

HYDROALKYLATION OF BENZENE: A STEP TOWARDS REFINERY PETROCHEMICAL INTEGRATION

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**DEPARTMENT OF CHEMICAL ENGINEERING
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by

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DEPARTMENT OF CHEMICAL ENGINEERING

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CERTIFICATE

This is to certify that the thesis entitled, “**Hydroalkylation of Benzene: A Step Towards Refinery Petrochemical Integration**” being submitted by **Mr. S A Kishore Kumar** to the **Indian Institute of Technology, New Delhi** for the award of **Doctor of Philosophy** is a bonafide record of original research work carried out by him under our guidance and supervision in conformity with the rules and regulations of the Institute. The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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(S A Kishore Kumar)

Abstract

Benzene is a known carcinogen and can cause serious health and environmental effects. EPA (Environmental Protection Agency) is constantly reducing the limit of benzene content in gasoline due to its health effects. To meet the EPA regulations, most refiners are saturating benzene in gasoline to cyclohexane. Benzene saturation not only consumes useful hydrogen but also leads to considerable octane loss for gasoline stream. In view of this, refiners are forced to explore alternate ways to valorize the benzene produced in the refinery. Cyclohexylbenzene (CHB) is a versatile chemical with numerous industrial applications. It is used as electrolytic additive in lithium ion batteries, liquid crystal displays and as non-carcinogenic fuel blending additive. Furthermore CHB is also excellent precursor for production of petrochemical intermediates like phenol cyclohexanone and biphenyl. Thus, converting benzene to CHB is more profitable option in view of the numerous benefits of CHB. This research is focused on development of a highly selective, stable and cost effective catalyst for hydroalkylation of benzene to CHB. This study also reports green route for the preparation of CHB avoiding the traditional two step alkylation of benzene and cyclohexene, using hazardous acid catalysts such as sulfuric acid and aluminium chloride. Theoretical understanding along with experimental studies on the effect of different physical and chemical properties of the catalyst on the hydroalkylation activity and selectivity is vital for designing efficient and cost effective hydroalkylation catalyst. Present study is attempted to evaluate hydroalkylation activity of different metal supported zeolites and discuss the results in terms of the effect of catalyst properties like zeolite acidity, zeolite pore structure, type and amount of metal and acid to metal ratio of the catalyst on the catalytic activity and CHB selectivity. Thus platinum, palladium, ruthenium and nickel modified zeolites (ZSM-5, ZSM-12, MOR, MCM-22, Y and Beta) were prepared and tested for hydroalkylation of benzene using fixed bed reactor at various operating conditions relevant to the industry. Activity of different metal loaded catalyst followed the sequence $Ru > Pt > Pd > Ni$ whereas, CHB selectivity of different metal loaded catalyst was governed by the interaction of the reaction intermediate cyclohexene with the metal surface. Furthermore, hydroalkylation reaction pathway was steered by the pore geometry of the zeolites employed in the catalyst preparation. Among all the zeolites tested, palladium modified FAU type zeolite showed highest hydroalkylation selectivity. In addition to this, activity and CHB selectivity of the hydroalkylation catalyst were also governed by the acidity and acid/metal mole ratio of the catalyst. Among all the catalysts tested, Pd(0.2 wt. %)/USY12 showed highest selectivity for CHB

at commercially viable benzene conversion due to its optimum acidity, acid to metal mole ratio and uni-modal large pore system. In spite of being mono metallic catalyst with lower metal loading, this catalyst system gave CHB selectivity of 75% in comparison to 71% for the best patented/ literature reported catalysts at similar benzene conversions. Furthermore, in order to demonstrate the proof of concept for the conversion of benzene to CHB, kinetic modelling, process modelling and scale up studies were carried out on the optimum catalyst formulation employing in-house designed process demonstration unit. Finally, it is discussed how hydroalkylation process will pave way for refinery petrochemical integration assisting in the production of useful petrochemicals like phenolic resins, bisphenol A, caprolactam, alkylphenols, biphenyl, adipic acid, cyclohexanone oxime, cyclohexanone resins and nylon.

