krishan Kumar, Mr. Vishesh Kumar, and Mr. N. K. Gupta for their constant help in every possible way to carry forward my research work.

U.G. and P.G. students of Catalytic Reaction Engineering Laboratory, IIT Delhi viz. Mr. Rahul Gupta, Mr. Dinesh Yadav, Mrs. Madhumita Patel, Mr. Mohit Khatri, Mr. Tarun Krishna Jindal, Mr. Omkarram Ajgaonkar, Mr. Kantesh Malviya, Mr. Ayunachew Zewdu, Mr. Pavan Dhamne, Mr. Manas Mishra, Mr. Satish Kumar Yadav and others are highly acknowledged for their concern and support.

Very special friends like Hariom, Jay, Dinu, Manish, Abhijeet, Kaushal, Amit, and Hitesh with whom life at IIT Delhi Campus and Noida become so memorable.

Mr. Abhijeet H. Thaker, Mr. Kaushal R. Parmar and Mr. Tarak Mondal are highly acknowledged for their kind help in formatting of this thesis and plagiarism verification.

Very special thanks to Mr. Suchit Kumar Pal and Mr. Vijay Pal Singh for their constant support whenever required.

I am grateful to Petrotech Society of India and IIT Delhi for encouraging my research work and providing me financial assistantship.

I wish to thank Library management staff, IIT Delhi for providing all the necessary material (books, e-journals, e-books etc.) to carry forward my research work.

I have no words to express motivation and inspiration given by my father and mother to me, whose courage through their life have been a spiritual inspiration to me and holds no bounds. Their encouraging words and deeds through these tough physical and emotional times will always remain in my heart and soul. I am very much grateful to my better half ‘Niyanta’ for her constant encouragement, support, love and care throughout my research work. I am also thankful to my grandfather, aunty, sisters, brother in-law, cousins, in laws, aunties and uncles and my sweet nephew ‘Jay’ for their constant moral support during my studies.

Herewith I would like to thank all of those, who have directly or indirectly contributed to the realization of this thesis.

Last but not the least, a note of heartfelt devotion to almighty GOD, who has made me capable of accomplishing this acclivitous task.

(Snehalkumar Parmar)

ABSTRACT

With emergence of stringent environmental norms as well as demand for superior quality of transportation fuels leads to melioration in the cold flow properties of winter grade Diesel, Aviation Turbine Fuels (ATF), Lube Oil fractions and hydro processed biofuels viz. biodiesel and bio-ATF are being targeted, respectively. Typically, hydroisomerization of n-Hexadecane, which is a major constituent of Lube Oil, Diesel and ATF fraction, is performed over noble metal loaded medium pore zeolites having optimum metal to acid balance. Thus, it is important to understand the criticalities involved *w.r.t.* zeolite textural properties and acidity in designing the hydroisomerization catalyst to obtain biofuel based diesel fraction with desired cold flow properties with maximum yield and minimal cetane/viscosity loss. In this context, present work is targeted to illustrate parameters viz. acidity and crystallite size in designing the catalyst for hydroisomerization of long chain n-paraffins ($n\text{-C}_{10+}$) and brings out challenges and future needs *w.r.t.* yield improvement as well as minimal fuel property loss.

As a first step, Hydroisomerization of n-Hexadecane has been investigated over ZSM-22 framework by varying bulk molar Si/Al ratio in the range of 30 to 90 at constant Platinum loading of about 0.45 wt%. Thus, ZSM-22 samples have been synthesized and characterized with respect to their crystallinity, textural parameters, and total acidity by means of X-ray diffraction, nitrogen adsorption desorption isotherm measurement at 77 K and temperature programmed desorption of ammonia technique, respectively. The effect of hydroisomerization reaction parameters namely temperature and weight hourly space velocity (WHSV) on n-hexadecane isomer selectivity and yield has been investigated. The optimal results over prepared catalysts demonstrated the best possible performance over ZSM-22 framework with bulk molar Si/Al ratio of 45 wherein maximum isomer selectivity and yield (82.7 and 74.8%, respectively) have been

achieved at conversion level of about 90% at 578 K. Based on the obtained results, the possible advantages of using ZSM-22 (bulk molar Si/Al $\sim$ 45) framework cold flow property improvement of long chain n-paraffins have been envisaged.

