A THESIS

ON

CATALYTIC HYDROALKYLATION OF BENZENE ON DUAL-FUNCTION CATALYST & CATALYTIC TRANSALKYLATION OF DCHB AND BENZENE

submitted by

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THESIS CERTIFICATE

This is to certify that the thesis titled **“CATALYTIC HYDROALKYLATION OF BENZENE ON DUAL-FUNCTION CATALYST & CATALYTIC TRANSALKYLATION OF DCHB AND BENZENE”** submitted by **NIKITA SHARMA**, to the Indian Institute of Technology, Madras for the award of the degree of **Master of Technology**, is a bonafide record of the research work done by her in **Corporate R&D Centre (CRDC), Bharat Petroleum Corporation Limited (BPCL), Greater Noida (UP) -201301.**

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ABSTRACT

Hydroalkylation of benzene is carried out using Nickel (Ni) supported HY zeolite with SiO_2/Al_2O_3 ratio 5-60. The different weight percentages of Ni is supported onγ-Al_2O_3using wet impregnation technique and the Ni/γ-Al_2O_3 has been incorporated with HY zeolite of different $SiO_2/Al_2O_3$and different weight percentage. Transalkylation of Di-cyclohexylbenzene and benzene is carried out using HY zeolite with SiO_2/Al_2O_3 ratio 5-60. Different HY zeolite catalysts are prepared using γ-Al_2O_3 as support. All catalysts are characterized using X-ray diffraction (XRD) techniques, BET surface area analysis, Scanning electron microscope (SEM), Temperature Programmed Desorption (TPD) of ammonia, and H_2 chemisorption experiments.

The catalyst testing for hydroalkylation reaction has been investigated in a fixed bed reactor under varying operating conditions. The effects of metal content, zeolite acidity, zeolite weight percent have been studied for the hydroalkylation reaction and effect of reaction temperature, pressure, WHSV, hydrogen to benzene mole ratio and stability have been investigated for the conversion of benzene to cyclohexylbenzene (CHB) in a fixed bed reactor under varying operating conditions. The best catalyst performance is obtained over Ni (5 wt %)/HY12 catalyst system as per reaction conditions: 423 K, 20 bar, 1.5 WHSV, and an H_2/C_6H_6 mole ratio of one. Typically, the selectivity of CHB was 74% at a benzene conversion of 45% over Ni (5 wt %)/HY12 catalyst which in turn indicated the requirement of the optimum balance of metal / acid site for enhancement in desired product selectivity. Based on the obtained results, the role of zeolite acidity and operating conditions are discussed for the maximization of benzene conversion as well as CHB selectivity.

The catalyst testing for transalkylation reaction has been investigated in a fixed bed reactor under varying operating conditions. The effect of zeolite acidity has been studied for transalkylation of Di-cyclohexylbenzene to Cyclohexylbenzene and the effect of reaction temperature, WHSV and time of stream have also been investigated in the fixed bed reactor. The best catalyst performance is obtained over HY60 catalyst system as per reaction conditions: 443K, 20bar, 2.29 WHSV, and a C_6H_6/DCHB mole ratio of 9. Typically, the selectivity of CHB was 81% at a benzene conversion of 87% over the HY60 catalyst which in turn indicated the requirement of large pore zeolites for transalkylation reaction. Based on the obtained results, the role of zeolite acidity and operating conditions are discussed for the maximization of DCHB conversion as well as CHB selectivity.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Abbreviations	Meaning
MCP	Methylcyclopentane
CHB	Cyclohexyl benzene
DCHB	Di-cyclohexyl benzene
MCPB	Methyl cyclo pentyl benzene
HY-5	H form of Y zeolite with SiO_2/Al_2O_3 ratio 5
HY-12	H form of Y zeolite with SiO_2/Al_2O_3 ratio 12
HY-60	H form of Y zeolite with SiO_2/Al_2O_3 ratio 60
XRD	X-ray Diffraction
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
SEM	Scanning electron microscope
GC	Gas chromatography
WHSV	Weight Hourly Space Velocity

1. Introduction

Benzene is a carcinogen, it can cause serious health and environmental effects with minimal exposure of Zero percent. In gasoline, the benzene content should be below 0.6 vol% and aromatics content should be below 38% according to Environmental hazards [41]. To follow these regulations, benzene in fuels or gasoline is saturated to produce cyclohexane which holds significant importance in the petroleum industry. The saturation of benzene to cyclohexane consumes more hydrogen and also has considerable octane loss for the gasoline stream. Different alternate ways are explored by industries to reduce the benzene content in gasoline. So hydroalkylation of benzene was introduced as a way to convert benzene present in fuel to a higher aromatic compound cycloalkylbenzene, improve octane number, and remove the potential hazard due to the presence of Benzene.

Cyclohexyl benzene (CHB) or Phenylcyclohexane is produced by Benzene hydroalkylation in the presence of hydrogen gas and metal-zeolite catalysts as reported in the literature [5-23]. Benzene can be hydroalkylated in the presence of other aromatic compounds like ethylbenzene to produce polystyrene [37]. CHB is used as a solvent and plasticizer in plastics, coatings, and adhesive fields. It is also used as an overcharge protecting agent in lithium-ion batteries and base material for LCD derivatives [4]. CHB is used as a blending agent for diesel fuels. It is an important industrial chemical intermediate and as starting material for the synthesis of several important products like phenolic resins, bisphenol-A, ε-caprolactam, and alkylphenols. Dehydrogenation of CHB produces Biphenyl which is used as heat transfer fluid and dye carrier. It is used in the production of phenol and cyclohexanone replacing cumene as the main reactant for phenol production [5-7]. Most of the phenol production is done using Cumene i.e. Hock process shown in the next point. Around 20% of Benzene used as a precursor in the production of Cumene. In this process, an equal amount of phenol and acetone formed. But in the current scenario demand of Phenol is increasing with a rapid rate in comparison to that of acetone also the price of propylene can affect the economy of the process. So an alternative route is developed as shown in the next point, in which the first step is Benzene hydroalkylated to form Cyclohexyl benzene. In the second step Cyclohexyl benzene (CHB) on further oxidation and acid cleavage produces Phenol and Cyclohexanone [1-3,5-10]. Cyclohexanone produced in this second step is a more valuable product as compared to acetone. Phenol is commonly used in organic synthesis as a precursor in the production of bisphenol-A, epoxy resins, phenolic resins, caprolactam, rubber, adipic acid, alkylphenols, aniline etc. [1]. It is also used in the manufacture of insulation materials, solvents, paints, dyes, adhesives, soaps, illuminating gases, perfumes

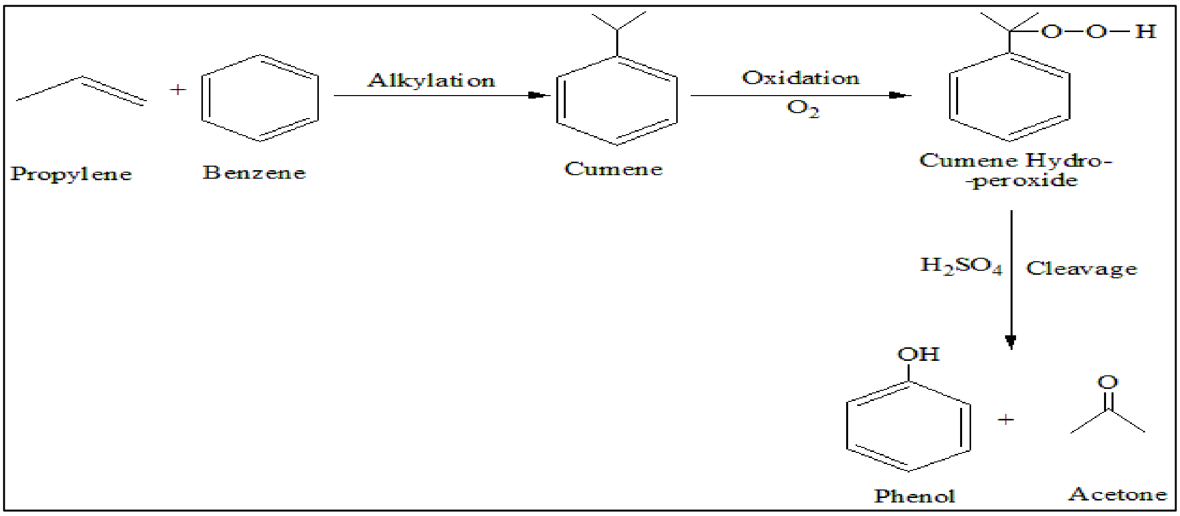
,etc. Also used in manufacturing commercial disinfectants, antiseptics, ointments. Phenol is also used in the medical industry as a topical anesthetic, in-ear drops, and as a sclerosing agent. Other medical applications of phenol include use as a neurolytic agent and in dermatology for chemical face peeling.

There are other products form in benzene hydroalkylation reaction such as Cyclohexane, Dicyclohexyl benzene (DCHB), methyl cyclopentane (MCP) and others. Cyclohexane can be converted dehydrogenated to form Benzene. The Di-cyclohexylbenzene (DCHB) can be transalkylated to form Cyclohexylbenzene (CHB). Transalkylation reaction is described as the transfer of one alkyl group from one compound to another. This reaction is used to increase the production of CHB in overall [18].

Hock process and Alternative process for phenol production consist of two steps i.e. Alkylation and oxidation with Acid Cleavage.

a) Hock Process:

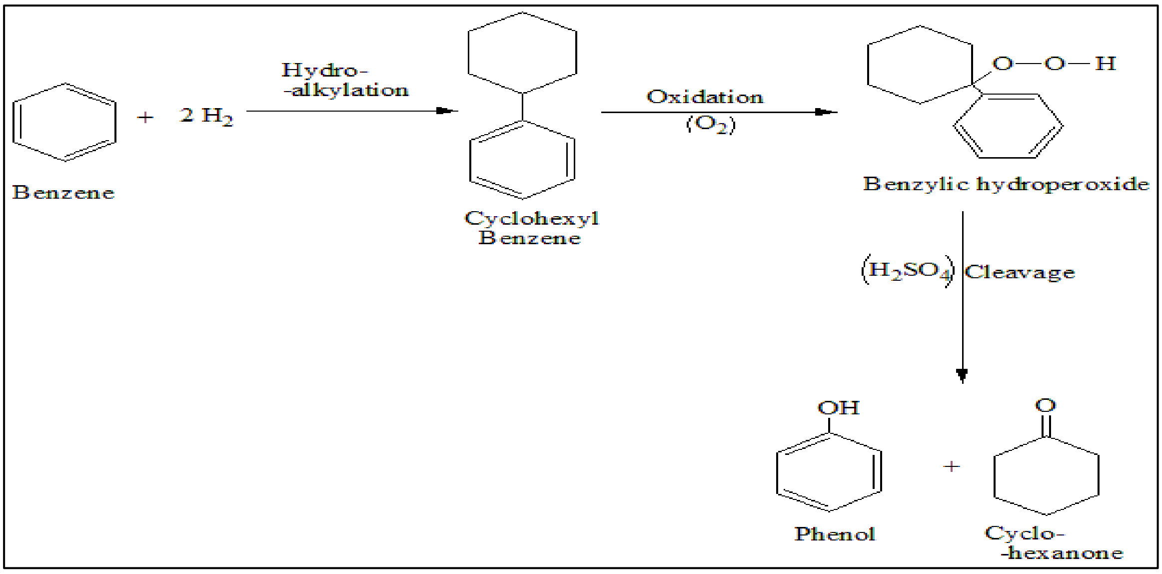
In the first step of this process, Benzene is alkylated with propylene to form Propylbenzene also known as Cumene and in the second step, Cumene is oxidized to Cumene hydroperoxide, which in the presence of acid breaks into an equal proportion of Phenol and acetone. The Hock process is shown in Scheme 1.



Scheme 1: Phenol production from Hock Process

b) Alternative Process:

In the first step of this process, Benzene is alkylated with hydrogen i.e. hydroalkylated to form Cyclohexylbenzene also known as Phenylcyclohexane. The second step includes Cyclohexylbenzene is oxidized to Benzylic hydroperoxide, which in the presence of acid breaks into an equal proportion of Phenol and Cyclohexanone. Hydrogen is less costly as compared to Propylene used in Hock Process Cyclohexanone can be used as a solvent, activator in oxidation reactions, and diluent for paints, inks, synthetic resins, and rubbers. It is majorly used as a raw material for Caprolactum and adipic acid production. It is used as an industrial solvent. Cyclohexanone can be dehydrogenated to form phenol i.e. a byproduct can be converted into the main product [38]. Oxidation of Cyclohexyl benzene (CHB) takes place at 343K to 473K and around 100 bar pressure. The cleavage process of Benzylic hydroperoxide takes place at a temperature of at least 458K and 10bar pressure [1-3]. An alternative route for Phenol production from Benzene is shown in Scheme 2.

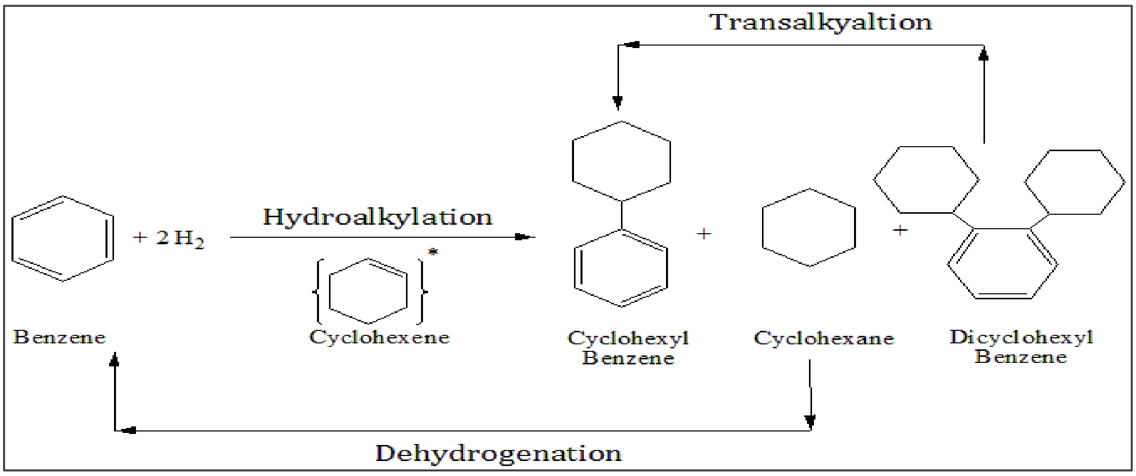


Scheme 2: Alternative route for Phenol production from Benzene Hydroalkylation

1.1 CHB production:

Truffault [11] first reported the production of CHB from nickel catalyzed hydrogenation of benzene in the presence of P_2O_5. CHB can be produced from hydrogenation of Biphenyl. CHB is also produced by the direct alkylation of benzene and cyclohexene using aluminium chloride or sulfuric acid as catalysts. This direct alkylation route not only uses hazardous acid catalysts such as sulfuric acid and aluminium chloride but also offer low selectivity (around 44%) for

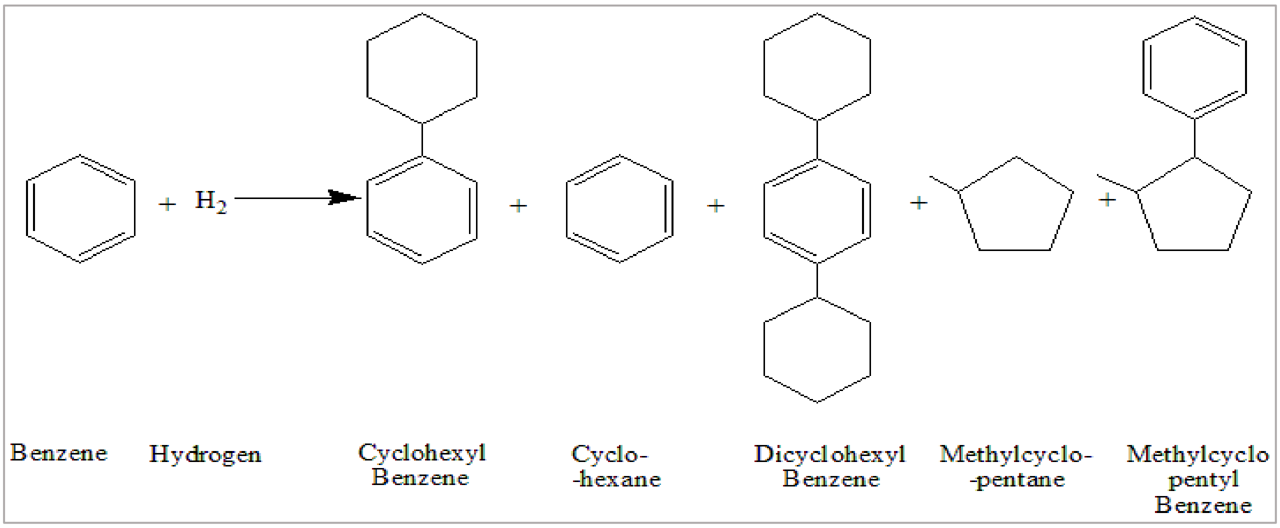
CHB [8,9]. Cyclohexyl benzene is produced from Benzene hydroalkylation. Biphenyl hydrogenation and alkylation of benzene with cyclohexene have high operating cost and low efficiency, so benzene hydroalkylation is used for high production of CHB. In the Hydroalkylation reaction, Cyclohexene is produced as an intermediate in this reaction. Cyclohexyl benzene, Cyclohexane, Dicyclohexylbenzene (DCHB), etc., are formed as products. DCHB can be transalkylated with Benzene to produce CHB thereby increasing CHB yield from the reaction. Cyclohexane can be dehydrogenated to form Benzene hence increasing the amount of raw material needed. An overall reaction is shown below in Scheme 3



Scheme 3: Different reactions possible to increase conversion and selectivity

1.2 CHB production from Benzene hydroalkylation reaction:

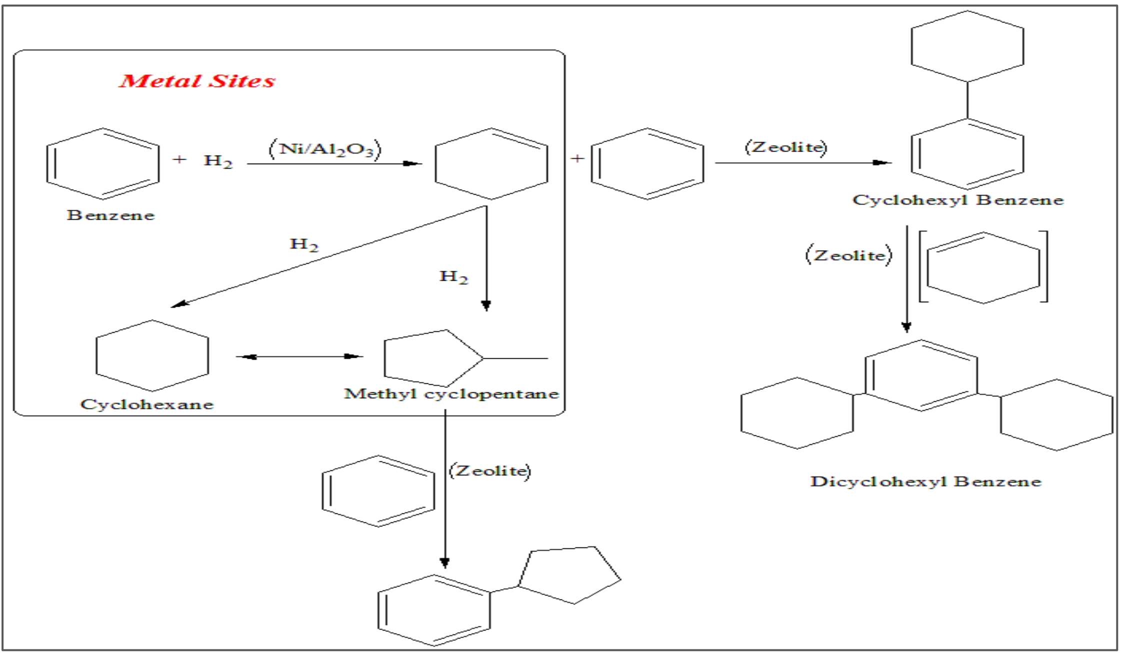
In this reaction shown in Scheme 4, benzene is partially reduced to form Cyclohexene as an intermediate. The partial hydrogenation of Cyclohexene takes place in the presence of metal sites. Cyclohexene reacts to form Cyclohexyl benzene (CHB) as the desired product for this reaction. Some undesired reactions such as complete hydrogenation of Benzene to form Cyclohexane and MCP, CHB alkylation to form DCHB and MCP alkylation to form MCPB can occur depending on the catalysts and experimental conditions like Temperature, hydrogen pressure and other reaction parameters [1-6]. Cyclohexyl benzene (CHB). Here, MCP means Methyl cyclopentane and MCPB means Methyl cyclopentyl Benzene. Benzene hydroalkylation to produce Cyclohexylbenzene (CHB) carried out on different catalysts and specific reaction conditions yield a number of useful chemicals as shown.



Scheme 4: CHB Production from Benzene Hydroalkylation.

Reaction pathway of <u>CHB production from Benzene hydroalkylation reaction</u>:

Benzene Hydroalkylation to form CHB is a two-step reaction i.e. Partial hydrogenation followed by Alkylation. This reactions, Partial hydrogenation and Alkylation of Benzene is carried out on the different catalyst surfaces. For partial hydrogenation metal is used as a catalyst and for alkylation reaction, acid type catalyst is used. Cyclohexene is formed as an intermediate in this reaction [5,7,17-18,21].

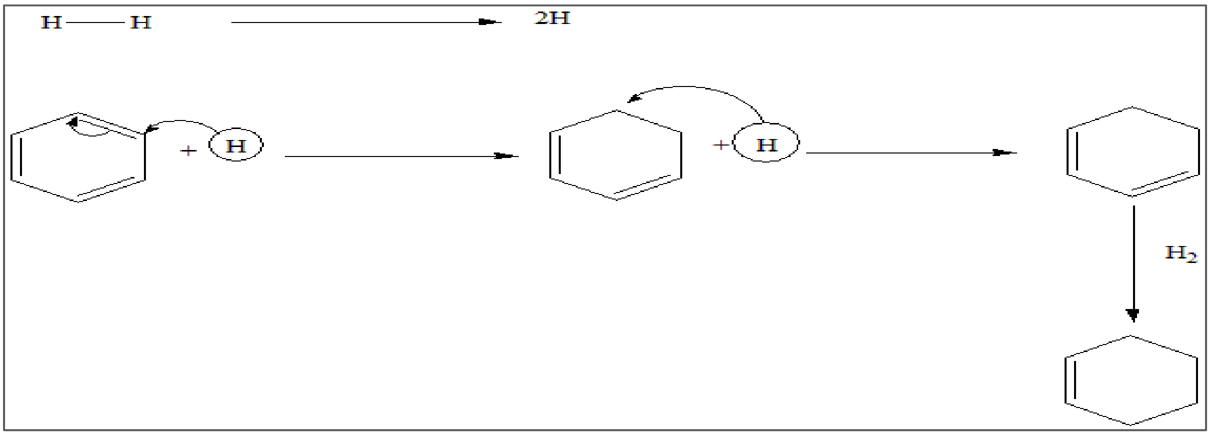


Scheme 5: Hydroalkylation reaction on metal and acid sites to produce different products.

