Olefin skeletal isomerization of *n*-butene, *n*-hexene and *n*-octene using alumina-based catalysts

by

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Abbreviations

AC	After calcination
Al	Aluminium
Al_2O_3/ SiO_2	Aluminium oxide to silica oxide
AlO (OH)	Boehmite
AlOH	Aluminium hydroxide
Å	Angstroms
Atm	Atmosphere/Atmospheric
Aux	Auxiliary
B	Boron
BET	Brunauer, Emmett and Teller
β-scission	Beta-scission
C	Cracks
Ca	Calcium
Cat/CAT	Catalyst
cm	Centimetre
cm^{-1}	Reciprocal centimetre
cm^3/g	Cubic centimetre to gram
CO	Carbon monoxide
CoAPO	Cobalt supported aluminophosphate
CFR	Cooperative Fuel Research
$C_{(s)}$	Solid coke
°C	Degree Celcius
°C/min	Degree Celcius per minute
D	Dimerize
Dim.	Dimension
dp	Particle size
DRIFT	Diffuse Reflectance Infrared Fourier Transform
DV	Dual View
e.g.	exempli gratia *for example*
EN	European National
et al.	et alibi *and elsewhere*
η – Al2O3	Eta-alumina
ETBE	Ethyl Tertiary Butyl Ether
etc.	et cetera *and so forth*
FCC	Fluid Catalytic Cracker
Fe	Iron
FID	Flame Ionization Detector
FT	Fischer–Tropsch
g	Gram
Ga	Gallium
GC	Gas Chromatography
GC-FID	Gas Chromatography – Flame Ionization Detector
GC-MS	Gas Chromatography – Mass Spectrometer
GC-RGA	Gas Chromatography – Refinery Gas Analysis
H^-	Hydride
h^{-1}	Reciprocal hour

H_2	Hydrogen
H_2O	Water
He	Helium
H_o	Indicates acid strength
HC	Hydrocarbons
HPLC	High Performance Liquid Chromatography
HTFT	High-Temperature Fischer-Tropsch
I	Isomerization
ICP	Inductively Coupled Plasma Analysis
i.e.	Id est *for that is*
i-Paraffins	*Iso*-Paraffins
K	Kelvin
K	Potassium
kg	Kilogram
kPa	Kilopascal
L/Dp	Length to particle size ratio
L/h	Litres per hour
LHSV	Liquid Hour Space Velocity
LPG	Liquefied petroleum gas
LTFT	Low-Temperature Fischer-Tropsch
Mass %	Mass percentage
max.	Maximum
m^2/g	Square meter per gram
MCT	Mercury Cadmium Telluride
MFI	Mordenite framework inverted
mg	Milligram
Mg	Magnesium
MgAPSO	Magnesium supported silicoaluminophosphate
Mg/kg	Milligram per kilogram
min.	Minimum
min	Minute
ml	Millilitre
ml/min	Millilitre per minute
mm	Millimetre
mmol	Milli-mole
MnAPO	Manganese supported aluminophosphate
Mo	Molybdenum
Mol %	Mole percentage
MON	Motor Octane Number
MPa	Mega Pascal
MS	Mass Spectrometer
MSD	Mass Spectrometer Detector
MSDS	Material Safety Data Sheets
MTBE	Methyl Tertiary Butyl Ether
N_2	Nitrogen
Na	Sodium
NH_3	Ammonia
Ni	Nickel
nm	Nanometer
NOx	Nitrogen Oxides
n-Paraffins	Normal Paraffins
NRTL	Non Random To Liquid
NV	Needle valve

O_2	Oxygen
OH	Hydroxide
OMe	Ether
P	Phosphorus
PI	Pressure Indicator
ppm m/m	parts per million mass to mass
PSRK	Predictive Redich-Kwong-Soave
Pt	Platinum
PV	Pore Volume
%	Percent
R	Alkyl group
R16	Reactor 16
RGA	Refinery Gas Analysis
RON	Research Octane Number
Rpm	Revolution per minute
RVP	Reid vapour pressure
rxn	Reaction
S/SL	Split/Splitless
SA	Surface Area
SAPO	Silicoaluminophosphate
SAPIA	South African Petroleum Industry Association
SA/V	Surface Area to Volume Ratio
Si	Silica
Si/Al	Silica to Alumina Ratio
SiC	Silicon Carbide
SiO_2/B_2O_3	Silica oxide to boron oxide
SiO_2/Al_2O_3	Silica oxide to aluminium oxide
SLO	Stabilised Light Oil
SPA	Solid Phosphoric Acid
STP	Standard Temperature and Pressure
TAEE	Tertiary Amyl Ethyl Ether
TAME	Tertiary Amyl Methyl Ether
TCD	Thermal Conductivity Detector
Temp.	Temperature
TGA	Thermal Gravimetric Analysis
Θ- Al_2O_3	Theta alumina
TMP	Trimethylphosphite
TPD	Temperature Programmed Desorption
µl	Micro-litres
µm	Micro-meter
µmole	Micro-mole
U.O.P	Universal Oil Products
US	United States
USA	United States of America
V	Valve
VICI	Valco Instruments Corporation Incorporated
vol%	Volume Percent
WHSV	Weight Hourly Space Velocity
Wt%	Weight percentage
XRD	X-Ray Diffraction Analysis