Then, ZSM-22 framework with bulk molar Si/Al ratio of 45 is synthesized by employing three different types of silica sources viz. colloidal silica (Ludox AS-40) , tetraethylorthosilicate (TEOS), fumed silica (CAB-O-SIL), respectively. The ZSM-22 samples thus obtained have been characterized in terms of crystallinity, morphology, crystal size, textural properties (external surface area), and acidity, respectively. The performance of the formed extrudates (0.5 wt% Pt over zeolite) has been judged in terms of their activity, selectivity and product distribution for the n-hexadecane hydroisomerization. Among the samples evaluated, catalyst based on ZSM-22 sample, obtained using colloidal silica as silica source, demonstrated the highest isomer selectivity ($\sim$ 83.7 %) and yield ($\sim$ 74.8 %) at 90% conversion level owing to its smaller crystallite size and higher external surface area.

Finally, Effect of tailoring the Brønsted acid sites was verified by ion-exchange with Group-II elements (i.e. Mg, Ca & Ba). The framework acidity w.r.t. Brønsted level was characterized and estimated using ammonia temperature programmed desorption (NH₃-TPD) and Fourier transform infrared spectroscopy of Pyridine (Py-FTIR) as a function of temperature, respectively. Hydroisomerization of n-hexadecane is performed over Pt ($\sim$ 0.5 wt %) /M-H-ZSM-22 samples (in extrudate form) in an up-flow fixed bed reactor and the effect of process parameters namely temperature and WHSV have been investigated. Based on the obtained results, Pt/Ca-H-ZSM-22 framework with calcium exchange level of about 10 % showed the optimum performance among all the prepared samples with maximum isomer selectivity, yield (85.8 and 77.8%, respectively) vis-à-vis Pt/H-ZSM-22 sample (79.3 and 70.5 %, respectively)

and more importantly branching index of 4 in favor of mono-branched isomers, at a conversion level of about 90% at 585 K.

In the same manner, another type of molecular sieve named ZSM-12 (MTW framework) was synthesized and characterized for hydroisomerization of n-Hexadecane. The framework Brønsted acidity is tailored with group II elements (M) viz. Ca, Ba and Mg, by means of ion-exchange method. Pt/Ba-H-ZSM-12 with tailored Brønsted acidity in the range of about 25% demonstrated the optimum performance among all the catalysts with an increased isomer selectivity and yield (89.2 and 80.3%, respectively) by about 4 wt% at a conversion level of about 90% vis-à-vis Pt/H-ZSM-12 framework at 568 K. Based on the obtained trend, the potential benefits of implementation of Pt/Ba-H-ZSM-12 (bulk molar ratio Si/Al $\sim$ 60) framework for cold flow property improvement of 'bio-ATF' have been envisaged.

TABLE OF CONTENTS

	Page No.
Certificate	i
Acknowledgments	ii
Abstract	v
List of Figures	xii
List of Tables	xvi
Nomenclature	xx
 CHAPTER 1: INTRODUCTION	 1
1.1 Objective of the Present work	19
1.2 Structure of the Thesis	20
 CHAPTER 2: LITERATURE REVIEW	 21
2.1. Hydroisomerization of paraffins and process chemistry	22
2.2. Hydroisomerization catalysts for heavy paraffins isomerization	22
2.2.1 Zeolites (ZSM-22, ZSM-23, ZSM-48, Mordenite, β)	25
2.2.1.1 Pore-mouth / Key-lock catalysis	28
2.2.1.2 Key factors influencing pore mouth / key lock catalysis	30
2.2.2 Silicoaluminophosphate molecular sieve (SAPO-11, SAPO- 31)	34
2.2.3 Mesoporous Materials (MCM-41, Al-MCM-41, Al-SBA-15)	36
2.2.4 Mixture of Oxides ($\text{ZrO}_2/\text{SO}_4^{2-}$)	37