As shown Scheme 5 above Benzene is partially hydrogenated to form Cyclohexene and also complete of Benzene produces cyclohexane and methylcyclopentane. There are three alkylation reactions possible i) Cyclohexene reacted with benzene to form Cyclohexylbenzene (CHB), ii) Cyclohexene on reacting with cyclohexylbenzene form Dicyclohexylbenzene and iii) Methylcyclopentane is reacted with benzene Methylcyclopentyl benzene, also an isomer of Di-cyclohexylbenzene (DCHB).

Reaction on Metal sites

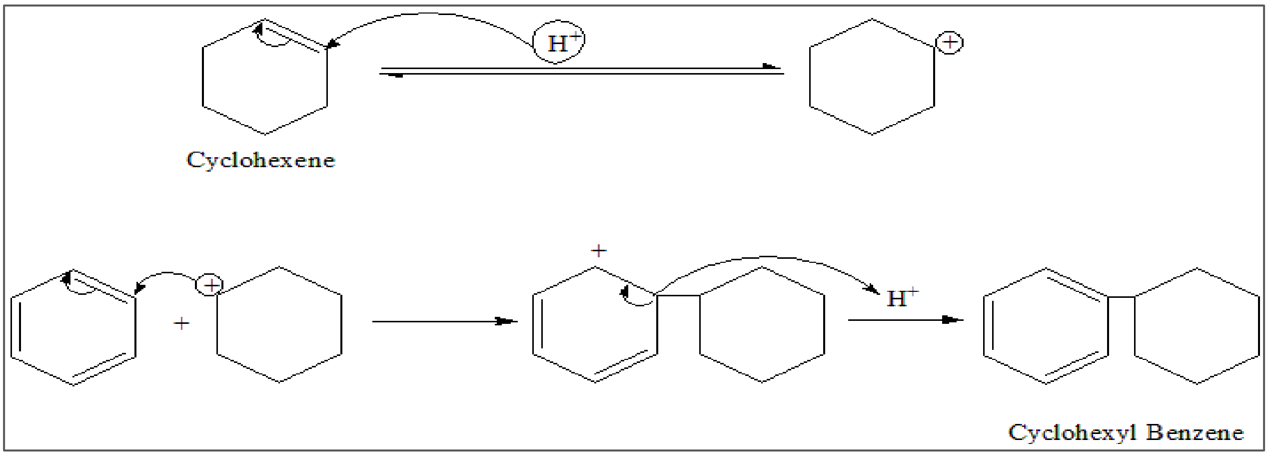
Hydrogen molecule dissociate on the surface of metal catalyst and this dissociated hydrogen then replace the double bond present in Benzene ring i.e. Hydrogenation reaction. Cyclohexene is formed as a result of the Partial hydrogenation of Benzene. Cyclohexane and methylcyclopentane are produced by the complete hydrogenation of Benzene.



Scheme 6: Reaction on metal sites

Reaction on acid sites

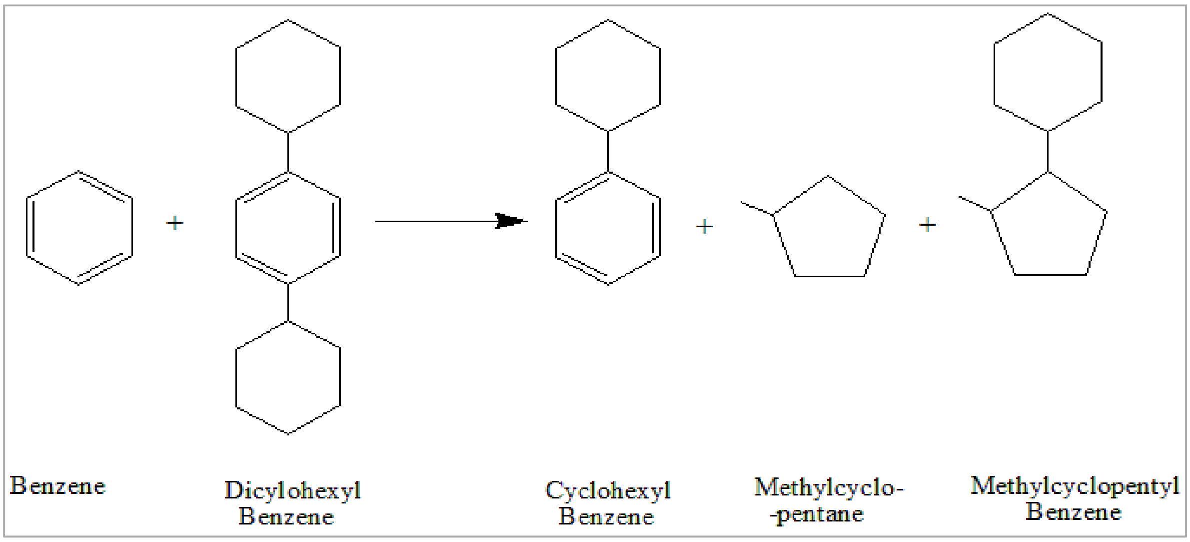
When one hydrogen of the Benzene ring is replaced by alkyl or cycloalkyl group i.e. Alkylation reaction. Hydrogen ion on acid sites reacts with cyclohexene to form a six-member hydrocarbon ring carbonium ion. It is known that carbonium ion is Carbon with a valency of five, is very reactive in nature. This carbonium ion is reacted with benzene ring to form Cyclohexylbenzene as shown below in Scheme 7.



Scheme 7: Reaction on Acid (Zeolite) sites

1.3 CHB production from DCHB transalkylation reaction:

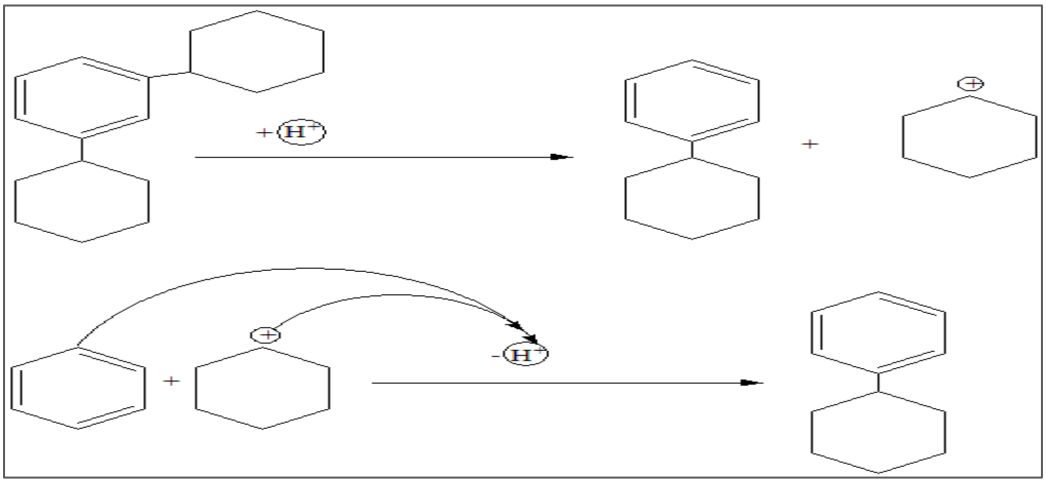
In this reaction shown in Scheme 8, Dicyclohexyl benzene (DCHB) is reacted with benzene to form Cyclohexyl benzene(CHB)[1-3,27]. The transition of one Cyclohexyl group from DCHB to Benzene leads to the term trans-alkylation i.e. transfer of alkyl group from one organic compound to another. Other than transalkylation reaction benzene is also reacted to form MCP and DCHB is isomerized to form Methylcyclopentyl benzene(MCPB). The products formed are Cyclohexyl benzene(CHB), Methyl cyclopentane(MCP), and higher cycloalkyl benzene.



Scheme 8 :CHB production from Transalkylation reaction

Reaction pathway of CHB production from DCHB transalkylation reaction:

In this reaction Di-cyclohexylbenzene (DCHB) is reacted to form a hydrogen ion on the surface of catalyst and produces Cyclohexylbenzene (CHB) and a six member hydrocarbon ring with carbonium ion. The ion reacts with the benzene ring to form Cyclohexyl benzene. One mole of DCHB and Benzene is used to produce two mole of Cyclohexylbenzene.



Scheme 9 :Reaction mechanism of DCHB transalkylation

1.4 Research objective

In benzene hydroalkylation, noble metals or precious metals such as Pd, Pt, W, Sn, Zn, etc. were used as catalyst for partial hydrogenation of benzene and Pd gives the best result for partial or controlled benzene hydrogenation. Also for hydroalkylation reaction, the first step is partial hydrogenation of benzene, without it the reaction cannot proceed with alkylation alone. Palladium is mostly used as a catalyst for partial hydrogenation of compounds but Pd is very costly and rarely available on earth. With the increasing demand for Palladium, the development of hydrogenation catalysts with non-noble metals such as Ni, Co was used as replacement for Pd. Because Nickel and Cobalt are available in abundance on the earth's surface and less costly than palladium and hence the reactions became economical.

- The main objective of this research is to develop a Nickel-based bi-functional catalyst for CHB production from Benzene hydroalkylation reaction and increase the yield and selectivity of Cyclohexylbenzene. In this study, a Nickel-based catalyst is developed to give almost similar hydroalkylation results as that of Pd based catalyst and to make hydroalkylation reaction more economical. Also for the second step of hydroalkylation reaction i.e. alkylation commercially available zeolites are used as an acid catalyst.

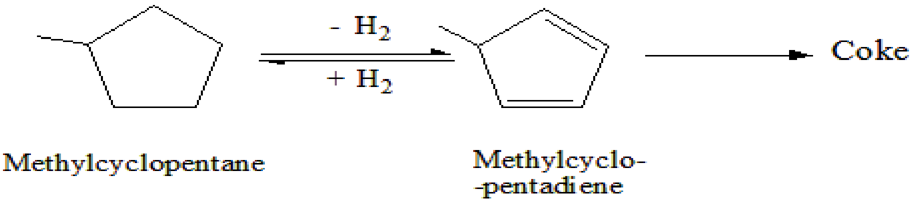
- The second objective is to develop a catalyst using different zeolites for benzene and DCHB transalkylation to produce cyclohexylbenzene with maximum yield.
- To study the effect of nickel content, acidity and zeolite content on the activity of benzene hydroalkylation reaction. Find out a particular catalyst proportion for best results and their physical & chemical properties.
- To study the effect of different reaction conditions like Temperature, hydrogen pressure, contact time, etc. on benzene conversion and CHB selectivity for benzene hydroalkylation reaction and obtain best-operating conditions for the reaction.
- To study the effect of acidity on the activity of DCHB transalkylation reaction and to obtain the best catalyst for the reaction and to study the physical & chemical properties of catalysts.
- To study the effect of operating conditions on the activity of DCHB transalkylation with benzene.

2. Literature Review

2.1 Bi-functional catalysts for Benzene Hydroalkylation reaction

Hydroalkylation reaction is divided into two parts as partial hydrogenation reaction and alkylation reaction. Two-step conversion of Benzene hydroalkylation with high yield and selectivity proceeds only in aqueous media in the presence of hydrogen and suitable bi-functional catalysts. For partial hydrogenation reaction,a metal catalyst with non-reactive support is used . The metal used for this part as a catalyst can be Pd, Ru, Ni, Co, Pt, Rh, Re, Sn, Zn, etc., supported on an inorganic oxide such as Alumina(Al_2O_3), TiO_2, ZrO_2, SiO_2, etc.. For Alkylation reaction, Zeolite is used as an acid catalyst. Zeolites used are MCM family such as MCM-22, MCM-49, MOR, Beta, 13X and H-form Y-zeolites for eg. commercially prepared CBV712 (SiO_2/Al_2O_3 =12), CBV760 (SiO_2/Al_2O_3 =60).

Truffault [11] first reported the small production of CHB with cyclohexane from nickel catalyzed hydrogenation of benzene in the presence of P_2O_5. several industrial companies like Exxon Mobil company and Phillips Petroleum Company studied the production of Cyclohexylbenzene as a replacement of cumene in producing phenol [12-15]. Suggitt and Crone concentrated on Ni and Co/W/zeolite-based catalysts [12]. In this study 4% to 25% VIII group metals impregnated on zeolites were used as hydroalkylation catalysts. The activity of these hydroalkylation catalysts decreases with the time on stream means slow deactivation. Regeneration or reactivation of catalysts can be done by heating catalyst at a high temperature of 700K. while Murtha and Zuech [13-15] focused on calcined, acidic, nickel and rare earth treated crystalline zeolites promoted by group VIII noble metals. Chang et.al. [7] developed hydroalkylation catalysts consisting of one or two metal for hydrogenation supported by zeolites for the alkylation process. The first metal having hydrogenating activity was selected from Pd, Ru, Ni and Co while the second metal was different from first metal and selected from Zinc, tin, nickel and cobalt used mainly as promoter of hydrogenation reaction on first metal. The zeolites may be selected from MCM-22, PSH-3 ,SSZ-25, MCM-36, MCM-49, and MCM-56 , with MCM-22 being particularly preferred because of its higher selectivity for CHB. The catalyst having 0.3%Pd/MCM-22 and 0.3% Ru-0.3% Sn/MCM-22 showed better activity for hydroalkylation reaction with respectively 48.6% and 43.9% benzene conversion and around 70% CHB selectivity ,detailed result is shown in Table 1. Although the use of MCM-22 family catalysts has afforded an increase in cyclohexylbenzene selectivity, significant amounts of cyclohexane and methylcyclopentane are nonetheless produced. The conditions of low temperature (less than 473 K) and high pressure (greater than 7.9 bar) typically employed in hydroalkylation processes also favor the competing reaction of benzene hydrogenation to cyclohexane. As a result, cyclohexane and methylcyclopentane selectivities of 5 to 20 wt % are commonly observed. The production of cyclohexane and methylcyclopentane results in the loss of valuable benzene feed and reduces the level of benzene conversion (typically 40 to 60 wt %), which necessitate recycle of unreacted benzene. Also dehydrogenation of methylcyclopentane forms methylcyclopentadiene, a very reactive precursor for coke formation and an accelerator of catalyst deactivation. Dakka et.al. [23] studied hydroalkylation reaction with an aim to reduce the formation of Cyclohexane and MCP. In their experiments effluent stream was divided in four parts as benzene to recycle back to hydroalkylation, cyclohexane and MCP to dehydrogenating reactor, and higher cycloalkylbenzene to be transalkylated back to CHB. Pd or any metal ion impregnated on γ-alumina using metal nitrates as precursor and gamma-alumina is non acidic in nature thereby not affecting acidity of zeolite used. The catalyst with Pd/MCM-49 showed better activity for benzene hydroalkylation with benzene conversion of 33.6% , CHB selectivity of 76%, and cyclohexane selectivity of 4%.



Slaugh et al.[10] studied the hydroalkylation of benzene over a range of supported metal catalysts. The different metal studied in this study include Ni, Pd, Pt, W supported on different inorganic oxide, zinc chloride, aluminium chloride and zeolites. The catalyst alumina impregnated with nickel produces cyclohexane predominantly and catalyst having alumina impregnated with tungsten exhibited no activity but the catalyst having alumina impregnated with both Ni and W showed better yield of cyclohexylbenzene for a benzene conversion of 20%. From this study it is concluded that tungsten present in Ni/Al_2O_3 as catalyst had a promotional effect on the formation of Cyclohexyl benzene .This effect may be due to the increase in acidity of catalyst by the addition of tungsten. Cyclohexane is added to reaction as a solvent, it served as an inert diluent in the yield of Cyclohexyl benzene. But in this study cyclohexane is proposed as an intermediate which can be desorbed easily from catalyst surface.

A four-component catalyst system containing Nickel, Platinum, rare earth metal and Zeolite 13X was developed for hydroalkylation reaction. The catalyst with low Ni content of less than 2 wt% was less active and catalyst with Ni content of more than 3 wt% gave higher selectivity of 70% for a benzene conversion of 20% but with the increase in Ni wt% of more than 7 wt% gave better selectivity of higher molecular weight products. This study also suggested that the small amount of platinum spillover on the surface of support helps in the reduction of nickel which in turn favors hydroalkylation at lower temperatures. The catalysts containing rare earth metals had no or minimal effect of acidity on the selectivity of CHB but the catalyst that doesn't include rare earth metal with high acidity produces a high yield of cyclohexane. Because addition of rare earth alters the electron transfer to the metal thereby reducing adsorption strength of benzene which in turn helps in hydroalkylation rather than hydrogenation [16]. Zeolite 13X was used because it has large pores for benzene to enter and hence favors hydroalkylation over hydrogenation reaction. It is also found out that the activity of hydroalkylation reaction decreases by approx 20% in the presence of hydrogen sulphide. The best catalyst, 5 wt% Ni/10 wt% Re/0.1 wt% Pt loaded on 13X zeolite showed a selectivity of 70% for CHB at 20% benzene conversion [16].

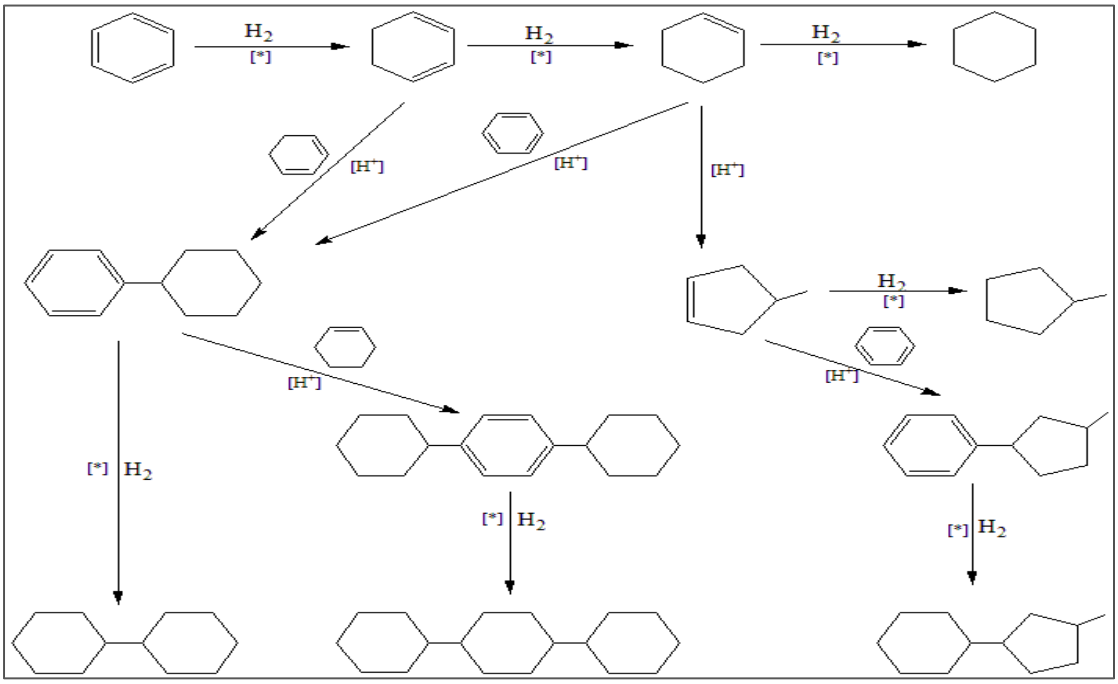
Palladium supported on Beta zeolite with different Si/Al ratio was also studied by Jun et.al. [5] . With the increase in SiO_2/Al_2O_3 ratio the number of weak and strong acid sites also decreases. The conversion of benzene and selectivity of cyclohexane increases with an increase in SiO_2/Al_2O_3 ratio while cyclohexylbenzene selectivity decreases, hence it was suggested that acidity of the Hβ zeolite with large pores or higher acidity (low SiO_2/Al_2O_3 ratio) favors selectivity of cyclohexylbenzene. They had also studied on the effect of different metal used for partial hydrogenation such as Pd, Ru, Rh and Ni. Catalysts with Rh and Ru as metal catalyst had high benzene conversion of ~98% but the selectivity for CHB is very less (~4%) and this catalysts favors hydrogenation with a cyclohexane selectivity of ~80%. The catalyst with 0.2% Ni/Hβ25 has almost same selectivity of 50% for cyclohexane and cyclohexylbenzene. While Pd on the catalyst has a favorable reduction activity and catalyst, 0.2%Pd/Hβ25 showed a selectivity of 67% for CHB and 25% for Cyclohexane at 28% conversion .

They have also studied the effect of operating conditions on the activity of benzene hydroalkylation. With the increase in reaction temperature the selectivity of by-products also increases because hydrogenation of benzene to cyclohexane and alkylation of Cyclohexylbenzene to produce di-cyclohexylbenzene is preferable at higher reaction temperature. The selectivity of CHB decreases with an increase in the contact or reaction time because of the hydrogenation of benzene and CHB. Higher hydrogen pressure promotes mass transfer process and increases the absorption of hydrogen on the catalyst surface, thereby increasing complete hydrogenation of benzene to cyclohexane [5].

Kralik et al. studied the effect of beta and mordenite zeolite on activity of hydroalkylation reaction in a batch reactor and reaction mechanism for the reaction. The catalysts with beta zeolite are more active for CHB and DCHB production while the catalysts with mordenite zeolite favor hydrogenation of benzene to cyclohexane and also increase in the yield of methylcyclopentane. This may be due to i) large pores and larger mesoporous surface area of beta zeolite, ii) ruthenium dioxide present on beta zeolite surface after reduction of catalyst prior to its calcination and iii) accessibility of acid catalytic sites on Zeolite surface. The obtained results are 60 to 40% CHB & DCHB selectivity at benzene conversion of 30 and 80%, by using 0.2 wt.% Ru/Beta zeolite [17]. The reaction route/mechanism proposed for hydroalkylation of benzene is shown in Scheme 10.

