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

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DEPARTMENT OF CHEMICAL ENGINEERING
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by

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DEPARTMENT OF CHEMICAL ENGINEERING

Submitted in fulfillment of
the requirements of the degree of

DOCTOR OF PHILOSOPHY

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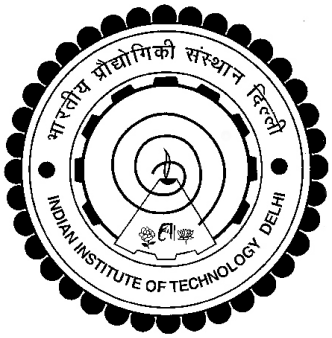

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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.

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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-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 ~ 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 (~ 83.7 %) and yield (~ 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 (NH_3-TPD) and Fourier transform infrared spectroscopy of Pyridine (Py-FTIR) as a function of temperature, respectively. Hydroisomerization of n-hexadecane is performed over Pt (~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 ~ 60) framework for cold flow property improvement of 'bio-ATF' have been envisaged.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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, $^oC/K$
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