2.2.5	Commercial catalysts	39
2.3.	Effect of crystallite size and its tailoring on isomerization of paraffins	40
2.3.1.	Conventional hydrothermal methods	43
2.3.1.1	Effect of crystallization conditions	43
2.3.1.2	Effect of synthesis gel composition	46
2.3.2.	Non-conventional methods for the synthesis of small crystal zeolites	48
2.3.2.1	Use of crystal growth inhibitors	49
2.3.2.2	Confined space synthesis	51
2.4.	Effect of Tailoring of acidity	51
2.4.1.	Tailoring of acidity through framework Si/Al ratio	52
2.4.2	Ion-exchange: Exchanging with alkali and alkaline earth metals	53
2.4.3	Acidity control through Silylation and dealumination	54
2.5.	Gaps identified from the literature	56
CHAPTER 3: EXPERIMENTAL DETAILS		58
3.1.	Synthesis of Zeolites	59
3.2.	Preparation of hydroisomerization catalysts	60
3.3.	Characterization techniques	63
3.4	Hydroisomerization of n-Hexadecane	65

CHAPTER 4: RESULTS AND DISCUSSION	68
4.1. Effect of tuning Si/Al ratio of H-ZSM-22 for n-Hexadecane hydroisomerization	69
4.1.1. Synthesis and characterization of ZSM-22	69
4.1.2. Hydroisomerization of n-hexadecane	82
4.1.2.1 Effect of Temperature	82
4.1.2.2 Effect of WHSV	86
4.1.2.3 Product distribution at constant conversion level for all the catalysts	88
4.1.3. Summary	90
4.2. Effect of silica source of H-ZSM-22 for n-Hexadecane hydroisomerization	90
4.2.1 Synthesis and characterization of ZSM-22	90
4.2.2 Hydroisomerization of n-Hexadecane	101
4.2.3 Summary	107
4.3. Effect of divalent cation exchange on H-ZSM-22 for n-Hexadecane hydroisomerization	107
4.3.1. Synthesis, modification and characterization of ZSM-22	108
4.3.2. Hydroisomerization of n-hexadecane	114
4.3.2.1 Effect of temperature	114
4.3.2.2 Effect of WHSV	120
4.3.3. Summary	123
4.4. Effect of divalent cation exchange over H-ZSM-12 for	124

hydroisomerization of n-Hexadecane	
4.4.1. Synthesis, modification and characterization of ZSM-12	124
4.4.2. Hydroisomerization of n-hexadecane	132
4.4.3 Summary	144
4.5. Kinetic modeling	144
4.5.1. Detailed kinetics	144
4.5.2. Lumped kinetics	150
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS	155
5.1. Conclusions	156
5.2. Recommendations	158
REFERENCES	159
APPENDICES	

LIST OF FIGURES

Fig. No.	Title	Page No
Fig. 1.1	Schematic flow diagram of a modern refinery	6
Fig. 1.2	Block diagram of the process for the production of lube oils during 1950s.	10
Fig. 1.3	Modified block diagram of the process for the production of lube oils during 1950s.	10
Fig. 1.4	Block diagram of the process for the production of lube oils during 1970s.	10
Fig. 1.5	Block diagram of the process for the production of lube oils during 1990s.	11
Fig. 2.1	Pathways for hydroisomerization of long chain n-alkane	24
Fig. 2.2	Pore geometry of (a) TON (b) MTT (c) AEL (d) MTW	27
Fig. 2.3	Schematic representation of various orientations of long chain paraffin for pore mouth catalysis	28
Fig. 2.4	Schematic representation of key-lock mechanism	29
Fig. 3.1	Synthesis of ZSM-22	60
Fig. 3.2	Synthesis of ZSM-12	61
Fig. 3.3	Typical procedure for the preparation of the catalyst	62
Fig. 3.4	Reactor set-up utilized for hydroisomerization of n-Hexadecane	66
Fig. 4.1	X-ray diffraction patterns of as-synthesized ZSM-22 with	69