Cyclohexyl benzene production from benzene hydroalkylation has two possible routes, one by the reaction of two molecules of cyclohexadiene while other by the alkylation of benzene with cyclohexene. But the formation of cyclohexylbenzene from two molecules of cyclohexadiene requires an aromatizing procedure featured with a relatively large reorganization of electron structures of reactants hence the second route for CHB production i.e. benzene alkylation with cyclohexene is more probable. The hydrogenation of CHB, DCHB and Methylcyclopentyl benzene (MCPB) is only possible when there is a change in the extent of reactions by molecules size and pores dimensions of the catalysts.

Kishore Kumar et al. [18] studied the effect of SiO_2/Al_2O_3 ratio in Pd/HY zeolite on the activity of Benzene hydroalkylation reaction. Catalyst Pd/HY5 (SiO_2/Al_2O_3=5) showed better hydroalkylation activity compared to the catalyst with SiO_2/Al_2O_3 of 12, 30, or 60 and the catalyst having Pd (0.2 wt%)/HY5 obtained a selectivity of 77% for CHB at 42% benzene conversion. The low content of metals Pd, Ru, Rh have high selectivity for CHB as reported in the literature, this is because of higher acidity with hydrogen spillover effect on the surface of catalyst. Zeolite with SiO_2/Al_2O_3 provided more acid sites that help in alkylation of cyclohexene and benzene to produce a higher yield of cyclohexylbenzene.



Scheme 10: Reaction mechanism for benzene hydroalkylation proposed by Kralik et.al. Here [*] and [H$^+$] represent metal sites for hydrogenation and acidic sites for alkylation & isomerization respectively.

The effect of operating conditions such as WHSV, hydrogen pressure, hydrogen to benzene ratio, reaction temperature, and time of stream [18] is also studied and the obtained results were similar to studies reported in previous researches[5,16]. Kinetic model based on surface reaction mechanism was also developed [18] i.e. mechanism with adsorption, reaction, and desorption steps. The obtained result showed that hydrogenation of benzene is much slower than alkylation of cyclohexene and benzene. This means that cyclohexene formed from benzene hydrogenation was quickly alkylated with benzene on acid sites to form CHB. They have also found out the absence of internal and external mass transfer limitations for the reaction.

Pd catalysts with H form of different types of zeolites such as β-zeolite, MCM-41, Y-zeolite, Mordenite, γ-Al_2O_3, SiO_2, and β-300 zeolite was developed by Li et al. [21]. The effect of Pd content in catalysts was also studied which showed with an increase in Pd wt% benzene conversion increases but the selectivity of CHB decreases and results have similar to as reported elsewhere [5,16,18]. The activity of benzene hydroalkylation on different metals Rh, Ru, and Ni supported by HBeta catalysts, Rh and Ru based catalysts showed a higher reaction rate than Pd/HBeta but lower selectivity for CHB.

Table 1: Previous work in the literature on Benzene Hydroalkylation reaction is detailed as follows

S. No.	**Catalysts**	**Operating Conditions**	**Benzene Conversion**	**Selectivity**	**Remarks**
1	Pt/Ni/Re-13X [16]	443K,3.50 bar,16LHSV (h^{-1}),H_2/HC = 1:1	20%	75% (CHB),20% (CH), 5% others	Poly-functional catalyst and low benzene conversion
2	0.2%Pd/Hβ25 [5]	473K, 50 bar, H_2/HC = 1:1	28.10%	67.2%(CHB),24.9% (CH), 7.9% (DCHB)	Batch study and low benzene conversion
3	0.2%Ru/Hβ25 [17]	443K, 10 bar	28%	40% (CHB), 50% (CH), 10% (DCHB)	Batch study and low selectivity for CHB
4	0.3%Ru/0.3%Sn/ MCM-22 [7]	393K,8 bar,1WHSV (h^{-1}),H_2/HC = 1:1	43.90%	71.4%(CHB),12.8% (CH),15.2%(DCHB), 0.6% others	Poly metal/functional catalyst with proprietary zeolite
5	0.3%Pd/MCM-22 [7]	423K 10 bar,2WHSV (h^{-1}) , H_2/HC=1:1	48.60%	70.3%(CHB),10.5% (CH),17.5%(DCHB), 1.7% others	Potential catalyst with proprietary zeolite
6	1.63%Ni/0.79%F /7.3%W/Al_2O_3-SiO_2[10]	423K, 55 bar, 90 m^3 of H_2 per m^3 of benzene	26.10%	62.6%(CHB),15.4% (CH),18.%(DCHB), 3.6% others	Batch process, poly metal/functional catalyst.
7	0.3%Pd/MCM-49 [23]	423K, 10 bar, 0.52 WHSV(h^{-1}), H_2/HC = 0.64	33.60%	75.8%(CHB),4.2% (CH),15.5%(DCHB), 4.5% others	Potential catalyst with proprietary zeolite
8	0.2 % Pd/HY5 [18]	423K,20 bar,0.5WHSV (h^{-1}), H_2/HC = 1	42.20%	77.3%(CHB),3.1% (CH),19.6% (DCHB & others)	Potential catalyst with Noble metal
9	0.2 %Pd@HBeta [21]	473K, 40 bar	34.40%	57.3%(CHB),40.80% (CH),1.8% (DCHB & others)	Potential catalyst with proprietary zeolite and Metal nanoparticles.

But catalysts Ni/HBeta showed lower reaction rates and benzene conversion with low conversion. There is no CHB yield for catalysts with γ-Al_2O_3 and SiO_2 as support because of the absence of acid sites and catalysts with Y-zeolite and MCM-41 have benzene conversion of 83.7% and 4.7% with lower selectivity for CHB of 21.4% and 0.1% respectively. Metal NPs enveloped/encapsulated in zeolite i.e. coating the Si-Al framework outside the Pd/HBeta catalyst, its acidic property will be changed and more acid sites will be available around the metal sites to enhance the hydroalkylation process [19-21]. Li et al. studied a Si-Al framework coated on the surface of Pd/Hβ catalyst (Pd@Hβ) where Pd is encapsulated into Hβ zeolite. Pd@Hβ catalysts showed a higher benzene conversion at the same reaction rate as compared to Pd/Hβ catalysts. Encapsulation of Pd nanoparticles (NPs) into HBeta zeolite, the Pd NPs reconstructed to a smaller diameter with uniform distribution, leads to improvement of Benzene reaction rate and an increase in the ratio of Bronsted to Lewis acid sites ratio. Due to the increase of acid sites, Pd@Hβ can absorb more quantities of benzene and cyclohexene hence prevents further hydrogenation of Cyclohexene and facilitates alkylation reaction [21]. The DFT calculations were also performed which showed that cyclohexene is easily desorbed from Pd NPs to HBeta zeolite channel in Pd@HBeta catalyst. It is effectively prevents the further hydrogenation of cyclohexene and facilitates the alkylation reaction. Pd@HBeta has better recyclability in the reaction as compared to Pd/HBeta catalysts and deactivation of Pd@HBeta is not encountered.

The hydroalkylation of other aromatic compounds was studied on Pd, Pt doped HY, La-BEA, H-BEA, and H-Mordenite zeolites [24-26]. The studies on hydroalkylation suggested that an optimum metal acid balance is required to achieve the highest hydroalkylation activity and selectivity. Their study also suggested that, Pd doped HY zeolite is more effective catalyst than any other metal-doped zeolites and is more active and selective for the hydroalkylation reaction.

2.3 Catalysts for DCHB Transalkylation

Transalkylation reaction of Di-cyclohexylbenzene with Benzene to form mono-Cyclohexyl benzene is a one-step reaction. The catalyst used in this reaction are Zeolites with inorganic oxide as support. Zeolites used can be MCM family such as MCM-22, MCM-45, TEA`1-Mordenite, H-Beta, 13X, or H-form Y-zeolites for example commercially prepared CBV712 (SiO_2/Al_2O_3 =12), CBV760 (SiO_2/Al_2O_3 =60), etc.. The inorganic oxide support can be Silica, Alumina, or group IVB metal oxide.

2.4 Literature review on Transalkylation reaction

Transalkylation of higher aromatic compounds over different zeolites has been reported in the literature. The zeolites used have medium and large size pores because the shape selectivity of the zeolites plays an important role through pore steric restrictions in producing alkyl aromatics [43-45].These reactions have components with higher molecular weights as reactants, which slowly diffuses through the pores and hence causes deactivation of catalysts from coke formation. Therefore, large pore zeolites such as Beta, mordenite, or USY are used as catalysts in alkyl aromatic processing. The activity and selectivity of these reactions depend on adsorption/desorption and pore-transport of reactants and products.

Transalkylation of Di-cyclohexyl benzene with benzene is suggested in the literature [1-3] as mixing effluent stream of benzene hydroalkylation reaction containing di-cyclohexylbenzene and fresh benzene to increase the yield of cyclohexylbenzene transalkyaltion of DCHB and Benzene to form Cyclohexylbenzene studied by Cheng et.al. [27]. This reaction takes place in the presence of a catalyst consisting of an acidic solid comprising of a group IVB metal oxide modified with an oxyanion of a group VIBA metal oxide, TEA-Mordenite, zeolite beta, and other zeolites. In this study, WO_x/ZrO_2 catalyst is very active for the reaction as compared to catalyst with zeolites TEA-Mordenite, Beta, and MCM-22 having 35% alumina as support. The catalysts were dried in the presence of nitrogen for some hours before reaction and feed contains benzene and di-cyclohexylbenzene in a weight ratio of 3:1. The obtained results are 96% selectivity for CHB with 63% DCHB conversion at an operating condition of around 200^0C, 20 bar, and WHSV of $4h^{-1}$. Several transalkylation reactions were carried on different zeolite surfaces with or without the corporation of metal.

Wang and Cheng studied the transalkylation of polycyclohexylbenzene to cyclohexylbenzene with a catalyst consisting of USY-zeolites. Ultra stable Y zeolites (USY-zeolites) with a silica to alumina ratio higher than six are produced by dealuminating Y zeolite. The term dealuminating is generally understood to mean the removal of aluminum from the Zeolite framework with minimal disturbance to the overall composition of the material since removed aluminum from the framework remains in the channels and cavities [28]. In this study, USY zeolites with silica-alumina ratio of 10-1000 were studied as transalkylation catalysts. The obtained results are 50% conversion of polycyclohexylbenzene and Cyclohexylbenzene selectivity of around 90% for a USY-Zeolite catalyst with silica to alumina ratio of 60 and unit cell size of 24.26.

Wang et al. also studied the production of cyclohexylbenzene from the dealkylation of di-cyclohexylbenzene in the presence of acid catalysts. The acid catalyst was selected from at least one alumino-silicate, alumino-phosphate, or silico-alumino-phosphate of the FAU, AEL, AFI, and MWW family[29]. Dealkylation of DCHB takes place in the absence of benzene and hydrogen was added to reduce coke formation in the process. Dealkylation of di-cyclohexylbenzene produces cyclohexylbenzene, cyclohexene, and also some amount of cyclohexane was formed due to the presence of hydrogen and also cyclohexene formed in the reaction can be recycled as an intermediate of hydroalkylation reaction. Absence of benzene in dealkylation reaction causes coke formation while in transalkylation of DCHB there is no formation of coke.

Different studies on transalkylation of higher aromatic compounds is done in literature. The transalkylation of Diethylbenzene with benzene was studied at different operating conditions on beta zeolite and in the presence of carbon dioxide [30]. In this study, deactivation of catalyst due to coke formation is also reported when catalyst is tested in super-critical conditions with CO_2. These results have been explained as the density and the Diethylbenzene diffusivity are lower than the corresponding to liquid and gas phases, respectively leading to coke formation and hence catalyst deactivation. High operating temperature and WHSV are favorable for transalkylation of Diethylbenzene and it is also reported that pressure has a negative effect at low temperature. Transalkylation of Trimethylbenzene with toluene was studied over different large pore zeolites Y-zeolites, beta zeolites, and mordenite for xylene production [30]. Zeolite Y has a higher conversion of trimethylbenzene as compared to zeolite beta and mordenite but with an increase in temperature conversion and xylene yield decreases rapidly. Zeolite beta also has higher conversion and yield of xylene as well as higher stability. Zeolite Beta is less affected by coke formation than mordenite and zeolite Y because of its unique structure and pore dimensions. In this study, it is suggested that for a lower operating temperature rate-limiting step is intrinsic reaction rates but for a higher temperature of around 673K, desorption of higher aromatic compounds also affected the rate-controlling step. Ali et al. studied transalkylation of Trimethylbenzene with Methylethylbenzene over mordenite and metal-based bi-functional catalysts [32]. They have studied the effect of Mordenite and Rheniumon on the dealkylation of Methylethylbenzene and transalkylation of Trimethylbenzene for Toluene and Xylene formation. Rhenium containing catalysts have higher Methylethylbenzene dealkylation and trimethylbenzene transalkylation as compared to molybdenum containing catalysts and also have higher hydrogen consumption with methane formation. The present research work focuses on the development of a highly selective, and stable HY zeolite as a catalyst for converting DCHB reacted with benzene to form CHB. The influence of catalyst properties and the reaction operating conditions were studied on the transalkylation activity of the catalyst. HY Zeolite (35% Alumina) with varied SiO_2/Al_2O_3 ratio were prepared and evaluated for the hydroalkylation activity.

3. Experimental work

Chemicals/Materials used:

Nickel nitrate hexahydrate [$Ni(NO_3).6H_2O$] were used. Pseudoboehmite from SudChemie was used as alumina binder. Zeolites CBV300 (SiO_2/Al_2O_3=5), CBV712 (SiO_2/Al_2O_3=12) and CBV760 (SiO_2/Al_2O_3=60) from Zeolyst International were used. Y zeolites CBV300, CBV712 and CBV760 is abbreviated as HY-5, HY-12 and HY-60 respectively.

3.1 Preparation of Catalysts

Our study focuses on the effect of catalyst preparation on hydroalkylation reaction. For this different types of catalysts were prepared using Ni as a base metal.

3.1.1 Preparation of Hydroalkylation Catalyst Employing different Ni content

Different weight percentage of Ni supported on Gamma alumina (Ni/γ-Al_2O_3) is prepared by wet impregnation method using Nickel nitrate hexahydrate and gamma alumina. A solution was prepared by adding some amount of Nickel nitrate hexahydrate in 20 ml deionised water. This solution was continuously stirred in a 50 ml beaker maintaining at room temperature for two hours. After two hours of mixing an amount of gamma alumina was added slowly to the solution. The mixture formed then was continuously stirred with the help of magnetic stirrer. After the impregnation, the mixture was placed in oven at 393K overnight to dry out excess water present in it. And the dried powder was calcined in Muffle furnace at 673K for 8 h in the presence of compressed air. The following Ni supported on Gamma alumina samples were produced: 5 wt% Ni/γ-Al_2O_3, 10 wt% Ni/γ-Al_2O_3, 20 wt% Ni/γ-Al_2O_3, and 30 wt% Ni/γ-Al_2O_3.

The catalysts with different Nickel content were prepared by using Ni/γ-Al_2O3 powder, HY-12 (SiO_2/Al_2O_3 = 12) Zeolite, and Binder alumina. A dry mixture was prepared by adding different Ni/γ-Al_2O_3 powder (5wt% Ni, 10wt% Ni etc.), HY-12 zeolite and Binder alumina. Prior to mixing HY12 zeolite was dried at 393K overnight and the ammonium form of HY-12 was calcined at 823K for 10 hours to convert to H form. This mixture was continuously mixed till homogeneity. After homogeneous mixing, dough was prepared by using a dilute solution of acetic acid (5%) as a kneading agent. Extrudates of 1.5 mm diameter and 3 cm length were formed from this dough using extrudater. The extrudates formed are dried at room temperature for around 10-12 h. The dried extrudates were calcined in a Tubular furnace at 673K for 4 h in the presence of Oxygen. The obtained extrudates were catalyst were mixed in the proportion as M/γ-Al_2O_3:HY-12: Binder in 1.67:4:1 weight ratio. The catalyst extrudates with different Ni/γ-Al_2O_3 powder are named as HAC-1, HAC-2, HAC-3, and HAC-4. A catalyst name HAC-1 is described in as 1.25 wt% Ni/ (γ-Al_2O_3-HY-12), HAC-2 as 2.5 wt% Ni/(γ-Al_2O_3-HY-12), HAC-3 as 5 wt% Ni /γ-Al_2O_3-HY-12, and HAC-4 as 7.5 wt% Ni /γ-Al_2O_3-HY-12. The various catalysts with different Ni weight percentage are described below in Table 2

Table 2: Hydroalkylation catalysts with different Ni weight Percent

S.No.	**Catalyst Name**	**Metal weight %**	**SiO_2/Al_2O_3**
1	HAC-1	1.25	12
2	HAC-2	2.5	12
3	HAC-3	5.0	12
4	HAC-4	7.5	12

3.1.2. Preparation of Hydroalkylation Catalyst with different SiO_2/Al_2O_3 Ratios

The catalysts with different SiO_2/Al_2O_3 were prepared by using 20 wt% Ni /γ-Al_2O_3 powder, H-form of different zeolites, and Binder alumina. A dry mixture was prepared by adding an amount of 20 wt% Ni/γ-Al_2O_3 powder, H-form Zeolites (HY-5, HY-12 and HY-60), and Binder alumina in the proportion of 1.67:4:1 weight ratio. Prior to mixing these zeolites were dried at 393K overnight and the ammonium form of zeolites was calcined at 823K for 10 hours to convert to H form. This mixture was continuously mixed till homogeneity. After homogeneous mixing, dough was prepared by using a dilute solution of acetic acid (5%) as a kneading agent. Extrudates of 1.5 mm diameter and 3 cm length were formed from this dough using extrudater. The extrudates formed are dried at room temperature for around 10-12 h. The dried extrudates were calcined in a Tubular furnace at 673K for 4 h in the presence of Oxygen. The catalyst extrudates with different zeolites are named HAC-5, HAC-3, and HAC-6 for zeolites HY-5, HY-12, and HY-60 respectively. The catalysts with different zeolite acidity are described below in Table 3

Table 3: Hydroalkylation catalysts with different SiO_2/Al_2O_3 ratio

S.No.	**Catalyst Name**	**Metal weight % (Ni wt%)**	**SiO_2/Al_2O_3 Ratio**
1	HAC-5	5	5
2	HAC-3	5	12
3	HAC-6	5	60

3.1.3. Preparation of hydroalkylation catalyst with different zeolite content

The catalysts with different zeolite content were prepared by using 20 wt% Ni/γ-Al_2O_3 powder, HY-12 (SiO_2/Al_2O_3 = 12) zeolite, γ-Al_2O_3, and Binder alumina. A dry mixture was prepared by adding an amount of 20Ni/γ-Al_2O_3 powder, HY-12 zeolite, and binder alumina in the proportion given in Table 4. Prior to mixing HY12 zeolite was dried at 393K overnight and the ammonium form of HY-12 was calcined at 823K for 10 hours to convert to H form. This mixture was continuously mixed till homogeneity. After homogeneous mixing, dough was prepared by using a dilute solution of acetic acid (5%) as a kneading agent. Extrudates of 1.5 mm diameter and 3 cm length were formed from this dough using extrudater. The extrudates formed are dried at room temperature for around 10-12 h. The dried extrudates were calcined in a Tubular furnace at 673K for 4 h in the presence of Oxygen. The catalyst extrudates with different zeolite weight percentage are named as HAC-7, HAC-8, HAC-9, HAC-3, and HAC-10 with a zeolite weight percent of 35%, 45%, 55%, 65%, and 74%. Gamma alumina is added to the mixture for balancing alumina to zeolite ratio to the required zeolite weight percent for example 1g of γ-Al_2O_3 is added to 5g of HY-12 for zeolite weight % of 55. The catalysts with different zeolite weight percentages are described below in Table 4.

Table 4: Hydroalkylation catalysts with different zeolite weight percent

S.No.	**Catalyst Name**	**Metal weight %**	**Zeolite:γ-Al_2O_3 :M/γ-Al_2O_3:Binder**	**Zeolite wt %**
1	HAC-10	5	14 : 0 : 5 : 1	74%
2	HAC-3	5	4 : 0 : 1.67 : 1	65%
3	HAC-9	5	3.33:0.67:1.67:1	55%
4	HAC-8	5	2.67:1.33:1.67:1	45%
5	HAC-7	5	2 : 2 : 1.67 : 1	35%

3.1.4. Preparation of transalkylation catalyst with different SiO_2/Al_2O_3 Ratios

The catalysts with different zeolites were prepared by using H-form of different Y-zeolites, and Binder alumina. A dry mixture was prepared by adding some amount of zeolite and binder alumina. Prior to mixing these zeolites were dried at 393K overnight and the ammonium form of zeolites was calcined at 823K for 10 hours to convert to H form. This mixture was continuously mixed till homogeneity. After homogeneous mixing, a dough was prepared by using dilute solution of acetic acid (5%) as a kneading agent. Extrudates of 1.5 mm diameter were formed from this mixture using extrudater. The extrudates formed are dried at room temperature for around 10-12 h. The dried extrudates were calcined in a Muffle furnace at 823K for 10 h. The catalyst extrudates with different SiO_2/Al_2O_3 are named as TAC-1, TAC-2, and TAC-3. A catalyst name TAC-1 is described in as zeolite HY-5 (SiO_2/Al_2O_3=5) with 35 wt% Alumina and so on.

Table 5: Transalkylation catalysts with different SiO_2/Al_2O_3 ratio

S.No.	**Catalyst Name**	**SiO_2/Al_2O_3 ratio**	**γ-Al_2O_3 to Zeolite ratio**	**Zeolite used**
1	TAC-1	5	35:65	HY-5
2	TAC-2	12	35:65	HY-12
3	TAC-3	60	35:65	HY-60

3.2 Catalyst characterization

3.2.1 X-Ray diffraction analysis

Room temperature X-ray diffraction patterns of the catalysts and metal on alumina powder were obtained using a PANalytical Aeris X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å, voltage = 40 kV and current = 7.5 mA). Scans were taken in the 2θ range 5° to 80° at increments of 0.01° with a time-step of 60s. The crystallite size of metal oxide is determine by using the Scherrer Equation i.e.

$$D = k.\lambda/(\beta.\cos\theta)$$

where, D = crystallite size ,k = 0.9 (Scherrer constant) ,λ = 0.15406 nm(wavelength), β = FWHM(Radians) and θ = Peak Position(Radians). Highscore software is used to determine the metal phases present in catalyst and also to compare the crystalline nature of zeolites.