γ -Al_2O_3	Gamma-Alumina
Zn	Zinc
ZnS	Zinc sulphide
Zn/SAPO	Zinc supported Silicoaluminophosphate
ZSM	Zeolite Socony Mobil

Abstract

Stringent standards to improve air quality and to protect human health are continuously implemented due to the environmental impact of auto emissions. As a result, researching options for alternative components or alternative processes are very important to continuously improve the octane number in the fuel pool.

Therefore, by exploiting the high olefin (butene, hexene and octene) content part of the feedstocks, the overall aim of this study was to obtain olefin skeletal isomerization for the improvement of the RON in the refinery fuel pool. The influence of temperature variation (350 °C, 400 °C and 450 °C) on the performance of the different alumina catalysts (eta (η)-alumina, H-ZSM-5 and silicated alumina) was investigated. All experiments were performed using a fixed bed reactor at atmospheric pressure and a constant weight hourly space velocity of 5 h^{-1}. The effect of the different conditions and additions on conversion and selectivity was determined.

Eta alumina and the silicated alumina (Siralox 40) were proved to be the catalysts that were most prone to cause skeletal isomerization when in contact with longer carbon chains. Butene did not isomerize to a significant extent when contacted over either Eta alumina or Siralox 40. In the case of the zeolite catalyst (ZSM-5), none of the feeds isomerized and it was speculated that it could have been due to the high activity of ZSM-5 which made this catalyst more likely to cause side reactions rather than the preferred skeletal isomerization reaction.

Opsomming

As gevolg van die omgewingsimpak van voertuiguitlaatgasse word strenger brandstofstandaarde deurgaans ingestel om lugkwaliteit te verbeter en gesondheid te beskerm. Navorsing spruit uit die strenger ingestelde standaarde om alternatiewe opsies aan die besigheidseenhede te bied. Hierdie alternatiewe sluit moontlike veranderinge in voerstroom komposisie in. Navorsing word gebou op die omskakeling van komponente na ander funksionele groepe in die voerstroom.

Die vooragfaande alternatief word beklemtoon vir die omskakeling van sekere lae oktaan voerstroom komponente na hoë oktaan komponente vir die verkryging van oktaan getal in die totale brandstof opbrengs vanuit die raffinadery. Die oorkoepelende tema vir hierdie studie is; olefien isomerisasie van buteen, hekseen en okteen. Die teenwoordigheid van die komponente in die geselekteerde geraffineerde produkte word geteiken waar omskakeling bewerkstellig word vir die verkryging van hoë oktaan komponente. Alle eksperimente is uitgevoer deur gebruik te maak van 'n statiese bed reaktor by atmosferiese druk en 'n konstante reagens voer snelheid van 5 h^{-1}. Die invloed van temperatuur verandering (350 ° C, 400 ° C en 450 ° C) op die verskillende alumina kataliste (eta (η)-alumina, H-ZSM-5 en silicated alumina), insluitend selektiwiteit en omskakeling van die verskillende kataliste was ondersoek.

Eta alumina en die silika alumina (Siralox 40) het getoon vanuit die eksperimentele resultate, die katalisators wat die meeste geneig was tot skeletale isomerisasie wanneer in kontak met langer koolstofkettings. Buteen het tot ‘n groot mate nie ge-isomeriseer wanneer dit in kontak was met Eta alumina en Siralox 40 nie. In die geval van die zeoliet katalisator (ZSM-5), het nie een van die voere ge-isomeriseer nie en die hipotese wat gedeeltelik aanspreeklik vir die bevinding aangevoer kan word is dat ZSM-5 ‘n hoë aktiwiteit onder beryfskondisies het en dus meer geneig was om newe-reaksies eerder as skeletale isomerisasie teweeg te bring.

Acknowledgements

When I started with my literature study I felt like I threw myself into deep waters and felt stupid from time to time, just wondering how to make sense of everything you read and how to place everything into perspective. I read an article written by Martin A. Schwartz in which he explained the importance of stupidity in scientific research. By reading this article I started feeling more relaxed and realised that what he stated was so true: He said that the more at ease we become with being stupid, the deeper we will paddle into the unknown and the more likely we are to make big discoveries.

Although I haven't made any big discoveries yet, I am very proud and can say with peace of mind that I have successfully completed this study. Saying this I want to acknowledge and thank all the people who played a role in this thesis, whether it was big or small; it most certainly helped me a great deal.

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I would like to dedicate this dissertation to my lifelong companion and great husband;

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This is small and it is little, but it is mine