	different bulk molar Si/Al ratio	
Fig. 4.2	Si NMR of (a) CAT-1 (Si/Al ~ 30) (b) CAT-2 (Si/Al ~ 45) (c) CAT-3 (Si/Al ~ 60) (d) CAT-4 (Si/Al ~ 90).	73
Fig. 4.3	Al MAS-NMR of (a) CAT-1 (Si/Al ~ 30) (b) CAT-2 (Si/Al ~ 60) (c) CAT-3 (Si/Al ~ 60) (d) CAT-4 (Si/Al ~ 90)	75
Fig. 4.4	NH ₃ -TPD of H-ZSM-22 having bulk molar Si/Al (a) 30, (b) 45, (c) 60, (d) 90	80
Fig. 4.5	Scanning Electron Micrograph of ZSM-22 samples having bulk molar Si/Al (a) 30, (b) 45, (c) 60 and (d) 90	81
Fig. 4.6	FT-IR spectra of different zeolite samples	82
Fig. 4.7	Effect of temperature variation on the conversion, selectivity & yield at WHSV = 1.1 g of n-Hexadecane / g of catalyst hr, H ₂ /HC = 10.9, p = 60 bar (a) CAT-1(Si/Al= 30) (b) CAT-2 (Si/Al=45), (c) CAT-3 (Si/Al=60) and (d) CAT-4 (Si/Al=90)	84
Fig. 4.8	Effect of WHSV variation on the conversion, selectivity & yield at H ₂ /HC = 10.9, p = 60 bar (a) CAT-1(Si/Al= 30 & T= 593 K) (b) CAT-2 (Si/Al=45 & T= 578 K), (c) CAT-3 (Si/Al=60 & T= 603 K) and (d) CAT-4 (Si/Al=90 & T= 623 K)	87
Fig. 4.9	Product distribution over various catalysts at constant conversion levels (~90%)	89
Fig. 4.10	Product distribution pattern for various catalysts at	89

	constant conversion levels (~90%)	
Fig. 4.11	XRD patterns of ZSM-22 (a) Colloidal Silica (b) TEOS (c) Fumed silica	93
Fig. 4.12	SEM of various ZSM-22 samples (a) CAT-5 (Colloidal Silica) (b) CAT-6 (TEOS) (c) CAT-7 (Fumed Silica)	95
Fig. 4.13	FT-IR spectra of pyridine adsorbed on various H-ZSM-22 zeolite samples (a) CAT-5 (Colloidal Silica) (b) CAT-6 (TEOS) (c) CAT-7 (Fumed Silica)	99
Fig. 4.14	Conversion, Selectivity & Yield as a function of temperature (WHSV = 1.1 g of n-Hexadecane / g of catalyst hr, $H_2/HC = 10.9$, $p = 60$ bar) (a) CAT-5 (b) CAT-6 (c) CAT-7	104
Fig. 4.15	Conversion, Selectivity & Yield as a function of WHSV ($H_2/HC = 10.9$, $p = 60$ bar) (a) CAT-5 ($T = 578$ K) (b) CAT-6 ($T = 583$ K) (c) CAT-7 ($T = 580$ K)	106
Fig. 4.16	Distribution of multi and mono branched isomers obtained for various catalysts at constant conversion levels (WHSV = 1.1 hr^{-1})	106
Fig. 4.17	X-ray diffraction patterns of (a) H-ZSM-22 (b) Ca-H-ZSM-22 (c) Ba-H-ZSM-22 (d) Mg-H-ZSM-22	109
Fig. 4.18	NH_3 -TPD spectra of (a) H-ZSM-22 (b) Ca-H-ZSM-22 (c) Ba-H-ZSM-22 (d) Mg-H-ZSM-22	111
Fig. 4.19	FT-IR spectra of (I) H-ZSM-22 (Base sample) (II) Ca-H-	116