3.2.2 Surface Area Measurement

The surface areas and porous characteristics of sorbents were tested by Micromeritics ASAP2020 gas adsorption analyzer. It used the principle of static volumetric technique and the measurements of standard nitrogen adsorption/desorption at 77 K after degassing samples (< 10−3 Torr) at 623 K for 3 h. The temperature is maintained at 77 K to test samples at a saturation pressure given by Nitrogen. The surface areas of materials can be calculated by BET (Brunauer–Emmett–Teller) equation. The BET equation is used to give the volume of gas needed to form a monolayer on the surface of the sample. The actual surface area can be calculated from a knowledge of the size and the number of the adsorbed gas molecules. Nitrogen is used most often to measure BET surface, but if the surface area is very low, argon or krypton may be used as both give a more sensitive measurement, because of their lower saturation vapor pressures at liquid nitrogen temperature. BET equation is given as

$$\frac{z}{(1\text{-}z)} * \frac{1}{V} = \frac{(c\text{-}1)*z + 1}{cV_{mono}}$$

Where, V is the volume of gas adsorbed at pressure p, V_{mono} is the amount of gas corresponding to one monolayer, z is the ratio of pressure of gas to saturation pressure and c is a constant. The surface area is calculated by V_{mono} and the specific surface area occupied by one molecule of adsorbed gas. The pore size distributions were obtained based on the BJH (Barret–Joyner–Halenda) method. The total pore volume, V_t, was estimated from the amount of N_2 adsorbed at a relative pressure of 0.95. The external surface area, micropore area, and micropore volume were estimated by employing the t-plot method [32].

3.2.3 Acidity Measurement

The structural acidity was determined by ammonia TPD using Altamira AMI 200 instrument. Prior to TPD studies, the catalyst was activated in helium flow for 2 h at 600 K. Then the sample was cooled to 373 K before the adsorption of ammonia. Subsequently, 6% NH_3 in helium (25 ml/min) was passed through the sample for 30 min followed by treatment in helium flow for 1 h. Desorption experiments were carried out in the temperature range of 373–873 K at a heating rate of 10 K/min [33]. The basic experiments in desorption is given as 1) Adsorption of one or more molecular species onto the sample surface at low temperature (frequently 300 K, but sometimes sub-ambient). 2) Heating of the sample in a controlled manner (preferably so as to give a linear temperature ramp) while monitoring the evolution of species from the surface back into the gas phase. The area under a peak is proportional to the amount originally adsorbed, i.e. proportional to the surface coverage and The position of the peak (the peak temperature) is related to the enthalpy of adsorption, i.e. to the strength of binding to the surface.

3.2.4 H_2 chemisorption

The reduction temperature was determined by Hydrogen TPR using Altamira AMI 200 instrument. Prior to TPR studies, the catalyst was activated in argon flow for 1 h at 623 K. Then the sample was cooled to 323 K before the adsorption of Hydrogen. Subsequently, 5% H_2 in argon (30 ml/min) was passed through the sample for 30 min followed by treatment in argon flow for 1 h. Reduction experiments were carried out in the temperature range of 323–973 K at a heating rate of 10 K/min [33].

3.2.5 Scanning electron microscope

Scanning electron microscope (SEM) is one of the common methods for imaging the microstructure and morphology of the materials. In SEM, an electron beam with low energy is radiated to the material and scans the surface of the sample. Several different interactions occur as the beam reaches and enters the material, which leads to the emission of photons and electrons from or near the sample surface [39]. It consists of an electron gun which is located on top of the column and emits electrons. The electrons are then accelerated to energy levels of typically 0.1-30 keV. With a hairpin tungsten gun which makes a high diameter electron beam to form high-resolution images and A high-vacuum environment that allows electrons moving without being scattered or absorbed by the air. The samples were placed on sample holder of Scanning Electron Microscope (INCA PentaFETx3) for studies and photographs were taken at the micrometer scale.

3.3 Catalyst Testing

3.3.1 Catalyst testing for Hydroalkylation reaction

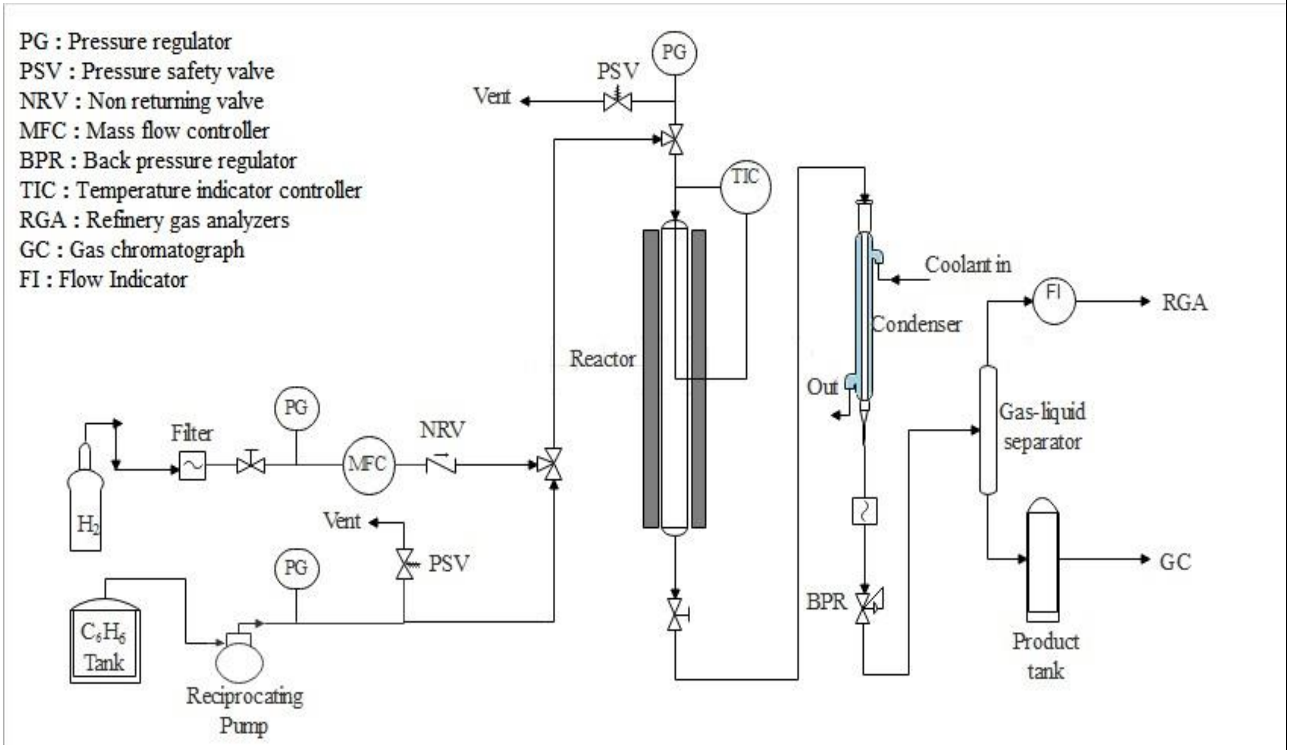


Figure 1: Reactor setup for catalyst testing of Benzene Hydroalkylation reaction.

Catalyst testing for Hydroalkylation reaction was carried out in a bench-scale unit as depicted in Fig. 1. The unit is equipped with a stainless steel fixed bed reactor of dimensions 47 cm × 1.1 cm with a thermowell for measurement of the catalyst bed temperature. Catalyst was placed in the reactor so as to have a minimum temperature gradient. Typically, about 5 g of catalyst extrudates were loaded in the reactor and during the loading process, the catalyst was divided into five batches. Following each batch of the catalyst, 80–120 mesh glass beads was packed into the void spaces of the catalyst bed to increase liquid hold up, improve catalyst wetting and reduce liquid back mixing and temperature gradient. Prior to the activity tests, catalyst was dried under H_2 flow overnight at 423 K followed by reduction at atmospheric pressure under 100 ml/min of H_2 at 573 K for 5 h. After reduction, the reactor was cooled to the desired temperature and then pressurized to the operating pressure and benzene was pumped using a high performance liquid chromatography pump (HPLC pump). The steady state products were collected and analyzed in the Gas chromatograph analyzer.

3.3.2 Catalyst testing for Transalkylation reaction

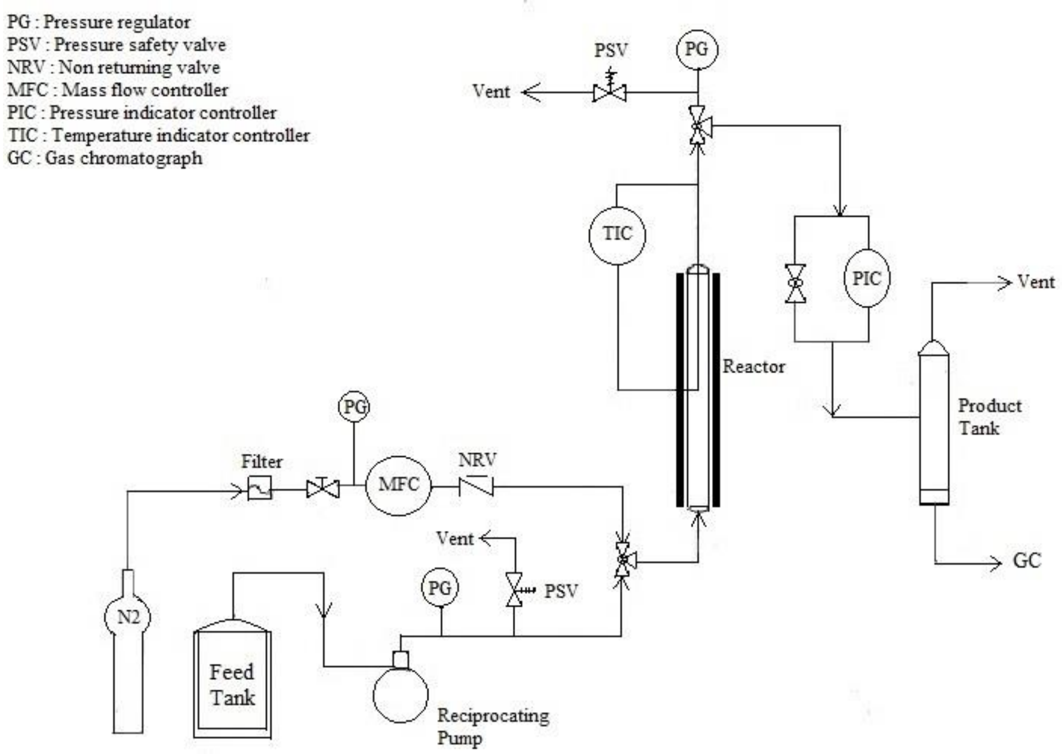


Figure 2: Reactor setup for catalyst testing of DCHB Transalkylation reaction.

Catalyst testing for Transalkylation reaction was carried out in a bench-scale unit as depicted in Figure 2. The unit is equipped with a stainless steel fixed bed reactor of dimensions 47 cm × 1.1 cm with a thermowell for measurement of the catalyst bed temperature. Catalyst was placed in the reactor so as to have a minimum temperature gradient. Typically, about 3.5 g of catalyst extrudates were loaded in the reactor and during the loading process, the catalyst was divided into three batches. Following each batch of the catalyst, 80–120 mesh glass beads were packed into the void spaces of the catalyst bed to increase liquid hold up, improve catalyst wetting and reduce liquid back mixing and temperature gradient. The reactor was pressurized to the operating pressure and the mixture of Benzene and Dicyclohexyl benzene (DCHB) was pumped using a high performance liquid chromatography pump (HPLC pump). The steady state products were collected and analyzed in the gas chromatograph analyzer.

3.4 Product analysis

The products were analyzed by employing GC technique (Agilent 6890N) gas chromatograph analyzer equipped with an FID and a DB-Petro column (100 m × 250 µm × 0.5 µm nominal).

The products are introduced as liquid form by using an injector. A volume of 1μl is injected into the instrument. FID is essentially a “carbon counter” it is invaluable for hydrocarbons in that it breaks the C-H bonds to form ions. Hydrogen and zero air are used for ignition and oxygen source respectively to produce the flame. Helium is used as carrier gas and compressed air is used for the cooling purpose. The sample is allowed to boil in the flame and the compound are going to appear on an online software attached to GC in increasing order of their boiling point.

3.4.1 Benzene Hydroalkylation reaction

Calculation of Conversion

The conversion of benzene for the hydroalkylation reactions are calculated as given. In this reaction, benzene is reacted with hydrogen gas. The conversion for this reaction is calculated on the weight of benzene converted to form the products.

$$\text{Benzene conversion (wt\%)} = \frac{((\text{Benzene wt\%})_{\text{feed}} - (\text{Benzene wt\%})_{\text{product}}) * 100}{(\text{Benzene wt\%})_{\text{feed}}}$$

Calculation of Selectivity

For Hydroalkylation reaction, product selectivity can be calculated as

$$\text{Product selectivity (wt\%)} = \frac{(\text{Product wt\%}) * 100}{(\text{wt\% of Benzene reacted})}$$

For this reaction, product yield(wt%) is the same as wt% of product. Here, (wt% of Benzene)$_{\text{Feed}}$ and (wt% of Benzene)$_{\text{product}}$ are the weight percent of Benzene present in Feed and Product stream respectively. The wt% of Benzene reacted is same as benzene conversion (wt%) and the calculation of Product selectivity is same for all the products like CHB, Cyclohexane, MCP, and others.

3.4.2 DCHB Transalkylation reaction

Calculation of Conversion

In this reaction, Benzene is reacted with Dicyclohexyl benzene(DCHB). The conversion for this reaction is calculated on the weight of Benzene and DCHB converted to form products.

$$\text{Benzene conversion (wt\%)} = \frac{((\text{Benzene wt\%})_{\text{feed}} - (\text{Benzene wt\%})_{\text{product}}) * 100}{((\text{Benzene wt\%})_{\text{feed}} + (\text{DCHB wt\%})_{\text{feed}})}$$

And,

$$\text{DCHB conversion (wt\%)} = \frac{((\text{DCHB wt\%})_{\text{feed}} - (\text{DCHB wt\%})_{\text{product}}) * 100}{((\text{Benzene wt\%})_{\text{feed}} + (\text{DCHB wt\%})_{\text{feed}})}$$

Calculation of Selectivity

For transalkylation reaction ,product selectivity can be calculated as

$$\text{Product selectivity (wt\%)} = \frac{(\text{Product wt\%}) * 100}{((\text{wt\% of Benzene reacted}) + (\text{wt\% of DCHB reacted})}$$

Here, the product in this reaction can be CHB, MCP, and other byproducts. And product yields(wt%) is calculated as the multiplication of Conversion and product selectivity (wt%). The $(\text{wt\% of Benzene})_{\text{feed}}$ and $(\text{wt\% of Benzene})_{\text{product}}$ are the amount of Benzene present in Feed and product respectively and the same is for DCHB. The Wt% of Benzene and DCHB reacted is same as Benzene conversion (wt%) and DCHB conversion (wt%) respectively.

4. Results and discussion

4.1 Effect of amount of metal on benzene hydroalkylation activity and selectivity

The catalysts with lower amount of metal content showed lower benzene conversion and CHB selectivity while the catalysts with higher amount of metal content showed high benzene conversion and low CHB selectivity with a higher selectivity of by-products. So an optimum amount of Ni content in Ni/HY-12 zeolite is required with a higher yield and selectivity for CHB. So the effect of nickel loading on the catalysts is studied on the activity and selectivity of benzene hydroalkylation is studied by using catalysts HAC-1, HAC-2, HAC-3, and HAC-4 having Nickel weight percent of 1.25, 2.5, 5, and 7.5 respectively.

4.1.1.Textural and chemical properties of catalysts

- **X-Ray diffraction**

The X-ray powder diffraction (XRD) is a rapid analytical technique primarily used are used to estimate phase identification of a crystalline material and can provide information on unit cell dimensions. The graphs obtained from XRD are analyzed in the Highscore application to determine the crystalline form of particular metals or zeolites.

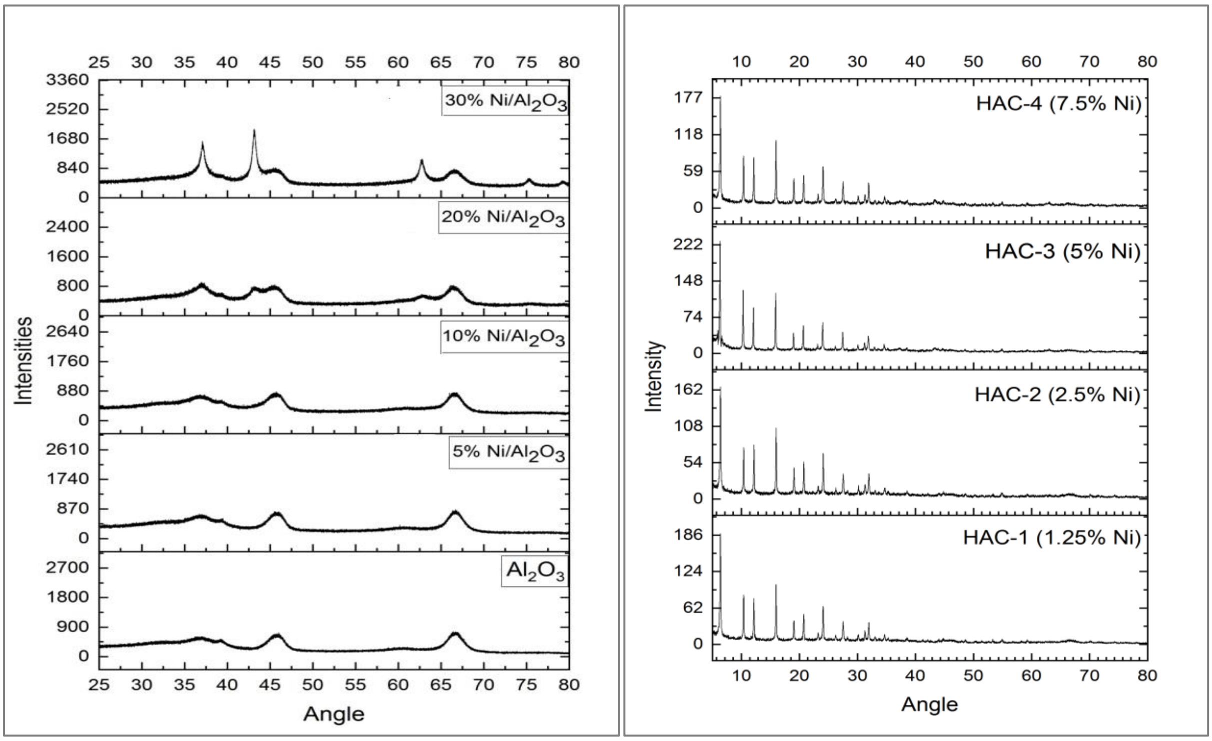


Figure 3: XRD pattern for (a) metal supported alumina with different metal % and (b) different metal % in catalyst.

In figure 3(a), X-ray diffraction spectra of Metal supported powders, the presence of peaks at 2θ = 37.10°, 43.20°, 75.2^0 corresponding diffraction planes confirmed the formation of a NiO and for a peak at 2θ value of 63^0 and 66^0 corresponding diffraction planes of Ni (101). In this figure sample with different weight % of metal supported by alumina is shown and as the metal percentage increases, the phases of NiO - Ni began to appear. Figure 3(b) shows the XRD pattern of catalyst with different metal % ranging from 1.25 wt% Ni to 7.5 wt% Ni.

- **BET Surface area and pore volume**

The BET surface area, external surface area, pore volume, and micropore volume data of the catalysts with different nickel content are shown in Table 6.

Table 6: Chemical and Physical properties of Hydroalkylation catalysts with different Ni wt%

S. No.	Catalyst	Ni wt%	BET Surface Area (m^2/g)		External Surface Area (m^2/g)		Micro Pore Area (m^2/g)		Pore Volume (cm^3/g)		Micropore volume (cm^3/g)	
			*	**	*	**	*	**	*	**	*	**
1	HAC-1	1.25	774	490	121	123	653	367	0.46	0.45	0.26	0.15
2	HAC-2	2.5	774	405	121	66	653	339	0.46	0.38	0.26	0.17
3	HAC-3	5	774	459	121	83	653	376	0.46	0.36	0.26	0.15
4	HAC-4	7.5	774	494	121	126	653	368	0.46	0.41	0.26	0.15

* Data for initial zeolite ** Data for the final catalyst

It can be observed that the surface area of the catalysts increases with an increase of nickel content in the catalyst. The prepared catalysts range from nickel content of 1.25 to 7.5 weight %. It is also observed that the pore volume of catalyst containing more nickel is greatest among them except for 1.25. It is observed that the surface area and pore volume of the support got reduced after the impregnation of metal. This is due to the dispersion of the metal oxide on the surface of silica-alumina which reduces the available area for N_2 Adsorption.

- **Acidity measurement**

NH_3-TPD was used to estimate the amount and the strength of acid sites formed on the surface of the catalyst. Figure 4(a) shows similar desorption patterns, with two distinct regions, from 373K to 600 K and 600 K to 873 K, respectively, indicating that the samples have two kinds of acid sites, weak acid sites and the strong acid sites. The high temperature peaks correspond to the NH_3 desorption at strong acid sites and low temperature peaks correspond to a number of reasons as desorption of weakly adsorbed NH_3 on weak acid sites, weak bronsted or lewis acid sites or to the formation of $NH_4^+(NH_3)_n$ ($n \geq 1$) groups as mentioned elsewhere [33,34].The corresponding low temperature peaks of 1.25, 2.5, 5, and 7.5wt % of nickel in samples are 504 K, 505 K, 507 K, and 500 K. The high temperature peaks are at 663 K, 647 K, 650 K, and 648 K. The total acid site concentration, weak acid site concentration, and strong acid site concentration are obtained from deconvoluting NH3 -TPD data of catalyst with different Ni content are listed in Table 7. The total number of acid sites decreases with increase in metal weight percentage of catalyst. This may be due to the impregnation of metal sites on the surface of acid sites thereby decreasing the number of acid sites available for the alkylation of cyclohexene.

- **H_2 chemisorption**

Temperature programmed reduction (TPR) tells us about the temperature of reduction of the catalyst which is in oxide form to its metallic state. The catalyst discussed here is the NiO impregnated on Zeolite-alumina. For reduction of the metallic species the possible transitions. Ni^{2+} - Ni^0 (NiO to Ni). Samples with lesser Nickel content have hydrogen adsorption at high temperature of 850K but these peaks are due to reduction of nickel aluminate present in samples. The absence of low reduction temperature may be due to less content of nickel oxide in it. Catalyst HAC-3 and HAC-4 are reducing at a temperature of around 740K indicate the presence of a high amount of nickel oxide.