सार

बेंजीन एक ज्ञात कैंसरकारक है और यह गंभीर स्वास्थ्य और पर्यावरणीय प्रभाव पैदा कर सकता है। ईपीए (पर्यावरण संरक्षण एजेंसी) इसके स्वास्थ्य प्रभावों के कारण गैसोलीन में बेंजीन की मात्रा की सीमा को लगातार कम कर रही है। ईपीए नियमों को पूरा करने के लिए, अधिकांश रिफाइनर गैसोलीन से साइक्लोएक्सेन में बेंजीन संतृप्त कर रहे हैं। संतृप्ति बेंजीन न केवल उपयोगी हाइड्रोजन का उपभोग करती है, बल्कि गैसोलीन धारा के लिए ओकटेन को काफी नुकसान भी पहुंचाती है। इसे देखते हुए, रिफाइनर रिफाइनरी में उत्पादित बेंजीन को वैध बनाने के वैकल्पिक तरीकों का पता लगाने के लिए मजबूर हैं। साइक्लोहेक्सिलबेनज़ीन कई औद्योगिक अनुप्रयोगों के साथ एक बहुमुखी रसायन है। इसका उपयोग लिथियम आयन बैटरी, लिक्विड क्रिस्टल डिस्प्ले में इलेक्ट्रोलाइटिक एडिटिव और गैर-कैंसर कारक ईंधन सम्मिश्रण योजक के रूप में किया जाता है। इसके अलावा साइक्लोहेक्सिलबेनज़ीन भी फिनोल साइक्लोहेक्सन और बाइफेनिल जैसे पेट्रोकेमिकल मध्यवर्ती के उत्पादन के लिए उत्कृष्ट अग्रदूत है। इस प्रकार, सीएचबी के कई लाभों को देखते हुए बेंजीन को सीएचबी में परिवर्तित करना अधिक लाभदायक विकल्प है। यह शोध सीएचबी के लिए बेंजीन के हाइड्रोकेलाइजेशन के लिए एक उच्च चयनात्मक, स्थिर और लागत प्रभावी उत्प्रेरक के विकास पर केंद्रित है। यह अध्ययन सल्फरिक एसिड और एल्यूमीनियम क्लोराइड जैसे खतरनाक एसिड उत्प्रेरक का उपयोग करके बेंजीन और साइक्लोहेक्सिन के पारंपरिक दो चरण क्षार से बचने के लिए सीएचबी की तैयारी के लिए हरे मार्ग की भी रिपोर्ट करता है। हैड्रोएलकाईलेसन गतिविधि और चयनात्मकता पर उत्प्रेरक के विभिन्न भौतिक और रासायनिक गुणों के प्रभाव पर प्रायोगिक अध्ययन के साथ सैद्धांतिक समझ कुशल, और लागत प्रभावी हैड्रोएलकाईलेसन उत्प्रेरक को डिजाइन करने के लिए महत्वपूर्ण है। वर्तमान अध्ययन में विभिन्न धातु समर्थित जिओलाइट्स की हैड्रोएलकाईलेसन गतिविधि का मूल्यांकन करने का प्रयास किया गया है और उत्प्रेरक गतिविधि के उत्प्रेरक गुणों जैसे जिओलाइट अम्लता, जिओलाइट छिद्र संरचना, उत्प्रेरक के धातु अनुपात के लिए धातु और एसिड की मात्रा और प्रकार के प्रभाव के परिणामों पर चर्चा की गयी है, उत्प्रेरक गतिविधि पर, उदाहरण के लिए प्लैटिनम, पैलेडियम, रूथेनियम और निकल संशोधित जिओलाइट्स (ZSM-5, ZSM-12, MOR, MCM-22, Y और Beta) तैयार किए गए थे और उद्योग के लिए प्रासंगिक विभिन्न ऑपरेटिंग परिस्थितियों में बेंजीन के हाइड्रोक्लोरिकेशन के लिए परीक्षण किया गया था। विभिन्न धातु भरी हुई उत्प्रेरक की गतिविधि ने अनुक्रम $Ru > Pt > Pd > Ni$ का अनुसरण किया, जबकि विभिन्न धातु लोड उत्प्रेरक की साइक्लोहेक्सिलबेनज़ीन चयनात्मकता को धातु की सतह के साथ प्रतिक्रिया मध्यवर्ती