	ZSM-22 (III) Ba-H-ZSM-22 (IV) Mg-H-ZSM-22	
Fig. 4.20	Conversion, Selectivity & Yield as a function of temperature (WHSV = 1.1 g of n-Hexadecane / g of catalyst hr, H ₂ /HC = 10.9, p = 60 bar) (a) CAT-8 (b) CAT-9 (c) CAT-10 (d) CAT-11	120
Fig. 4.21	Conversion, Selectivity & Yield as a function of temperature (H ₂ /HC = 10.9, p = 60 bar) (a) CAT-8 (b) CAT-9 (c) CAT-10 (d) CAT-11	122
Fig. 4.22	Distribution of multi and mono branched isomers obtained for various catalysts at constant conversion levels	123
Fig. 4.23	X-ray diffraction pattern of as-synthesized ZSM-12 phase	125
Fig. 4.24	SEM image of H-ZSM-12 crystallites	126
Fig. 4.25	NH ₃ -TPD spectra of (a) H-ZSM-12 (b) H-Ba-ZSM-12 (c) H-Ba-ZSM-12 (Higher degree of exchange) (d) H-Ca-ZSM-12 (e) H-Ca-ZSM-12 (Higher degree of exchange) (f) H-Mg-ZSM-12 (g) H-Mg-ZSM-12	128
Fig. 4.26	FT-IR spectra of [a] H-ZSM-12 (Base sample) at (a) 120 °C (b) 250 °C (c) 450 °C [b] Ba-H-ZSM-12 at (a) 120 °C (b) 250 °C (c) 450 °C [c] Ba-H-ZSM-12 (Higher Degree of exchange) at (a) 120 °C (b) 250 °C (c) 450 °C [d] Ca-H-ZSM-12 at (a) 120 °C (b) 250 °C (c) 450 °C [e] Ca-H-ZSM-12 (Higher degree of exchange) at (a) 120 °C (b) 250 °C (c) 450 °C [f] Mg-H-ZSM-12 at (a) 120 °C (b) 250 °C	132

	(c) 450 °C [g] Mg-H-ZSM-12 (Higher degree of exchange) at (a) 120 °C (b) 250 °C (c) 450 °C	
Fig. 4.27	Conversion, Selectivity & Yield as a function of temperature (WHSV = 1.1 g of n-Hexadecane / g of catalyst hr, H ₂ /HC = 10.9, p = 60 bar) (a) CAT-12 (b) CAT-13 (c) CAT-14 (d) CAT-15 (e) CAT-16 (f) CAT-17 (g) CAT-18	139
Fig. 4.28	Conversion, Selectivity & Yield as a function of temperature (H ₂ /HC = 10.9, p = 60 bar) (a) CAT-12 (T = 568 K) (b) CAT-13 (T = 568 K) (c) CAT-14 (T = 575 K) (d) CAT-15 (T = 573 K) (e) CAT-16 (T = 577 K) (f) CAT- 17 (T = 583 K) (g) CAT-18.(T = 585 K)	142
Fig. 4.29	Distribution of multi and mono branched isomers obtained for various catalysts at constant conversion levels (~ 90%) (p=60 bars, WHSV = 1.1 hr ⁻¹)	143
Fig. 4.30	Typical mechanism for hydroisomerization reaction over bifunctional catalyst	145
Fig. 4.31	Reaction scheme for n-Hexadecane hydroisomerization	151
Fig. 4.32	Comparison of concentration profile, molar yield of mono- , multibranched isomers and cracked products at 583 K for (a) CAT-8 (Pt/H-ZSM-22) (b) CAT-9 (Pt/Ca-H-ZSM-22)	154

LIST OF TABLES

Table No.	Title	Page No
1.1	Gasoline Fuel Specifications	2
1.2	Diesel Fuel Specifications	3
1.3	Research Octane Numbers (RON) of various paraffins and isoparaffins	8
2.1	Hydroisomerization of n-Dodecane over Pt/HZSM-22 (base as well as modified with NH_4^+ ion-exchange, treatment with HNO_3 and $(\text{NH}_4)_2\text{SiF}_6$)	32
2.2	Hydroisomerization of n-Hexadecane over various catalysts	33
2.3	Hydroisomerization of n-Hexadecane over MTEABr, BTMACl and TEABr templated Pt/H-ZSM-	34
2.4	Hydroisomerization of n-decane over Pt, Pd, and Pt-Pd/Al-MCM-41 catalysts	38
2.5	Hydroisomerization of n-C ₁₆ over Pt (0.5 wt%)/SO ₄ /ZrO ₂ and Pt (0.5 wt%)/WO ₃ /ZrO ₂ (6.5 wt% W)	38
2.6	Various catalyst systems reported for hydroisomerization of heavy paraffins in the literature	41
2.7	Effect of crystallite size on external surface area of nanosilicalite-1	40
2.8	Effect of crystallization temperature on crystallite size of CHA type zeolite	44
2.9	Effect of dilution on ZSM-5 crystal size	47