Table 7: Acidity data of Hydroalkylation catalysts with different Ni weight percent

S.No.	Catalyst name	Total acid sites concentration (μmol NH_3/g cat)	Peak Temperatures Tmax TPD (K)	Weak acid sites (μmol/g)	Strong acid sites (μmol/g)
1	HAC-1	225.3	504, 663	55.46	169.84
2	HAC-2	210.9	505, 647	55.74	155.16
3	HAC-3	184.5	507, 650	45.63	138.87
4	HAC-4	163.53	500, 648	38.56	124.97

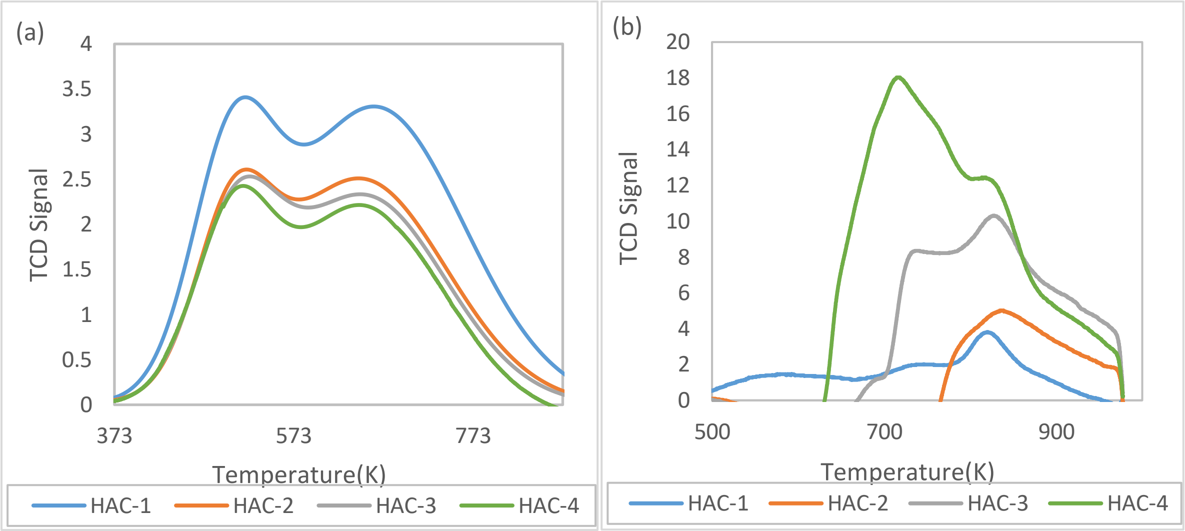


Figure 4: (a) TPD profile of different Ni wt% on alumina (b) TPR profile of different Ni wt% on alumina.

4.1.2 Effect of metal on activity and selectivity for benzene hydroalkylation

To study the effect of Ni loading on the catalytic activity, benzene hydroalkylation reaction was conducted at WHSV=1–1.5 h^{-1}, P=20 bar, T=423 K, and H_2/C_6H_6 mole ratio of 1. The catalytic performance of catalysts with different Ni wt% was compared and the observed result is shown in Table 8.

Table 8: Effect of metal loading on hydroalkylation product distribution

Catalyst	**HAC-1**	**HAC-2**	**HAC-3**	**HAC-4**
Benzene conversion %	4.45	8.94	45.11	44.63
WHSV (h^{-1})	1	1	1.5	1.5
Selectivity %				
Cyclohexane	0.23	0.11	9.28	9.97
CHB	85.04	94.21	74.2	74.9
DCHB& Others	14.73	5.68	16.52	15.13
CHB Yield, Wt.%	3.79	8.42	33.47	33.43

Operating conditions: P=20 bar, Temp= 423K, H_2/C_6H_6 (mole ratio) = 1, and Time on stream(TOS)=24 hrs

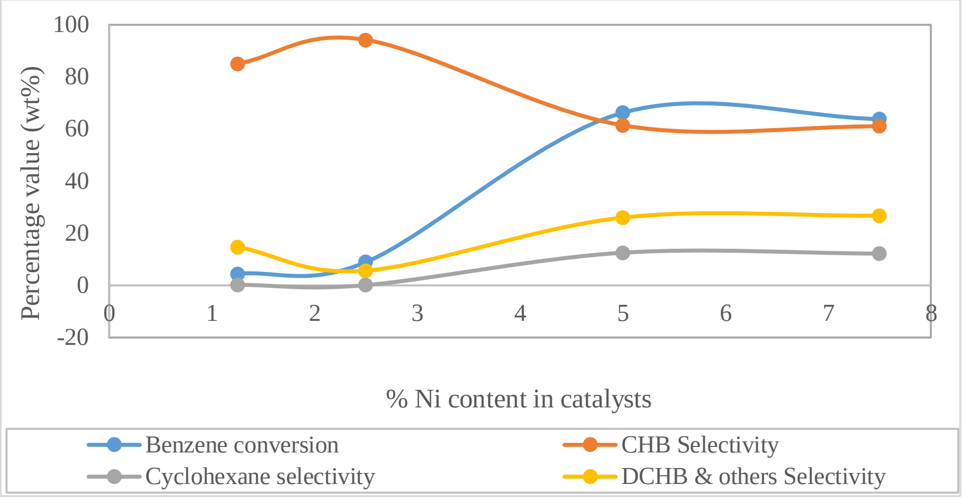


Figure 5: Effect of Ni content on Benzene conversion and selectivity of hydroalkylation products.

The catalysts with low metal content have less sites for hydrogenation of benzene to cyclohexene, which is reported for catalysts HAC-1 (1.25 wt% Ni) & HAC-2 (2.5 wt% Ni). For a catalyst with lower Ni wt % such as 1.25% and 2.5%, benzene conversion is observed as 4.45 wt% and 8.94 wt %. With higher metal content in catalysts benzene can be completely hydrogenated to cyclohexane i.e. low selectivity for Cyclohexylbenzene, so an optimum amount of metal (Ni) is required for partial hydrogenation of benzene as reported for catalysts HAC-3 (5wt% Ni) & HAC-4 (7.5 wt% Ni). For catalysts with higher Ni wt % of 5 % and 7.5%, around 45% of benzene is converted to give a higher CHB selectivity as shown in figure 5.

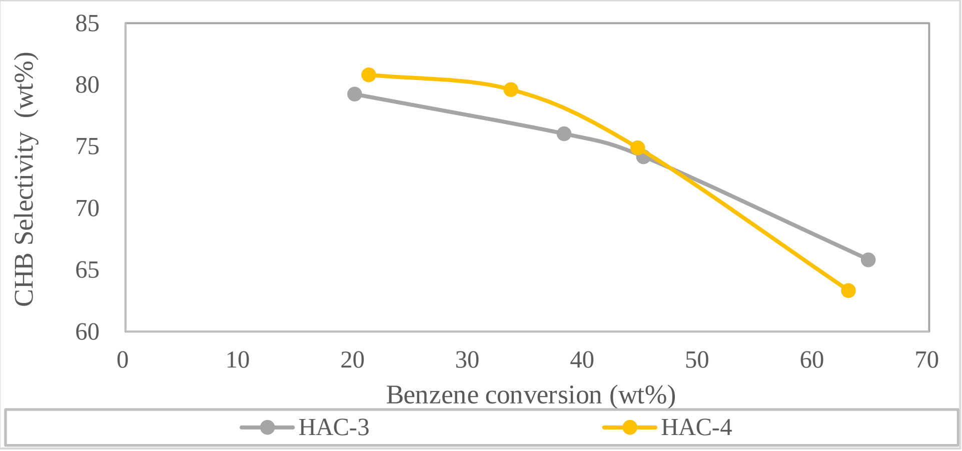


Figure 6: Benzene conversion versus CHB selectivity data of catalysts with different Nickel content.

The catalyst HAC-3 and HAC-4 gave higher CHB Selectivity at low benzene conversion and contact time higher than 0.5 hours. These catalysts gave almost the same cyclohexylbenzene selectivity for similar benzene conversion and operating conditions as shown in figure 6. With the increase in benzene conversion leads to higher amount cyclohexene present on metal sites of catalyst that reacts with hydrogen and cyclohexylbenzene i.e. higher selectivity of by-products such as cyclohexane, di-cyvlohexylbenzene, etc.. So benzene conversion of around 45%-50% is desired for a higher CHB selectivity as suggested in the literature [5, 12, 18, 22].

4.1.3 Summary

The catalysts HAC-3 and HAC-4 have reported similar physical and chemical properties such as BET surface area, micropore volume, and reduction temperature. The catalysts HAC-3 & HAC-4 showed good activity for benzene hydroalkylation at same WHSV of $1.5h^{-1}$. But the catalyst with 1.25 Ni wt% and 2.5 wt % have a lower benzene conversion for a higher contact time which is similar to the results given by Fahy et al..HAC-3 and HAC-4 gave around 45% Benzene conversion with 74% CHB Selectivity at similar reaction conditions. So the catalyst with 5 wt% Ni is considered as the best catalyst as on increasing Ni wt % to 7,5% there is no change in activity of reaction.

4.2 Effect of zeolite acidity on hydroalkylation product distribution

The catalysts with different acidity i.e. zeolite with different Si/Al ratio was studied in the literature [5-23]. Pd impregnated Y-zeolites and beta zeolites have given the best results for benzene hydroalkylation reaction [18,22]. Li et al. have stated that the acidity of catalyst is necessary for the alkylation of cyclohexene with benzene to form Cyclohexylbenzene. So the effect zeolite acidity on the activity and selectivity of benzene hydroalkylation is studied by using catalysts HAC-5, HAC-3, and HAC-6 having the silica-alumina ratio of 5, 12, and 60 respectively.

4.2.1 Textural and Chemical properties of catalysts

- **X-Ray Diffraction**

The X-ray powder diffraction (XRD) is a rapid analytical technique primarily used are used to estimate phase identification of a crystalline material such as zeolites. Figure 7 shows XRD pattern of the nickel-based catalyst with zeolites of different acidity and it similar to the respective zeolite.

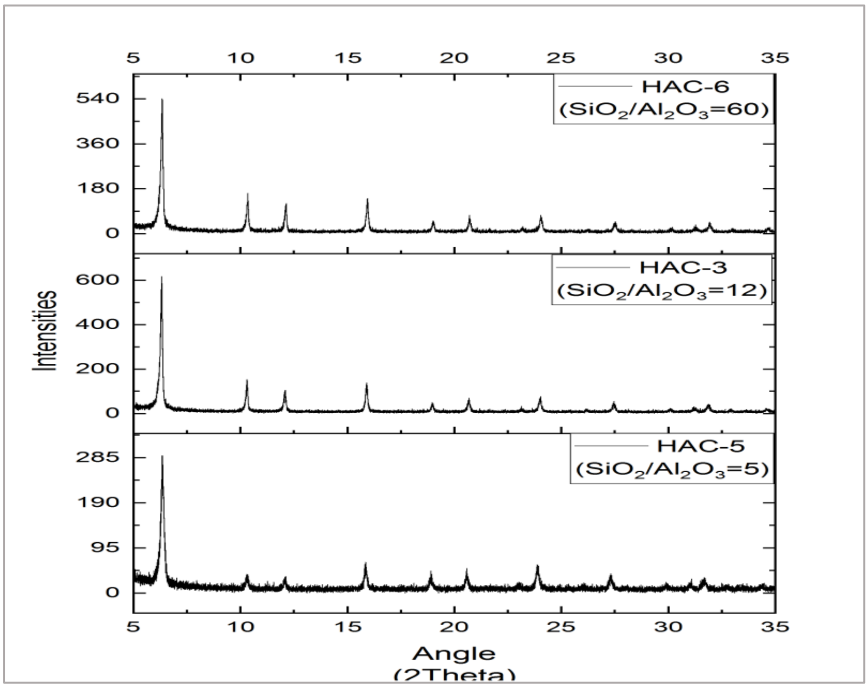


Figure 7: XRD Pattern of Catalyst with different SiO_2/Al_2O_3 ratio

- **BET surface area and pore volume**

The BET surface area, external surface area, pore volume, and micropore volume data of the catalysts with different acidity are shown in Table 9.

Table 9: Chemical and physical properties of catalysts with different SiO_2/Al_2O_3 ratio

S. No.	**Catalyst**	**SiO_2/Al_2O_3 ratio**	**BET Surface Area (m^2/g)**		**External Surface Area (m^2/g)**		**Micro Pore Area (m^2/g)**		**Pore Volume (cm^3/g)**		**Micropore volume (cm^3/g)**	
			*	**	*	**	*	**	*	**	*	**
1	HAC-5	5	841	436	134	129	707	307	0.38	0.33	0.32	0.13
2	HAC-3	12	774	459	121	83	653	376	0.46	0.36	0.26	0.15
3	HAC-6	60	720	586	107	231	613	355	0.55	0.49	0.34	0.15

* Data for initial zeolite ** Data for the final catalyst

The catalysts being meso structured have pores in the range of 2-50 nm. The pores are usually cylindrical in shape but can be partially distorted. The BET surface area and pore volume of the catalysts increase with an increase in acidity(SiO_2/Al_2O_3)of Y-zeolite.

- **Acidity measurement**

NH_3-TPD was used to estimate the amount and the strength of acid sites formed on the surface of the catalyst. Figure 8(a) shows similar desorption patterns, with two distinct regions, from 373K to 600 K and 600 K to 873 K, respectively, indicating that the samples have two kinds of acid sites, weak acid sites and the strong acid sites. The peaks represent the temperature at which NH_3 is desorbed from the surface of the catalyst. The corresponding low temperature peaks of SiO_2/Al_2O_3 ratio of 5, 12, and 60 samples are 503 K, 507 K, and 503 K. The high temperature peaks are at 649 K, 650 K, and 659 K. In Figure 8(a) NH_3-TPD pattern for catalysts having different acidity is shown. From this figure, it is clearly known that HAC-5 contains higher number acid sites as compared to others. The number of strong and weak acid sites decreases with an increase in the ratio of SiO_2/Al_2O_3.

- **H_2 chemisorption**

TPR tells us about the temperature of reduction of the catalyst which is in oxide form to its metallic state. The catalyst discussed here is the NiO impregnated on Zeolite - alumina. For reduction of the metallic species the possible transitions. Ni^{2+} - Ni^0 (NiO to Ni).

Table 10: Acidity data of hydroalkylation catalysts with different SiO_2/Al_2O_3 ratio.

S. No.	**Catalyst**	**Total acid sites concentration (µmol NH_3/g cat)**	**Peak Temperatures T_{max}TPD (K)**	**Weak acid sites (µmol/g)**	**Strong acid sites (µmol/g)**
1	HAC-5	414.4	503, 649	123.79	290.61
2	HAC-3	184.5	507, 650	45.63	138.87
3	HAC-6	158.2	503, 659	37.40	120.8

The samples with moderate alumina content (SiO_2/Al_2O_3=12) have low reduction temperature as compared to low(SiO_2/Al_2O_3=60) and high(SiO_2/Al_2O_3=5) alumina content. Catalyst HAC-3 reduced at a lower temperature as compared to other catalysts. The second peak in reduction temperature is because of the formation of Ni-Al Compounds as shown in figure 8(b).

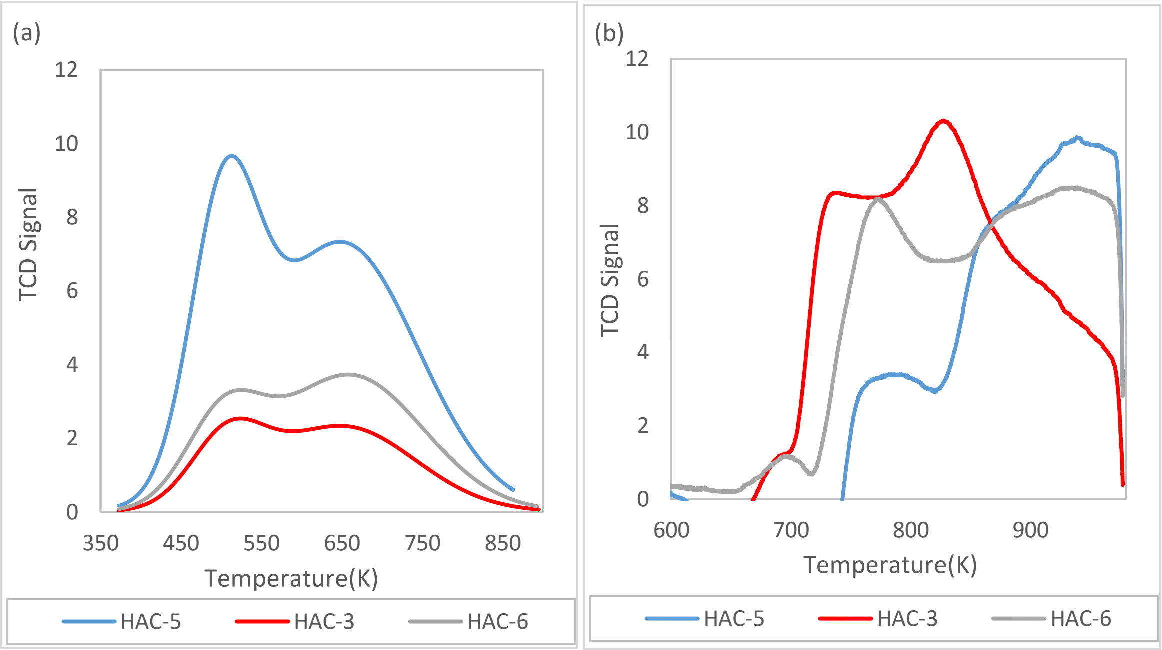


Figure 8: (a) TPD profile of catalysts with different SiO_2/Al_2O_3 ratio (b)TPR profile of catalysts with different SiO_2/Al_2O_3.

4.2.2 Activity of different Ni/HY catalysts for benzene hydroalkylation

To study the effect of zeolite acidity on the hydroalkylation products distribution, benzene hydroalkylation was carried out at P=20bar, T= 423K, H_2/C_6H_6 mole ratio = 1 and WHSV of around 0.5 (h^{-1}) to $2h^{-1}$on 5 wt% Ni loaded HY5, HY12 and HY60. The obtained results are presented in Table 11.

Table 11: Effect of catalyst acidity on the activity of hydroalkylation reaction.

Catalyst	**HAC-5**	**HAC-3**	**HAC-6**
Benzene conversion %	43.86	45.11	43.5
WHSV (h^{-1})	2	1.5	0.7
Selectivity %			
Cyclohexane	26.2	9.28	6.77
CHB	57.88	74.2	65.11
DCHB& Others	16.92	16.52	28.12
CHB Yield, Wt.%	25.38	33.47	28.32

Operating conditions : P=20 bar, Temp= 423K, H_2/C_6H_6 (mole ratio) = 1 and TOS=24 hrs

In Table 11, comparison of catalysts with different zeolite at the same benzene conversion is shown. For a catalyst HAC-5 having a silica-alumina ratio of 5, selectivity of cyclohexane is highest as compared to others at the same benzene conversion of hydroalkylation reaction. The selectivity of higher alkyl aromatics compounds is more for catalyst with silica to alumina ratio of 60. Zeolite with Silica to alumina ratio of 12 gave the highest selectivity and yield for cyclohexylbenzene as compared to other Y- zeolite having the same hydroalkylation activity.

Table 12 : Effect of zeolite on hydroalkylation activity at similar operating conditions

Catalyst	HAC-5	HAC-3	HAC-6
Benzene conversion %	43.86	38.20	21.74
WHSV (h^{-1})	2	2	2
Selectivity %			
Cyclohexane	26.2	8.65	8.39
CHB	57.88	76.04	77.06
DCHB& Others	16.92	15.31	14.55
CHB Yield, Wt.%	25.38	29.05	16.75

Operating conditions : P=20 bar, Temp= 423K, H_2/C_6H_6 (mole ratio) = 1 and TOS=24 hrs

The activity of hydroalkylation reaction decreases with the increase of Silica to alumina ratio in catalyst at the same operating conditions such as similar temperature, pressure, feed ratio, and contact time as shown in Table 12. Cyclohexylbenzene selectivity increases with increase in silica to alumina ratio. The catalyst HAC-5 has very low CHB selectivity for high benzene conversion at different contact time. The catalyst HAC-3 have moderate benzene conversion with highest selectivity of cyclohexylbenzene as compared to HAC-5 and HAC-6 as shown in figure 9(b). The catalyst with silica to alumina ratio of 60 also gave higher CHB selectivity for low benzene conversion of 18%, but the selectivity for CHB is decreasing more with an increase in benzene conversion and contact time as compared to catalyst HAC-3 as shown in figure 9(b). The catalyst HAC-5 provided more acidic sites as compared to HAC-3 & HAC-6 that leads to fast alkylation of cyclohexene with cyclohexylbenzene to produce di-cyclohexylbenzene.

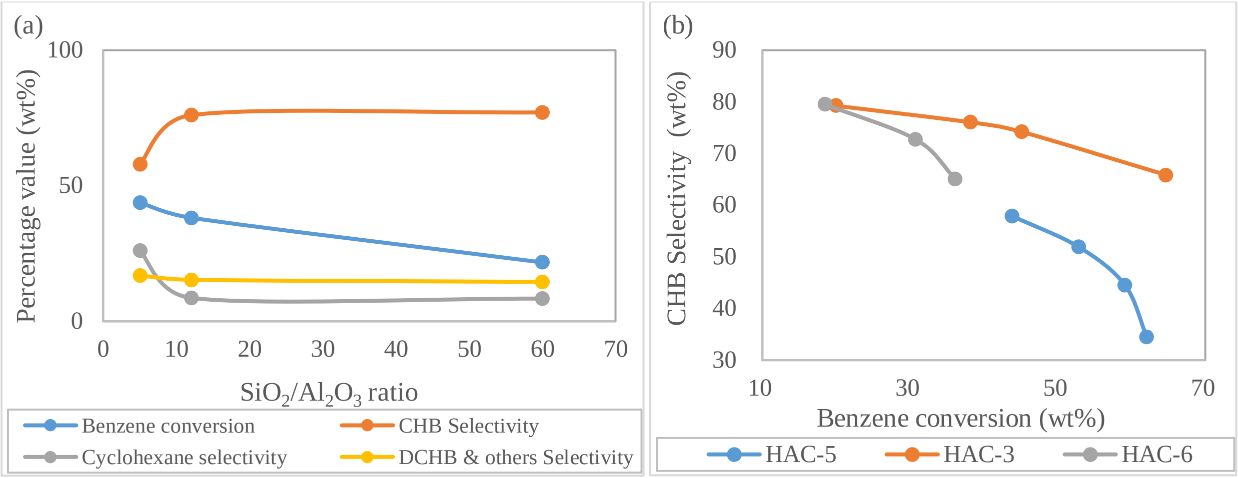


Figure 9: (a) Effect of acidity on Benzene conversion and CHB selectivity (b) Benzene conversion versus CHB selectivity for catalysts with different acidity.