स्यक्लोबेंजीन की क्रिया से नियंत्रित किया गया था। इसके अलावा, उत्प्रेरक तैयारी में कार्यरत जिओलाइट्स के छिद्र ज्यामिति द्वारा हैड्रोएलकाईलेसन प्रतिक्रिया मार्ग का संचालन किया गया था। परीक्षण किए गए सभी जिओलाइट्स के बीच, पैलेडियम संशोधित एफएयू प्रकार जिओलाइट ने सबसे अधिक हैड्रोएलकाईलेसन चयनात्मकता दिखाई। इसके अलावा, हैड्रोएलकाईलेसन उत्प्रेरक की गतिविधि और सीएचबी चयनात्मकता भी उत्प्रेरक की अम्लता और एसिड / धातु के मोल अनुपात द्वारा शासित होती थी। परीक्षण किए गए सभी उत्प्रेरकों में, Pd (0.2 भार.%) / USY12 ने साइक्लोहेक्सिलबेनज़ीन के लिए व्यावसायिक रूप से व्यवहार्य बेंजीन रूपांतरण में इसकी अधिकतम अम्लता, अम्ल से धातु मोल अनुपात और यूनी-मोडल बड़े छिद्र संरचना सिस्टम के कारण उच्चतम चयनात्मकता दिखाई। कम धातु लोडिंग के साथ मोनो मेटालिक उत्प्रेरक होने के बावजूद, इस उत्प्रेरक प्रणाली ने समान बेंजीन रूपांतरणों में सर्वश्रेष्ठ पेटेंट / साहित्य रिपोर्टेड उत्प्रेरक के लिए 71% की तुलना में 75% की साइक्लोहेक्सिलबेनज़ीन चयनात्मकता दी। इसके अलावा, सीएचबी के लिए बेंजीन के रूपांतरण के लिए अवधारणा के प्रमाण को प्रदर्शित करने के लिए, गतिज मॉडलिंग, प्रोसेस मॉडलिंग और स्केल अप स्टडीज को इन-हाउस डिजाइन प्रक्रिया प्रदर्शन इकाई में काम करने वाले इष्टतम उत्प्रेरक तैयार करने पर किया गया था। अंत में, यह चर्चा की गई है कि कैसे फेनोलिक रेजिन, बिसफ़ेनॉल ए, कैप्रोलैक्टम, अल्काइलेफेनोल्स, बाइफेनिल, एडिपिक एसिड, साइक्लोहेक्सेनॉन ऑक्सिन, साइक्लोहेक्सन रेजिन जैसे उपयोगी पेट्रोकेमिकल्स के उत्पादन में सहायता करने वाली रिफाइनरी पेट्रोकेमिकल एकीकरण के लिए हैड्रोएलकाईलेसन प्रक्रिया मार्ग प्रशस्त करेगी।

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NOMENCLATURE

EPA	Environmental protection agency
FCC	Fluid catalytic cracking
VGO	Vacuum gas oil
CHB	Cyclohexylbenzene
DCHB	Dicyclohexylbenzene
Pt	Platinum
Pd	Palladium
Ru	Ruthenium
Ni	Nickel
MCM	Mobil composite material
ZSM	Zeolite Socony Mobil
Beta	Zeolite Beta zeolite
MOR	Mordenite zeolite
Y	Y-zeolite
HY	Proton form of Y zeolite
USY	Ultra stable Y zeolite
B/L	Brønsted/Lewis
MR	Membered Ring
TEAOH	Tetraethylammonium hydroxide
HMI	Hexamethyleneimine
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission electron microscopy
TGA	Thermal Gravimetric Analysis
TPD	Temperature Programmed Desorption
BET	Brunauer-Emmett-Teller
ICP	Inductively coupled plasma
n	Order of reflection
d	Lattice spacing, Å
λ	Wave length of X-rays, Å
θ	Angle between the incident rays and the surface of the crystal
MFC	Mass Flow controller
WHSV	Weight hourly space velocity (h^{-1})
TOF	Turnover frequencies (h^{-1})
TOS	Time on stream (hr)
D_{AB}	Molecular diffusivity (cm^2/s)
D_k	Knudsen diffusivity (cm^2/s)
D_e	Effective diffusivity (cm^2/s)
$\emptyset$	Thiele modules

η	Effectiveness factor
r_{hyd}	Reaction rate of hydrogenation step (mol/hr g-catalyst)
r_{hydalk}	Reaction rate of hydroalkylation step (mol/hr g-catalyst)
r_{alk}	Reaction rate of alkylation step (mol/hr g-catalyst)
F	Molar flow rate of feed, mol h ⁻¹
W	Mass of catalyst, gm
K_i	Adsorption coefficient
R_i	Rate of transformation of the component i (mol g ⁻¹ h ⁻¹)
$k_{i,0}$	Reaction rate constant for reaction i, mole/g catalyst hr
$E_{i,0}$	Activation energy for reaction i, kJ/mol