2.10	Hydroisomerization of n-hexadecane over normal and nano-form of Pt/SAPO-11	49
2.11	Role of Si/Al ratio on activity of the catalyst for n-hexadecane hydroisomerization	53
2.12	Conversion and selectivity of hydroisomerization of n-C ₁₆ over modified and non-modified MTT based catalysts	55
2.13	Hydroisomerization of n-decane over un-modified and modified MTT based catalysts	55
4.1	Textural properties of H-ZSM-22 with different Si/Al ratio	70
4.2	Physico-chemical characteristics for prepared Pt/ZSM-22 catalyst samples: Pt content and its dispersion (D) estimated by H ₂ chemisorption	76
4.3	Total acidity measured by NH ₃ -TPD for H-ZSM-22 with different Si/Al ratio	78
4.4	Textural properties of H-ZSM-22 synthesized using various silica sources	93
4.5	Total acidity of H-ZSM-22 synthesized using various silica sources obtained by NH ₃ -TPD	97
4.6	Comparison of Brønsted and Lewis acid sites determined by Pyridine adsorbed FT-IR spectra of H-ZSM-22 zeolite samples	97
4.7	Estimation of Platinum and its dispersion determined by ICP and H ₂ chemisorption techniques for various ZSM-22 based catalysts	98
4.8	Textural parameters of M-H-ZSM-22 sample	108

4.9	Estimation of metal content, total acidity and its distribution for M-H-ZSM-22 samples determined by ICP, NH ₃ -TPD and Py-FTIR methods	112
4.10	Pt content and dispersion for different catalyst samples	114
4.11	Comparison catalyst performance with reported literature data for hydroisomerization of n-paraffin	124
4.12	Textural properties of H-M-ZSM-12 samples	127
4.13	Estimation of metal content, total acidity and its distribution for H-M-ZSM-12 samples determined by ICP, NH ₃ -TPD and NH ₃ -FTIR methods	133
4.14	Pt content and dispersion for various H-M-ZSM-12 catalyst formulations	133
4.15	Comparison catalyst performance with reported literature data for hydroisomerization of n-paraffin	143
4.16	Rate constant (k) and TOF values for n-Hexadecane hydroisomerization over CAT-8 (Pt/H-ZSM-22) and CAT-9 (Pt/Ca-H-ZSM-22)	153

NOMENCLATURE

d	distance between crystal planes, XRD, Å
F	molar flow rate of feed, mol s ⁻¹
P	operating pressure, atm
P_i	partial pressure of component i, atm
r_i	rate of reaction of component i, mol m ² s ⁻¹
S_{BET}	surface area of catalyst, m ² g _{cat} ⁻¹
V_{pore}	pore volume, cm ³ g ⁻¹
W	mass of catalyst, kg
F_{obj}	objective function
r_i	reaction rate, kmol/kg _{cat} .h
R	constant of ideal gas, 8.314 J/mol K
T	temperature, °C/K
k	reaction rate constant, s ⁻¹
n	reaction order

Greek letters

κ	X-ray wavelength
φ	constant in XRD
θ	radiation angle
β	peak width at half height

Subscripts

i, i+1 branching degrees

Superscripts

' species adsorbed on active site

Acronyms

ATF	Aviation Turbine Fuel
BTMACl	Benzyl Tri Methyl Ammonium Chloride
BET	Brunauer-Emmett-Teller
FT-IR	Fourier Transform Infra-Red Spectroscopy
FID	Flame Ionization Detector
MTEABr	Methyl Tri Ethyl Ammonium Bromide
MTW	Mobil Twelve
MTT	Mobil Twenty Three
IZA	International Zeolite Association
RDS	Rate Determining Step
RON	Research Octane Number
SAPO	Silica Alumino Phosphate
SEM	Scanning Electron Microscopy
STP	Standard Temperature and Pressure
TCD	Thermal Conductivity Detector
TEABr	Tetra Ethyl Ammonium Bromide

TGA	Thermal Gravimetric Analysis
TON	Theta One
TPD	Temperature Programmed Desorption
VGO	Vacuum Gas Oil
XRD	X-ray Diffraction
ZSM	Zeolite Socony Mobil