4.2.3 Summary

HAC-3 is having moderate surface area as well as acidity as compared to HAC-5 and HAC-6. The catalyst with moderate acidity i.e. HAC-3 gave better activity of Benzene hydroalkylation followed by HAC-6, HAC-5 for WHSV of around 0.7h^{-1} to 2h^{-1}. CHB selectivity (wt%) and yield (wt%) of HAC-3 is higher as compared to that of HAC-5, HAC-6, and for almost same benzene conversion. It is noticed that for a 5 wt% Ni catalyst, moderate acid i.e. HAC-3 is best as support for hydroalkylation reaction.

4.3 Effect of zeolite content on benzene hydroalkylation

In the literature reported, several researchers have discussed the importance of zeolites as acid catalysts for the alkylation of cyclohexene and benzene. Different zeolites and inorganic oxide was used as a support for the hydrogenating metal [7-23]. In this research, γ-Al_2O_3 is used as non-acidic support and a particular percent of zeolite as acidic support is required. So to determine the amount of zeolite in the catalyst for best activity and selectivity of benzene hydroalkylation is studied by using catalysts HAC-10, HAC-3, HAC-9, HAC-8, and HAC-7 having Zeolite weight percentage of 74, 65, 55, 45, and 35 respectively.

4.3.1 Textural and Chemical properties of catalysts

- **X- Ray Diffraction**

The X-ray powder diffraction (XRD) is a rapid analytical technique primarily used are used to estimate phase identification of a crystalline material such as zeolites. The intensity and the crystallanity (clarity of peaks) of sample increases with increases in the zeolite content of 5 wt% nickel catalyst from 35% to 74% as shown in figure 10.

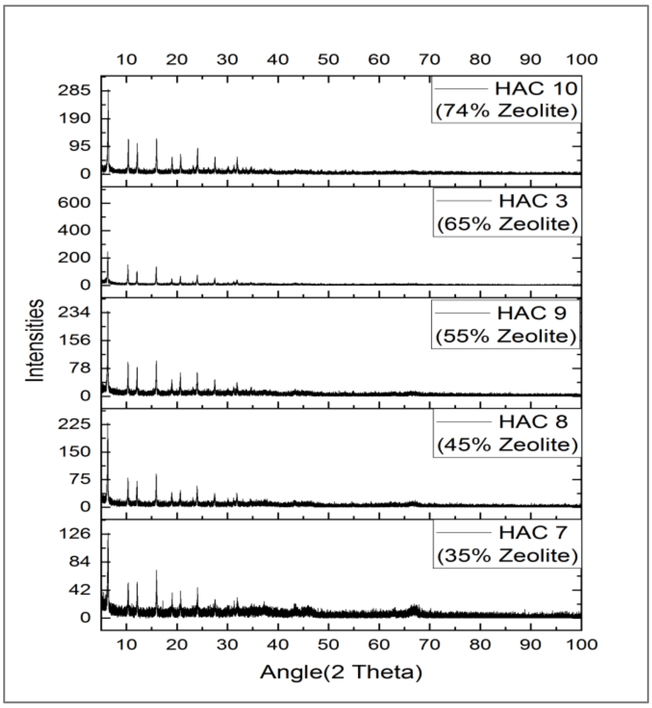


Figure 10: XRD pattern of Hydroalkylation catalysts with different zeolite weight percent.

- **BET surface area and pore volume**

The BET surface area, external surface area, pore volume, and micropore volume data of the catalysts with different zeolite weight percent are shown. Also surface area and micropore volume of the catalysts increases with increase in the ratio of Zeolite to alumina content in catalysts. This is due to increase in the surface available for metal impregnation.

Table 13: Chemical & Physical properties of Hydroalkylation catalysts with different zeolite weight percent.

S. No	**Catalyst**	**Zeolite weight %**	**BET Surface Area (m^2/g)**		**External Surface Area (m^2/g)**		**Micro Pore Area (m^2/g)**		**Pore Volume (cm^3/g)**		**Micropore volume (cm^3/g)**	
			*	**	*	**	*	**	*	**	*	**
1	HAC-10	74%	774	549	121	113	653	436	0.46	0.45	0.26	0.18
2	HAC-3	65%	774	459	121	83	653	376	0.46	0.36	0.26	0.15
3	HAC-9	55%	774	470	121	156	653	314	0.46	0.48	0.26	0.13
4	HAC-8	45%	774	391	121	144	653	247	0.46	0.43	0.26	0.10
5	HAC-7	35%	774	318	121	148	653	170	0.46	0.46	0.26	0.07

* Data for initial zeolite ** Data for the final catalyst

- **Acidity measurement**

NH_3-TPD was used to estimate the amount and the strength of acid sites formed on the surface of the catalyst. Figure 11(a) shows similar desorption patterns, with two distinct regions, from 373K to 600K and 600K to 873K, respectively, indicating that the samples have two kinds of acid sites, weak acid sites and the strong acid sites. The peaks represent the temperature at which NH_3 is desorbed from the surface of the catalyst. The corresponding low temperature peaks of 74, 65, 55, 45, and 35wt % of Zeolite in samples are 497 K, 507 K, 491 K, 504 K, and 503 K. The high temperature peaks are at 669 K, 650 K, 651 K, 645 K, and 655 K. The total number of acid sites increases with increase in zeolite content of nickel-based catalyst. The strong and weak acid sites for nickel-based catalysts also increases with the increase in zeolite content of catalysts.

Table 14: Acidity data of Hydroalkylation catalysts with different zeolite weight percent

S.No.	**Catalyst**	**Total acid sites concentration (µmol NH_3/g cat)**	**Peak Temperatures T_{max} TPD (K)**	**Weak acid sites (µmol/g)**	**Strong acid sites (µmol/g)**
1	HAC-10	205	497, 669	44.97	160.03
2	HAC-3	184.5	507, 650	45.63	138.87
3	HAC-9	173.1	491, 651	36.37	136.83
4	HAC-8	171.8	504, 645	36.58	135.22
5	HAC-7	142.9	503, 655	29.07	113.87

- **H_2 chemisorption**

TPR tells us about the temperature of reduction of the catalyst which is in oxide form to its metallic state.The catalyst discussed here is the NiO impregnated on Zeolite - alumina. For reduction of the metallic species the possible transitions. Ni^{2+} - Ni^{0} (NiO to Ni). There is no change in reduction temperature for the catalysts with different zeolite-alumina ratio.

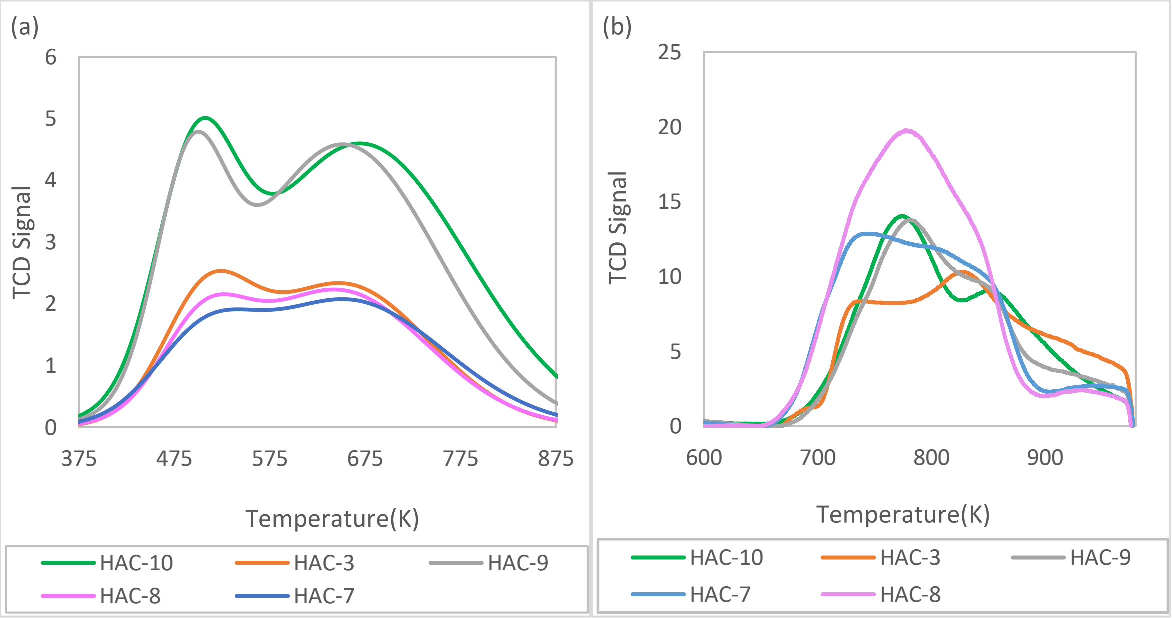


Figure 11: (a) TPD Profile of hydroalkylation catalysts with different zeolite weight percent. (b) TPR Profile of hydroalkylation catalysts with different zeolite weight percent.

- **Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (SEM) is used to determine the physical representation of catalyst i.e. the shape of pores on the surface of catalyst. The shape can be square, rectangle, hexagonal, circle depending on the crystalline nature of sample. In figure 12, The zeolite with a silica-alumina ratio of 12 is shown with pore shape similar to rectangle or hexagonal.

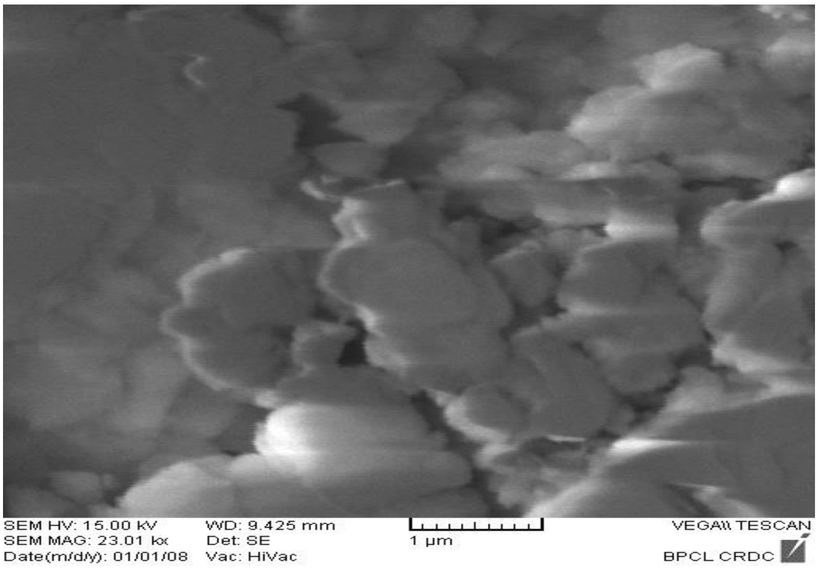


Figure 12: SEM image of zeolite CBV-712.

4.3.2 Activity of different catalysts for benzene hydroalkylation

To study the effect of zeolite content of the catalyst on the hydroalkylation product distribution, benzene hydroalkylation was carried out at P=20bar, T= 423 K, H_2/C_6H_6 mole ratio = 1 on 5 wt% Ni loaded HY12 with different zeolite to alumina ratio. The obtained results are presented in Table 15.

Table 15: Effect of zeolite content of the catalyst on hydroalkylation activity

Catalyst	HAC-10	HAC-3	HAC-9	HAC-8
Benzene conversion %	44.12	45.11	41.14	38.84
WHSV (h^{-1})	2.5	1.5	1.6	1
Selectivity %				
Cyclohexane	8.58	9.28	9.24	5.41
CHB	77.88	74.2	68.20	68.17
DCHB& Others	13.54	16.52	22.56	26.42
CHB Yield, Wt.%	34.32	33.47	28.06	26.67

Operating conditions: P=20 bar, Temp= 423 K, H_2/C_6H_6 (mole ratio) = 1 and TOS=24 hrs

The catalyst with 74 wt% Zeolite (HAC-10) gave CHB Selectivity of 77% for a benzene conversion of 44%and catalyst with 65wt% Zeolite (HAC-3) gave an almost similar result for a Benzene conversion of 45%. But catalysts with less weight percentage of zeolite such as HAC-9, HAC-8 & HAC-7 are not stable during the reaction, benzene conversion for these catalysts is continuously decreasing.

Table 16: Effect of zeolite content of the catalyst on hydroalkylation product distribution

Catalyst	**HAC-10**	**HAC-3**	**HAC-9**
Benzene conversion %	50.35	38.20	30.83
WHSV (h^{-1})	2	2	2
Selectivity %			
Cyclohexane	8.72	8.65	9.48
CHB	72.69	76.04	69.29
DCHB & Others	20.59	15.31	21.23
CHB Yield, Wt.%	33.47	29.05	21.36

Operating conditions: P=20 bar, Temp= 423 K, H_2/C_6H_6 (mole ratio) = 1 and TOS=24 hrs

In figure 13 (b), it is shown that catalysts with zeolite weight percent 65 wt% and 74 wt% have a higher selectivity for cyclohexylbenzene at moderate benzene conversion for a contact time of 0.5 hours. The catalyst HAC-9 with zeolite weight percent of 55 wt% gave low CHB selectivity as compared to HAC-3 and HAC-10 as shown in Table 16.

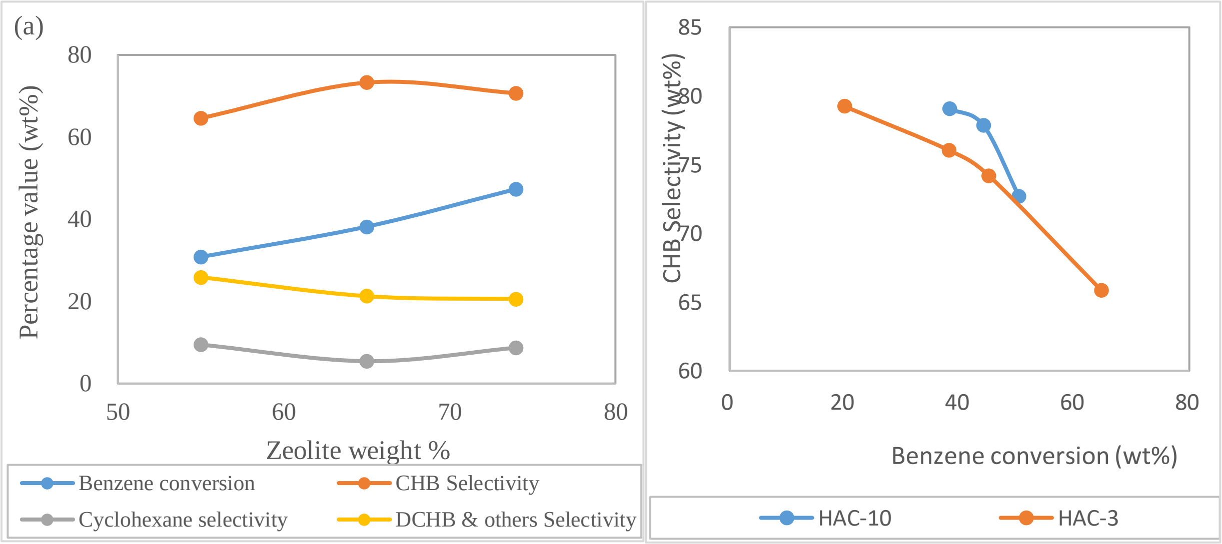


Figure 13: (a) Effect of zeolite content on hydroalkylation activity and selectivity. (b) Benzene conversion versus CHB selectivity for catalyst with different zeolite weight percent.

The catalyst with zeolite wt% of 65 (HAC-3) gave similar results as that of the catalyst with 74 wt% zeolite at higher benzene conversion of 48%. So there is no need to increase the zeolite content and it will also make reaction economical.

4.3.3 Summary

The selectivity and yield of CHB increase with an increase in the weight percentage of zeolite in catalysts for similar benzene conversion. Catalyst HAC-9 also show some of these signs but after reduced at a higher temperature, it becomes stable. The instability in the reaction is due to lower number of acid sites for reaction and a particular metal to acid sites ratio is required for benzene hydroalkylation reaction to proceed [17].

5. Effect of operating conditions on hydroalkylation of benzene

To find the best operating conditions on the activity and selectivity of the catalyst HAC-3 for benzene hydroalkylation.

5.1 Effect of contact time

Benzene conversion increases with the increase in contact time but CHB selectivity decreases. To study the effect of contact time (1/WHSV) of Ni-based catalyst on the hydroalkylation product distribution, benzene hydroalkylation was carried out at P=20bar, T= 423 K, and H_2/C_6H_6 ratio of one on 5 wt% Ni loaded HY12 by varying Weight hourly space velocity from 1 h^{-1} to $3h^{-1}$. The obtained results are presented in figure 14.

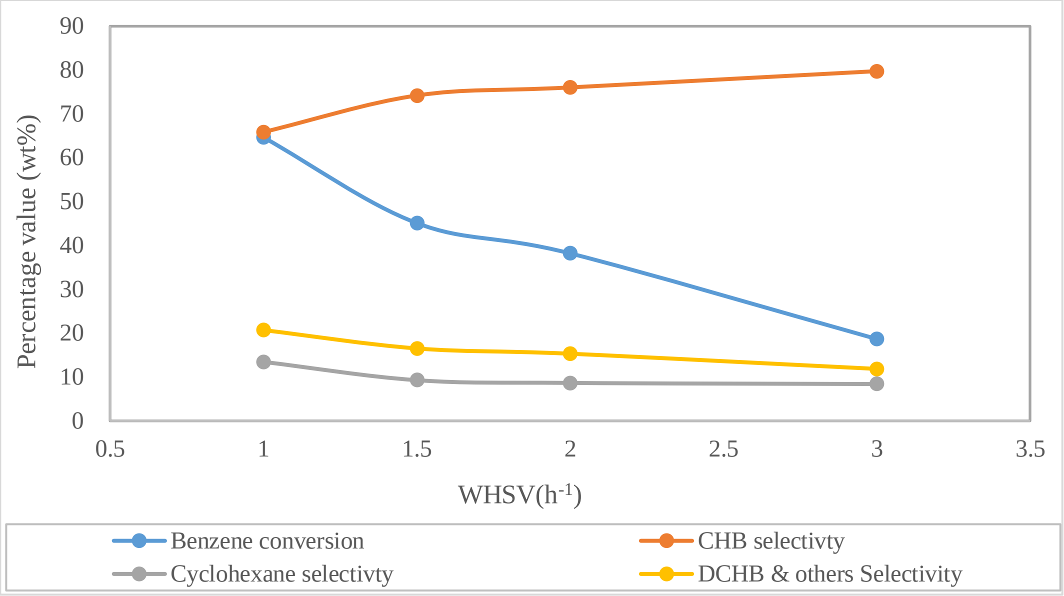


Figure 14: Effect of contact time on Activity of catalyst HAC-3 on hydroalkylation reaction operating conditions: P=20 bar, Temp= 423 K, H_2/C_6H_6 =1 and TOS=24 hrs

On increasing the contact time of feed, Benzene conversion is also increasing from 21% to 66% but CHB selectivity remains around 70 wt% because of the increase in production of other products. At WHSV value of 1 h^{-1}there is drop-in the selectivity of CHB from 74% to 61% due to the formation of higher cycloalkyl groups and hence the benzene conversion has to be limited to around 45%, in order to produce CHB with high selectivity. For catalyst HAC-3, selectivity of CHB was around 74% at a benzene conversion of 45% at a contact time of 0.67 h (WHSV= 1.5 h^{-1}) and this is the best possible selectivity for CHB at considerably good benzene conversion for the present catalyst system.

5.2 Effect of hydrogen pressure

Benzene conversion increases with increase in hydrogen pressure due to its effect on hydrogenation activity as reported in the literature. So to study this effect of hydrogen pressure of Ni-based catalyst on the hydroalkylation product distribution, benzene hydroalkylation was carried out at T= 423 K, H_2/C_6H_6 ratio of one, and WHSV of around 1.5 (h^{-1}) on 5 wt% Ni loaded HY12. The obtained results are presented in Table 17.

Table 17: Effect of Hydrogen pressure on activity of catalyst HAC-3 on Hydroalkylation reaction.

Catalyst	**HAC-3**		
Hydrogen pressure	**12 bar**	**20 bar**	**30 bar**
Benzene conversion %	35.33	45.11	46.73
WHSV (h-1)	1.5	1.5	1.5
Selectivity %			
Cyclohexane	8.98	9.28	16.13
CHB	76.85	74.20	62.17
DCHB & Others	14.17	16.52	21.70
CHB Yield, Wt.%	21.85	33.47	29.05

Operating conditions: Temp = 423 K, H_2/C_6H_6 (mole ratio) = 1, WHSV= 1.5h^{-1} and TOS=24 hrs

Benzene conversion increases from 35 % to 46.7 % with an increase in hydrogen pressure from 12 bar to 30 bar. An increase in the pressure from 20 bar to 30 bar, increases the adsorption of hydrogen on the catalyst surface leading to further hydrogenation of benzene to form cyclohexane leading to the drop in selectivity for CHB. At lower pressure of 12 bar benzene conversion is low and at higher pressure of 30 bar benzene is hydrogenated to cyclohexane. Hence a Hydrogen pressure of around 20 bar is best suited for the reaction. These results shown in figure 15 concluded that at high pressure adsorption of hydrogen increases leads to the higher selectivity of cyclohexane than cyclohexylbenzene.

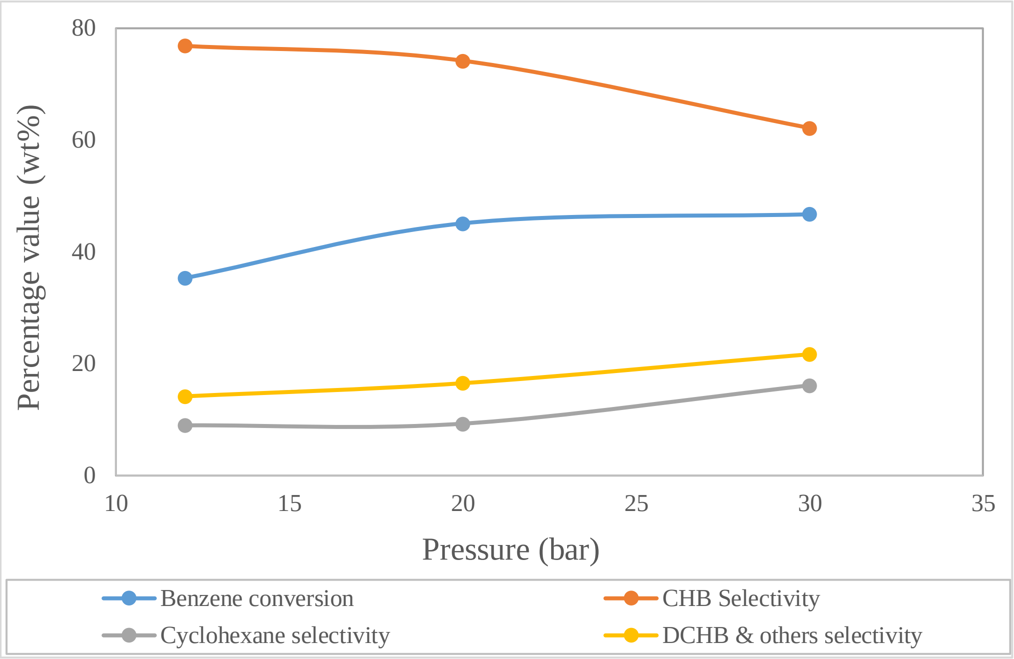


Figure 15: Effect of Hydrogen pressure on the hydroalkylation activity

5.3 Effect of hydrogen to benzene mole ratio

To study the effect of Feed ratio of Ni-based catalyst on the hydroalkylation product distribution, benzene hydroalkylation was carried out at P=20bar, T= 423 K, and WHSV of around 3 (h^{-1}) on 5 wt% Ni loaded HY12 with various feed ratio of 1 to 4. The obtained results are presented in Table 18.

Table 18: Effect of feed ratio on hydroalkylation product distribution

Catalyst	**HAC-3**			
H_2/ Benzene ratio	**1**	**2**	**3**	**4**
Benzene conversion %	38.20	40.17	41.33	42.50
WHSV (h^{-1})	2	2	2	2
Selectivity %				
Cyclohexane	8.65	4.17	3.73	3.45
CHB	76.04	71.50	69.78	68.70
DCHB & Others	15.31	24.33	26.49	27.85
CHB Yield, Wt.%	29.05	28.72	28.84	29.20

Operating conditions: P=20 bar, Temp= 423K and TOS=24 hrs

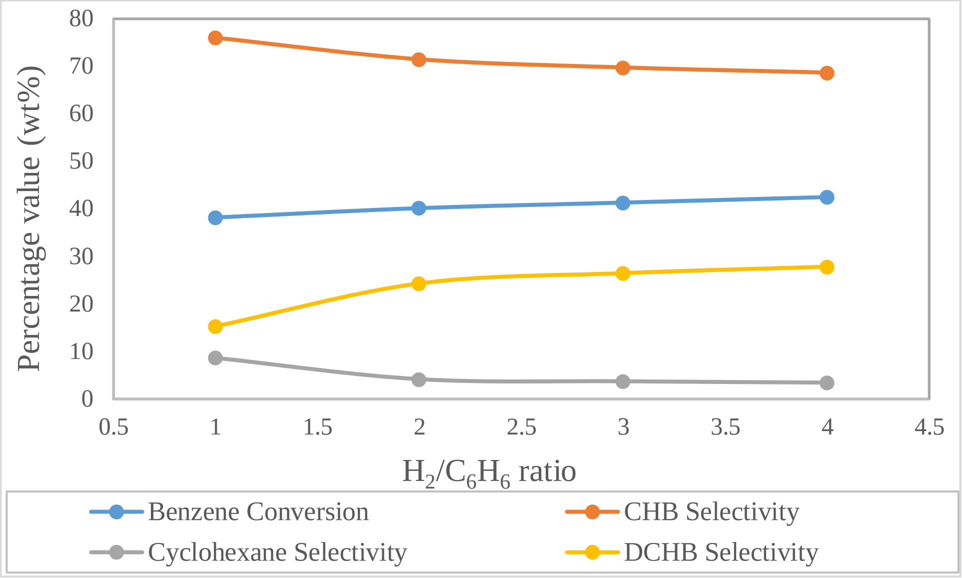


Figure 16: Effect of feed ratio on hydroalkylation activity

Benzene conversion increases by a small amount from 38% to 42.5% and CHB selectivity decreases from 73% to 69% with the increase in feed ratio from 1 to 4 as shown in figure 16. An H_2/C_6H_6 mole ratio of around 1 is found to be the best. Any decrease in this value may promote catalyst deactivation and an increase in H_2/C_6H_6 mole ratio beyond 1, will promote the formation of higher cycloalkyl groups [35].

5.4 Effect of temperature

Benzene hydroalkylation is known to be an exothermic reaction i.e. with an increase in reaction temperature benzene conversion is also increasing. To study the effect of reaction temperature on the hydroalkylation product distribution, benzene hydroalkylation was carried out at P=20bar, H_2/C_6H_6 mole ratio = 1 on 5 wt% Ni loaded HY12 reacted at different temperatures from 403K to 453K and the obtained results are presented in Table 19.

Benzene conversion increases with increase in reaction temperature. The selectivity of CHB decreases with an increase in temperature due to the formation of by-products at higher temperature. At higher temperature benzene hydrogenation is more promoted than alkylation reaction so a temperature of 423K (150^0C) is best for the reaction with higher CHB selectivity at a benzene conversion of 45% as shown in figure 17.

Table 19: Effect of reaction temperature on hydroalkylation product distribution

Catalyst	**HAC-3**			
Reaction Temperature	**403K**	**423K**	**443K**	**453K**
Benzene conversion %	38.41	45.11	66.62	73.31
WHSV (h-1)	1.5	1.5	1.5	1.5
Selectivity %				
Cyclohexane	9.19	9.28	14.21	17.26
CHB	74.71	74.20	44.06	39.47
DCHB & Others	16.10	16.52	41.73	43.27
CHB Yield, Wt.%	27.76	33.47	29.35	28.93

Operating conditions: P=20 bar , H_2/C_6H_6 (mole ratio) = 1, WHSV(h^{-1}) =1.5 and TOS=24 hrs

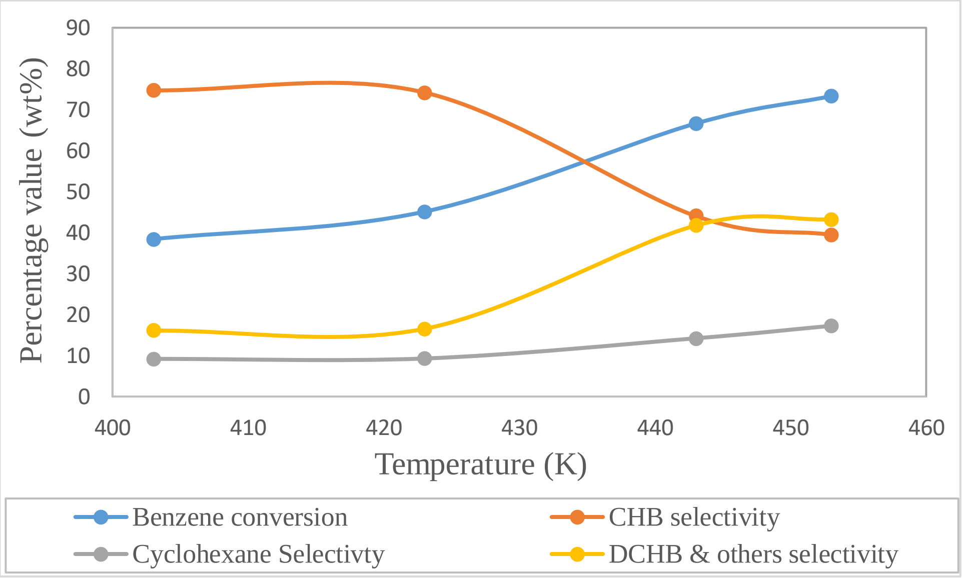


Figure 17: Effect of reaction temperature on hydroalkylation activity

5.5 Effect of time on stream

To study the deactivation of catalyst on the hydroalkylation product distribution, benzene hydroalkylation was carried out at P= 20bar, T=423 K ,H_2/C_6H_6 mole ratio = 1, and WHSV of 1.5h^{-1} on 5 wt% Ni loaded HY12 reacted for a time of stream of 58 hours. The obtained results are presented in figure 18. There is a change of 5% in benzene conversion over a period of 58 hours with a 1 or 2% change in CHB selectivity.

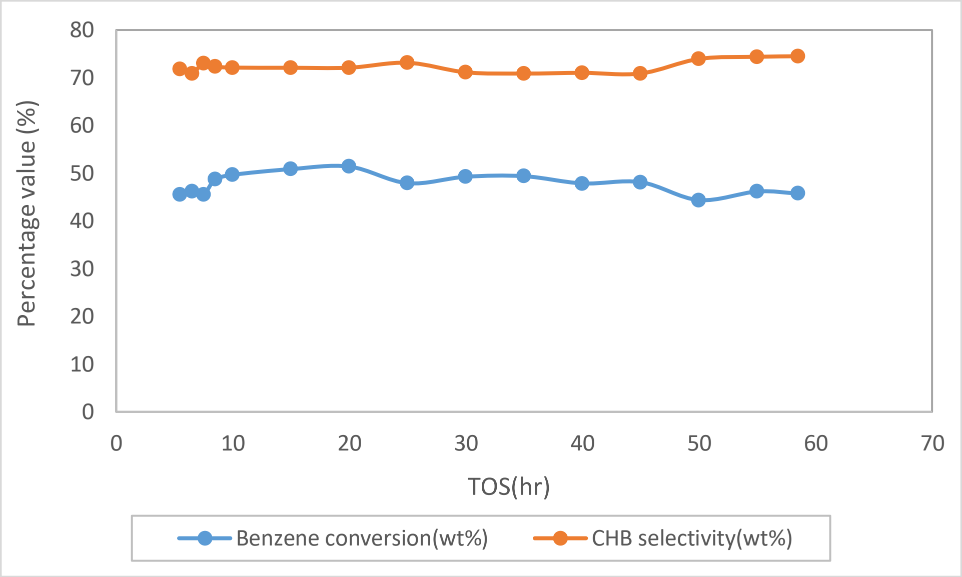


Figure 18: Effect of Time of Stream (TOS) on benzene conversion and CHB selectivity for catalyst HAC-3

5.6 Effect of catalyst reduction temperature and reduction time on hydroalkylation of benzene

To study the effect of catalyst reduction temperature on the hydroalkylation product distribution, benzene hydroalkylation was carried out at P=20bar, T= 423 K, and H_2/C_6H_6 mole ratio = 1 on 5 wt% Ni loaded HY12 reduced at different reduction temperatures. The obtained results are presented in Table 20.

Table 20: Effect of catalyst reduction temperature on hydroalkylation activity

Catalyst	**HAC-3**				
Reduction Temperature	**523K**	**573K**		**623K**	
Benzene conversion %	9.45	45.11	64.67	40.68	62.68
WHSV (h^{-1})	1.2	1.5	1	3	2
Selectivity %					
Cyclohexane	3.57	9.28	13.45	20.35	24.62
CHB	79.43	74.2	65.86	57.91	49.68
DCHB & Others	17	16.52	20.69	21.74	25.7
CHB Yield, Wt.%	7.51	33.47	42.59	23.56	31.14

Operating conditions: P=20 bar, Temp= 423 K, H_2/C_6H_6 (mole ratio) = 1 and TOS=24 hrs

Table 21: Effect of catalyst reduction temperature on hydroalkylation product distribution

Catalyst	**HAC-3**		
Reduction Temperature	**523K**	**573K**	**623K**
Benzene conversion %	9.45	64.67	91.98
WHSV (h^{-1})	1.2	1	1
Selectivity %			
Cyclohexane	3.57	13.45	35.69
CHB	79.43	65.86	34.95
DCHB & Others	17	20.69	29.36
CHB Yield, Wt.%	7.51	42.59	32.15

Operating conditions: P=20 bar, Temp= 423 K, H_2/C_6H_6 (mole ratio) = 1 and TOS=24 hrs

At low reduction temperature of 523K, the metal oxide sites present on the surface of catalyst are not completely reduced to active metal sites. The presence of lower amount of metal sites leads to lower benzene conversion as shown in Table 21. The number of metal sites on the catalyst surface increases with increase in reduction temperature that leads to an increase in benzene conversion at similar operating conditions. But CHB selectivity decreases due to the formation of other by-products beacause of higher amount of active metal and acid sites at higher reduction temperature as shown in figure 19.

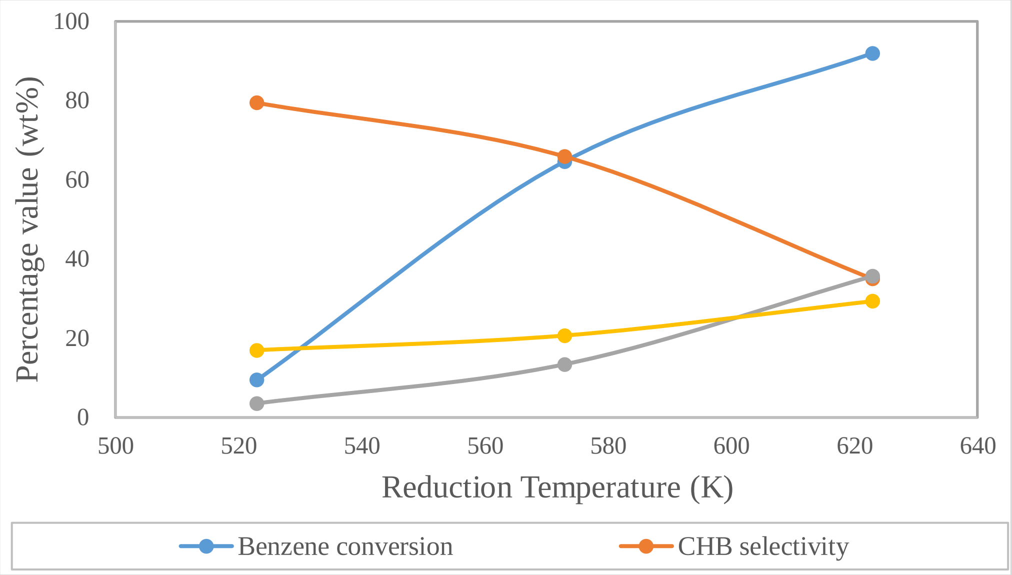


Figure 19: Effect of Reduction temperature on benzene conversion and CHB selectivity for catalyst HAC-3

To study the effect of catalyst reduction temperature on the hydroalkylation product distribution, benzene hydroalkylation was carried out at P=20bar, T= 423 K, and H_2/C_6H_6 mole ratio = 1 on 5 wt% Ni loaded HY12 reduced at 573K for different reduction time. The obtained results are presented in Table 22.

Table 22: Effect of reduction time on hydroalkylation activity and selectivity.

Catalyst	**HAC-3**			
Reduction Time	**5h**	**8h**	**12h**	**17h**
Benzene conversion wt %	45.11	43.14	43.29	41.61
WHSV (h^{-1})	1.5	2.5	2.5	3
Selectivity %				
Cyclohexane	9.28	6.80	5.81	5.80
CHB	74.2	72.42	71.72	69.66
DCHB & Others	16.52	20.78	24.09	24.54
CHB Yield, Wt.%	33.47	31.24	32.89	28.98

Operation conditions: T= 423K, P= 20Bar, H_2/C_6H_6=1 and TOS = 24h.

The conversion of benzene increases with the increase in reduction time and selectivity of CHB decreases after an increase in reduction time from 5 hours as shown in Figure 20. The increase in reduction time leads to an increase in metal sites that leads to high benzene conversion to cyclohexene which immediately reacts to form cyclohexylbenzene.

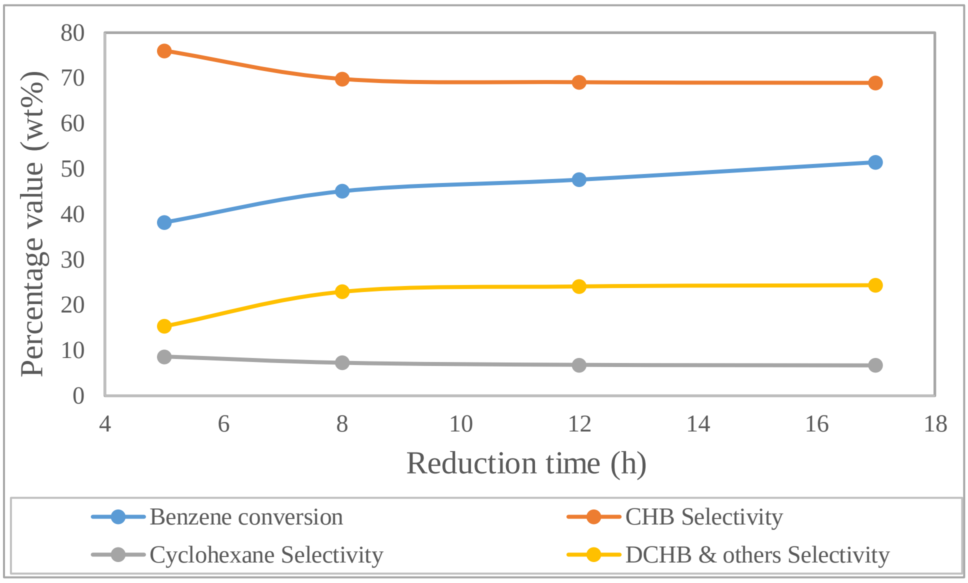


Figure 20: Effect of Reduction time on benzene conversion and CHB selectivity for catalyst HAC-3

Table 23: Effect of reduction time on hydroalkylation product distribution at similar operating conditions.

Catalyst	**HAC-3**			
Reduction Time	**5h**	**8h**	**12h**	**17h**
Benzene conversion wt %	38.2	43.14	43.29	51.45
WHSV (h^{-1})	2	2.5	2.5	2.5
Selectivity %				
Cyclohexane	8.65	6.80	5.81	6.70
CHB	76.04	72.42	71.72	68.94
DCHB & Others	15.31	20.78	24.09	24.36
CHB Yield, Wt.%	29.05	31.24	31.04	35.47

Operation conditions: T= 423K, P= 20Bar, H_2/C_6H_6=1 and TOS = 24h.

But dicyclohexylbenzene has higher selectivity because of the alkylation of cyclohexene and cyclohexylbenzene for catalyst reduced for higher reducing time.This may be due to increase in reduction of metal sites and acid sites and hence, alkylation of cyclohexene to higher cycloalkyl benzene as shown in Table 23.

6. Comparing Nickel based catalysts with Palladium based catalysts on the activity of hydroalkylation reaction

Palladium was mostly studied as hydrogenation catalyst for hydroalkylation reaction in previous literature reported [5, 7, 10, 18, 22, 23, and others]. The catalyst with 0.2 wt% Pd/HY5 has best activity for the reaction with higher CHB selectivity of 77% and Benzene conversion of 42% was developed by Kishore Kumar et al.[18]. In this research, our main objective is developing Nickel-based catalyst having similar activity for hydroalkylation reaction as that of palladium-based catalyst. The catalyst developed with 5 wt% Ni/HY-12 i.e. HAC-3 have the best activity and selectivity for hydroalkylation reactions as compared to other Ni-based catalysts prepared. HAC-3 gave 74 wt% CHB selectivity for a benzene conversion of 45 wt% at operating conditions of 423 K, 20 bar, 1.5 WHSV(h^{-1}), and H_2/C_6H_6 mole ratio of 1, which is similar to that reported [18]. The comparison of Ni catalysts with different Pd catalysts reported in the literature is listed in Table 24.

Table 24: Comparison of Ni based catalyst with palladium based catalysts for hydroalkylation activity

S.No.	Catalyst	Benzene conversion	Product selectivity	Operating conditions
1	5 %Ni/HY12*	45.11%	74.2%(CHB),9.28% (CH),16.52% (DCHB & others)	423K, 20 bar,1.5WHSV(h-1), H2/HC = 1
2	0.5 %Pd/HY12*	45.95%	72%(CHB), 6.32%(CH), 21.66% (DCHB & others)	423K, 20 bar,1.5WHSV(h-1), H2/HC = 1
3	0.2 wt%Pd/Hβ25 [5]	28.10%	67.2%(CHB),24.9%(CH), 7.9% (DCHB)	473K, 50 bar, H2/HC = 1:1
4	0.2 wt%Pd/HY5 [18]	42.20%	77.3%(CHB),3.1%(CH),19.6% (DCHB & others)	423K, 20 bar,0.5WHSV(h-1), H2/HC = 1
5	0.3%Pd/MCM-22 [7]	48.60%	70.3%(CHB),10.5%(CH),17.5%(DCHB),1.7% others	423K 10 bar,2WHSV(h−1) , H2/HC=1:1
6	0.3%Pd/MCM-49 [23]	33.60%	75.8%(CHB),4.2%(CH),15.5%(DCHB),4.5% others	423K, 10 bar, 0.52 WHSV(h−1), H2/HC = 0.64
7	0.2 %Pd@HBeta [22]	34.40%	57.3%(CHB),40.80%(CH),1.8% (DCHB & others)	473K, 40 bar

* Catalysts prepared in this study.

The catalyst with Palladium as hydrogenation metal catalyst is also developed using preparation method as reported in the literature[39]. This catalyst 0.25 wt% Pd/HY-12 is reacted at same operating conditions as that 5 wt% Ni/HY-12 catalyst, gave 72% selectivity for CHB with 46% benzene conversion.

7. Effect of zeolite acidity on transalkylation product distribution

The catalysts with different acidity i.e. zeolite with different Si/Al ratio was studied in the literature [27-33]. So the effect of Y-zeolites with different acidity on the activity and selectivity of DCHB Transalkylation is studied by using catalysts TAC-1, TAC-2, and TAC-3 having the silica-alumina ratio of 5, 12 and 60 respectively.

7.1 Textural and Chemical properties of catalysts

- **X-Ray Diffraction**

The X-ray powder diffraction (XRD) is a rapid analytical technique primarily used are used to estimate phase identification of a crystalline material such as zeolites. Figure 21 shows the XRD pattern of catalyst with zeolites of different acidity with alumina weight percent of 35 and it similar to the respective zeolites.

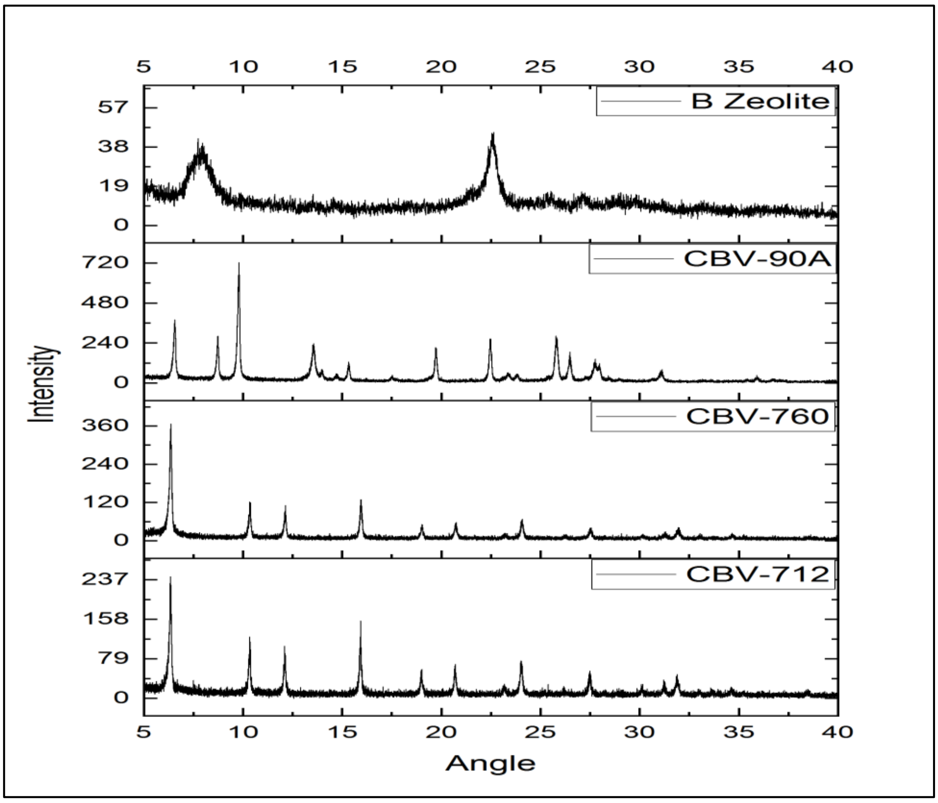


Figure 21: XRD pattern of different Zeolites with 35 wt% Alumina.

- **BET Surface area and pore volume**

The BET surface area, external surface area, pore volume, and micropore volume data of the catalysts with different acidity are shown in Table 25. The catalysts being meso structured have pores in the range of 2-50 nm. The pores are usually cylindrical in shape but can be partially distorted. The BET surface area and pore volume of the catalysts increase with an increase in acidity of zeolite.

Table 25: Chemical & Physical properties of Transalkylation catalysts with different SiO_2/Al_2O_3 ratio

S.No	**Catalyst**	**SiO_2/ Al_2O_3 ratio**	**BET Surface Area (m^2/g)**		**External Surface Area (m^2/g)**		**Micro Pore Area (m^2/g)**		**Pore Volume (cm^3/g)**		**Micropore volume (cm^3/g)**	
			*	**	*	**	*	**	*	**	*	**
1	TAC-1	5	841	436	134	129	707	307	0.38	0.41	0.22	0.13
2	TAC-2	12	774	473	121	153	653	320	0.46	0.43	0.26	0.15
3	TAC-3	60	720	582	107	231	613	351	0.55	0.47	0.34	0.15

* Data for initial zeolite ** Data for the final catalyst

Pore volume of catalysts increases with an increase in Silica to alumina ratio and it is also reported in the literature [27-33] that zeolites with large pores size are favorable for transalkylation of higher aromatic compounds to proceed.

- **Acidity measurement**

NH_3-TPD was used to estimate the amount and the strength of acid sites formed on the surface of the catalyst. NH_3 TPD had with two distinct regions, from 373K to 600K and 600K to 873K, respectively, indicating that the samples have two kinds of acid sites, weak acid sites and the strong acid sites. The peaks represent the temperature at which NH_3 is desorbed from the surface of the catalyst. The corresponding low temperature peaks of SiO_2/Al_2O_3 ratio of 5, 12, and 60 samples are 503 K, 507 K, and 503 K and high temperature peaks are at 649 K, 650 K, and 659 K. The acidity of catalyst decreases with increase in silica to alumina ratio. Total number of acid sites, as well as weak and strong acid sites, decreases with an increase in silica to alumina ratio and the results are similar to that reported elsewhere [32-33].

Table 26: Acidity data of Transalkylation catalysts with different SiO_2/Al_2O_3 ratio

S.No	**Catalyst**	**Total acid sites concentration (µmol NH_3/g cat)**	**Peak Temperatures T_{max} TPD (K)**	**Weak acid sites (µmol/g)**	**Strong acid sites (µmol/g)**
1	TAC-1	408	503, 649	121	287
2	TAC-2	184.5	507, 650	50.63	133.87
3	TAC-3	151.8	503, 659	27.50	124.3

- **Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (SEM) is used to determine the physical representation of catalyst i.e. the shape of pores on the surface of catalyst. The shape can be square, rectangle, hexagonal, circle depending on the crystalline nature of sample. In figure 22, the zeolite with silica-alumina ratio of 60 (HY-60 zeolite) is shown with pore shape similar to circle or hexagonal. The amorphous nature of alumina present in catalyst is also shown in the figure.

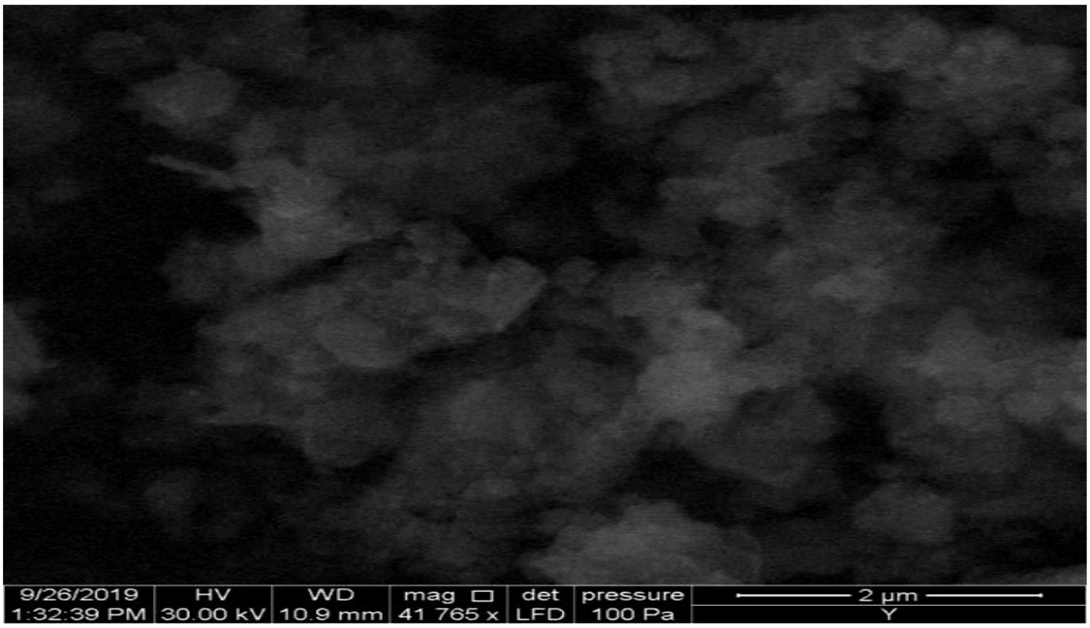


Figure 22: SEM images of Transalkylation catalysts TAC-3 having 35 wt% Alumina

7.2 Activity of different catalysts of Transalkylation reaction

To study the effect of catalyst acidity on the transalkylation product distribution, DCHB transalkylation with benzene was carried out at P=20bar, T= 453 K, feed ratio (mole) Benzene to DCHB of 9 on catalysts with different acidity. The obtained results are presented in Table 27.

Table 27: Effect of acidity on Activity of Transalkylation reaction

Catalyst	**TAC-1**	**TAC-2**	**TAC-3**
DCHB conversion %	91.17	-5.57	86.78
Benzene conversion %	13.13	3.73	16.83
WHSV (h^{-1})	2.28	2.28	2.28
Selectivity %			
MCP	3.25	0.38	1.21
CHB	68.66	46.19	78.77
Others	28.08	53.41	20
CHB Yield,Wt.%	62.59	-2.57	68.36

Operating conditions: P=20 bar, Temp= 453 K, C_6H_6/DCHB=9 and TOS=24 hrs

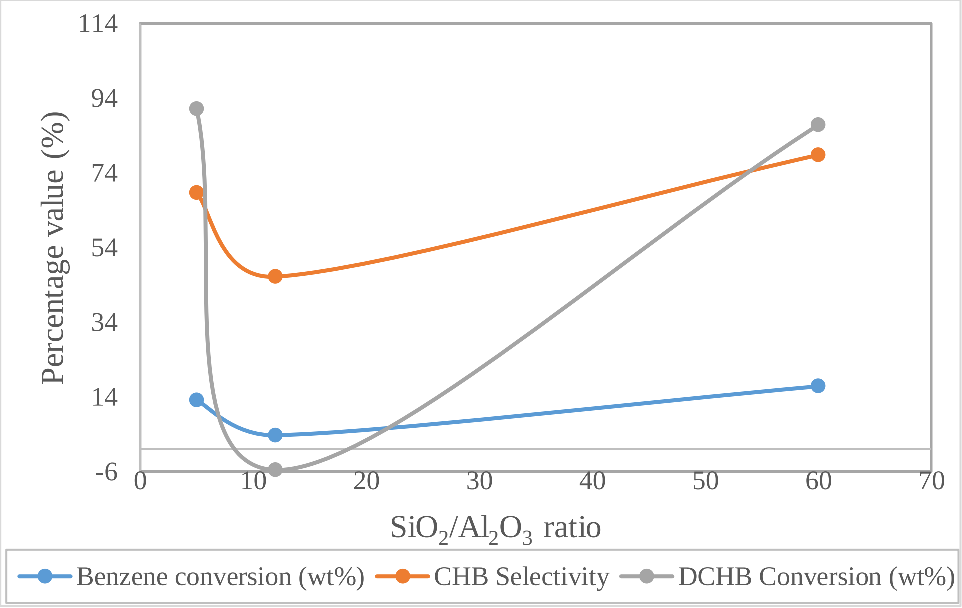


Figure 23: Effect of acidity on transalkylation activity and selectivity.

7.3 Summary

Benzene conversion and CHB selectivity(wt%) are highest for a silica-alumina ratio of 60 i.e. catalyst TAC-3. Catalyst TAC-2 has a negative conversion of DCHB which shows the formation of it on the catalyst surface and hence it is not desirable as a transalkylation catalyst. TAC-1 catalyst had lower CHB selectivity for a DCHB conversion of 91% as compared to TAC-3 catalyst. The selectivity of by-products increases with a decrease in silica-alumina ratio from 60 to 5, this may be due to the isomerization effect is more for catalysts with lower silica-alumina ratio.

8. Effect of operating conditions on transalkylation product distribution

Effect of operating conditions for a catalyst TAC-3 on transalkylation product distribution is shown below:

8.1 Effect of temperature

To study the effect of reaction temperature on the transalkylation product distribution, DCHB transalkylation with benzene was carried out at P=20bar, feed ratio (mole) Benzene to DCHB of 9. CHB selectivity(wt%) decreases with an increase in temperature from 443K and 453K. But on further increasing temperature benzene conversion, CHB selectivity and yield decreases. This change is may be due to the sintering effect on catalyst surface. The obtained results are presented in Table 28.

Table 28: Effect of reaction temperature on activity of transalkylation product distribution

Catalyst	**TAC-1**	**TAC-3**	**TAC-1**	**TAC-3**	**TAC-3**
Reaction Temperature	443K		453K		473K
DCHB conversion %	90.09	86.61	91.17	86.78	71.50
Benzene conversion %	12.17	13.84	13.13	16.83	5.50
WHSV (h^{-1})	2.28	2.28	2.28	2.28	2.28
Selectivity %					
MCP	2.17	0.88	3.25	1.21	2.58
CHB	76.37	81.35	68.66	78.77	36.96
Others	21.46	16.96	28.09	20	60.45
CHB Yield, Wt.%	68.81	70.45	62.59	68.36	26.43

Operating conditions: P=20 bar, Temp= 443 K- 473K and TOS=24 hrs

For both the catalysts TAC-1 & TAC-3, with the increase in temperature CHB selectivity & DCHB conversion decreases and benzene conversion increases as shown in figure 24. This may be due to the breaking of DCHB at a higher temperature which leads to the formation of other by-products.

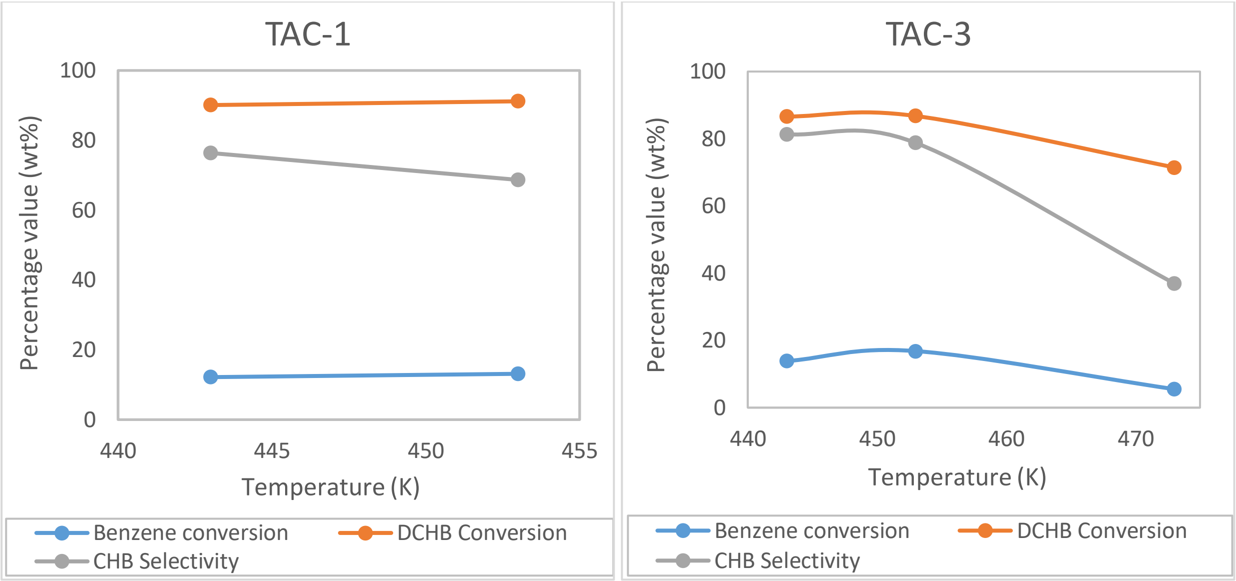


Figure 24: Effect of reaction temperature on activity of catalyst (a) TAC-1 and (b) TAC-3 on transalkylation product distribution.

8.2 Effect of contact time

To study the effect of WHSV on the transalkylation product distribution, DCHB transalkylation with benzene was carried out at P=20bar, feed ratio (mole) Benzene to DCHB of 9. The obtained result is shown in Table 29.

Table 29: Effect of WHSV on activity of catalyst TAC-3 on transalkylation product distribution

Catalyst	**TAC-3**					
WHSV(h^{-1})	2.28		3.5		4.57	
Temperature	443K	453K	443K	453K	443K	453K
DCHB conversion %	86.61	86.78	77.98	78.54	69.46	70.84
Benzene conversion %	13.84	16.83	11.08	11.83	7.68	8.55
Selectivity %						
MCP	0.88	1.21	0.41	0.59	0.31	0.42
CHB	81.35	78.77	78.07	77.9	73.86	74.4
Others	17.77	20.02	21.52	21.51	25.83	25.18
CHB Yield, Wt.%	70.45	68.36	60.88	61.19	51.3	52.71

Operating conditions: P=20 bar, Temp= 443K-453 K and TOS=24 hrs.

In figure 25, it is presented that with the increase in contact time (1/WHSV), the DCHB conversion & Benzene conversion increases while the selectivity of CHB decreases. The catalyst TAC-3 with a temperature of 443K, nitrogen pressure of 20 bar, Feed ratio of 9, and WHSV of 2.28 h^{-1} gave the best result for DCHB transalkylation to CHB.

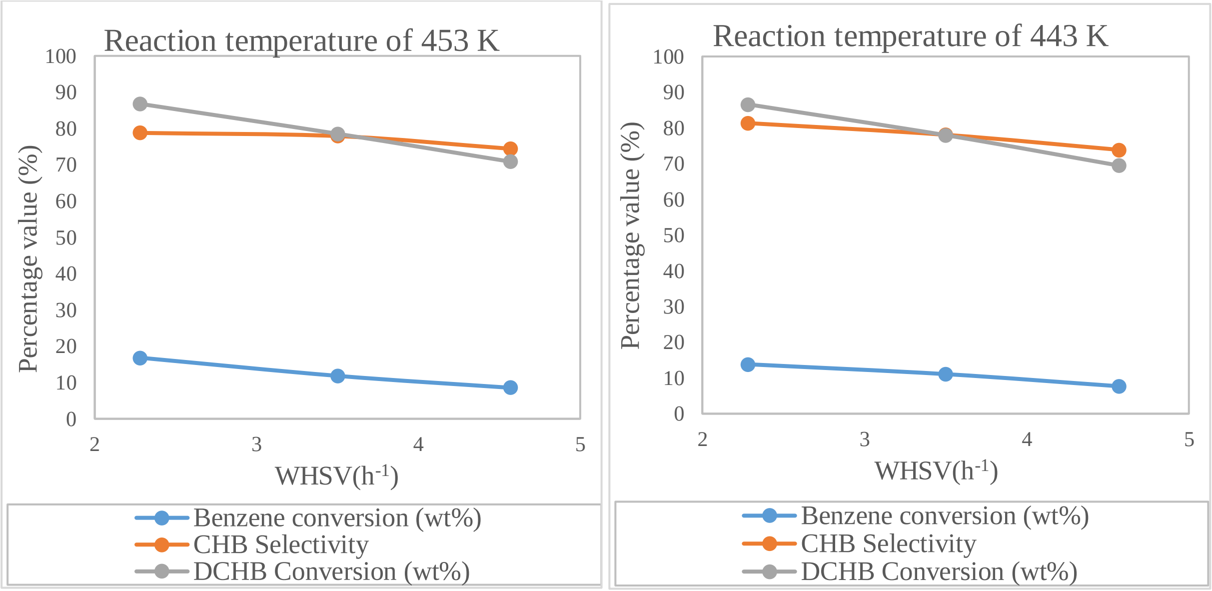


Figure 25: Effect of WHSV on activity of catalyst TAC-3 at temperature (a) 443 K & (b) 453 K.

8.3 Effect of time on stream

To study the deactivation of catalyst on the Transalkylation product distribution, the reaction was carried out at P= 20bar, T=443 K, C_6H_6/DCHB mole ratio = 9, and WHSV of 2.29h^{-1} on TAC-3 reacted for a time of stream of 50 hours. The obtained results are presented in figure 26. There is a change of 9% in DCHB conversion and 2% in benzene conversion over a period of 50 hr with a 1 or 2% change in CHB selectivity.

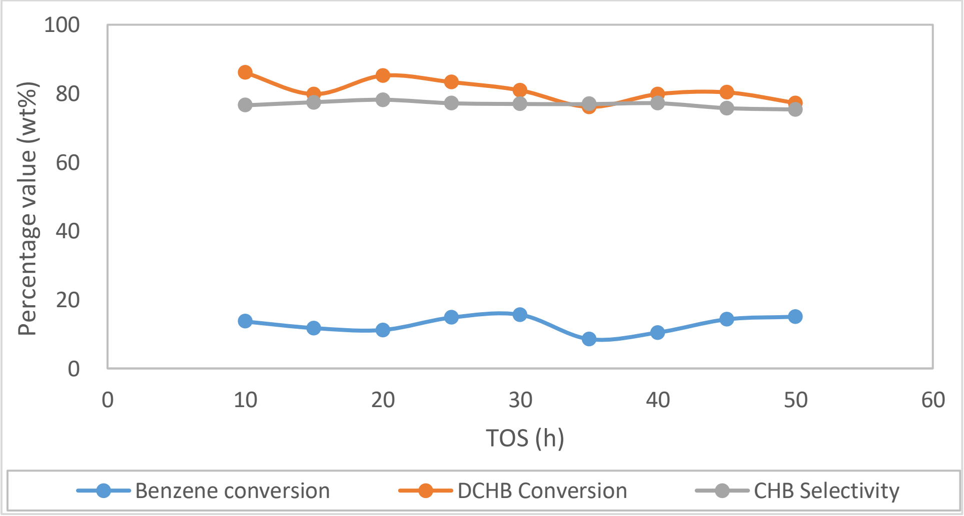


Figure 26: Effect of time of stream on activity of catalyst TAC-3

9. Conclusions and recommendations for future work

9.1 Conclusions

Hydroalkylation of benzene is carried at Ni/HY catalysts having different Nickel weight percent, different zeolite weight percent and different HY zeolites. The catalysts with Ni content below 2.5% has not shown any activity for hydroalkylation reaction while catalysts with 5 wt% Ni and 7.5 wt% Ni showed similar activity. Y-Zeolite HY-12 having SiO_2/Al_2O_3 ratio of 12 has better activity as compared to Y-Zeolites HY-5 and HY-60, and hence it is evident that the acidity and proper balance between the active metal sites and the acid sites of the catalyst is vital for the activity and the selectivity of the hydroalkylation catalyst. The total weight percentage of zeolite as support in catalysts should be equal to or greater than 65%, for maintaining the stability of catalysts taking part in the reaction. Among all the tested catalysts, HAC-3 (5 wt%Ni/HY12) having 65 wt% zeolite proved to be most active, selective, and stable catalyst for the hydroalkylation of benzene. The reaction operating conditions for the best possible CHB selectivity at reasonably good benzene conversions are 423K, 20 bar, 1.5 WHSV, and H_2/C_6H_6 mole ratio of 1. At these operating conditions, the selectivity for CHB was 74% at 45% Benzene conversion. The results for HAC-3 is similar to that of 0.2 wt% Pd/ HY-5, hence producing a catalyst with metal (Ni) to obtain a result similar to a catalyst with noble metal (Pd).

Transalkylation of DCHB & Benzene was carried on different HY zeolites with 35% alumina as support. Y-Zeolite HY-60 having SiO_2/Al_2O_3 ratio of 60 has better activity as compared to Y-Zeolites HY-5 and HY-12, similar to the data reported in the literature [28-29]. Among all the tested catalysts, TAC-3 (SiO_2/Al_2O_3) proved to be most active, selective, and stable catalyst for the transalkylation of DCHB. The reaction operating conditions for the best possible CHB selectivity at reasonably good DCHB conversions are 443K, 20 bar, 2.28 WHSV, and C_6H_6/DCHB mole ratio of 9. At these operating conditions the selectivity for CHB was 81% at 87% DCHB conversion.

9.2 Recommendations for future work

A kinetic model is to be developed to determine the reaction mechanism, either assuming Power law or Lanmuir - Hinshelwood mechanism or Eley - Riedal mechanism and kinetic parameters. Develop the kinetic model for Ni-based catalyst using analysis data of Hydroalkylation reaction system. Develop the kinetic model for Transalkylation reaction using analysis data.

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