Catalytic Performance Of Modified HZSM-5 On Synthesis Of Ethyl Phenol: A kinetic study

A

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In the partial fulfillment of the requirement for the degree of

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Submitted by

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Under the supervision

of

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July 2017

CERTIFICATE

This is to certify that the dissertation entitled **'Catalytic Performance Of Modified HZSM-5 On Synthesis Of Ethyl Phenol: A kinetic study'** being submitted by **Ms. Renuka Saharan** in partial fulfillment of requirements for the award of degree of **M.Sc. Chemistry** in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafied work carried out by her under my supervision. The work has reached the standard, necessary for submission. The contents of this dissertation have not been submitted for the award of any other degree or diploma.

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This is certify the above statement made by student concerned is correct and true to the best of my knowledge.

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CANDIDATE'S DECLARATION

I, hereby declare that the work presented in the thesis entitled **'Catalytic Performance Of Modified HZSM-5 On Synthesis Of Ethyl Phenol: A kinetic study'**, in partial fulfillment of the requirement for the award of the degree of Master's of Science, School of Chemistry and Biochemistry, Thapar University, Patiala, India, is an authentic record of my own work during the period of January 2017 to June 2017 under the supervision of Dr. Sanghamitra Barman, Associate Professor, Department of Chemical Engineering, Thapar University, Patiala, Punjab. The matter embodied in this thesis has not been submitted in any part or full to any other university or institute for the award of any degree in India or abroad.

Date: 17 July, 2017

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It is certified that above statement made by the student is true to the best of my knowledge and belief.

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ABSTRACT

The selective synthesis of p-ethylphenol from vapor phase alkylation of phenol with ethanol was investigated in a fixed bed reactor on cerium modified zeolite HZSM5 at temperature 693K. A series of CeZSM-5 were prepared by modifying with 4%, 6%, 8% and 10% cerium ammonium nitrate solution. ZSM-5 exchanged with 10% cerium nitrate solution was proved to be the best of all the catalyst used. The modified catalyst were further characterized by SEM, XRD. Phenol reacted with ethanol to form ethylphenyl ether by O-alkylation, and p- and o-ethylphenol by C-alkylation; secondary products were m-ethylphenol and dialkylated compounds. Reactions were carried out in the temperature 623K-693K, phenol to ethanol reactant mole ratio 1-10 over both cerium modified ZSM-5 modified. From the study of the effects of various parameters, the optimum operating condition for maximum selectivity of p-ethyl phenol were obtained at space time-0.0384kgh/kmol, phenol to ethanol reactant mole ratio of 1:3, nitrogen to feed mole ratio, 0.16. 1 atm pressure. A systematic and detailed kinetic study were carried out for the alkylation reaction. From the product distribution pattern, a kinetic model was developed following Langmuir–Hinshelwood approach. The kinetic and adsorption parameters of the rate equation were determined by non-linear regression analysis. From the kinetic analysis of the experimental data, the apparent activation energy for the reaction was determined to be 43.27 kJ/mol.

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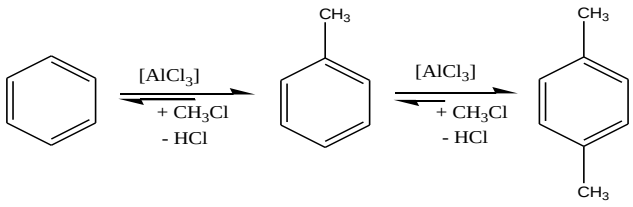
NOMENCLATURE

Ce	Cerium
EPE	Ethylphenylether
p-$_{ep}$	para-ethylphenol
m-$_{ep}$	meta-ethylphenol
p-$_{ep}$	ortho-ethylphenol
HZSM5	ZSM5 zeolite
k_1,k_2,k_3	Kinetic constant,kgmol/kgh
K_{ph}	Adsorption constant for phenol,atm^{-1}
K_{Et}	Adsorption constant for ethanol,atm^{-1}
CeZSM5	Cerium modified HZSM5 zeolite
P	Total pressure, atm
p_{EPE}	Partial pressure of ethylphenylether,atm
p_{Ph}	Partial pressure of phenol,atm
p_{Et}	Partial pressure of ethanol,atm
$p_{p\text{-}ep}$	Partial pressure of p-ethylphenol,atm
$p_{m\text{-}ep}$	Partial pressure of m-ethylphenol,atm
$p_{o\text{-}ep}$	Partial pressure of o-ethylphenol,atm
$p_{Diethylether}$	Partial pressure of diethylether,atm
$p_{ethylene}$	Partial pressure of ethylene,atm
X_{Ph}	Moles of phenol produced,kgmol
X_{Et}	Moles of ethanol produced,kgmol
$X_{p\text{-}ep}$	Moles of p-ethylphenol produced,kgmol
$X_{m\text{-}ep}$	Moles of m-ethylphenol produced,kgmol
$X_{o\text{-}ep}$	Moles of o-ethylphenol produced,kgmol
X_{EPE}	Moles of ethylphenylether produced,kgmol
$X_{Dieyhylether}$	Moles of diethylether produced,kgmol
$X_{ethylene}$	Moles of ethylene produced,kgmol
T	Space-time,kgh/kgmol
$-r_{Ph}$	Rate of formation of phenol
$r_{\ Dieethylether}$	Rate of formation of diethylether
$y_{i,o}$	Molar fraction of aromatic product
$y_{Ph,o}$	Outlet molar fraction of phenol

CHAPTER-1 INTRODUCTION

1.1 Alkylation

Alkylation of aromatic substrates catalyzed by solid acids such as zeolites constitutes a class of reactions having both academic and industrial importance. Alkylation of phenol is one of such important alkylation reactions producing both C-alkylated products and O-alkylated product [1]. The p-ethyl phenol are used as chemical intermediate for the manufacture of Wine and beer, P-coumaric acid, 4-vinylphenol, food and flavor ingredient. Alkylation of phenol with ethanol over zeolite is an attractive synthetic route for the production of ethyl phenol compared to the conventional Friedel–Crafts alkylation. The alkylating agent originally used in the Friedel-Crafts reaction was alkyl halide [2]. Later on, alkenes came into prominence as an alkylating agents followed by alcohols in recent years. The use of alcohol instead of alkenes as an alkylating agent has some advantages. A long stable life of the catalyst is observed when alcohol, rather than olefin, is used as an alkylating agent. Moreover, choice of alkenes (which stay in gas phase) as alkylating agents is usually associated with high storage and transportation costs.



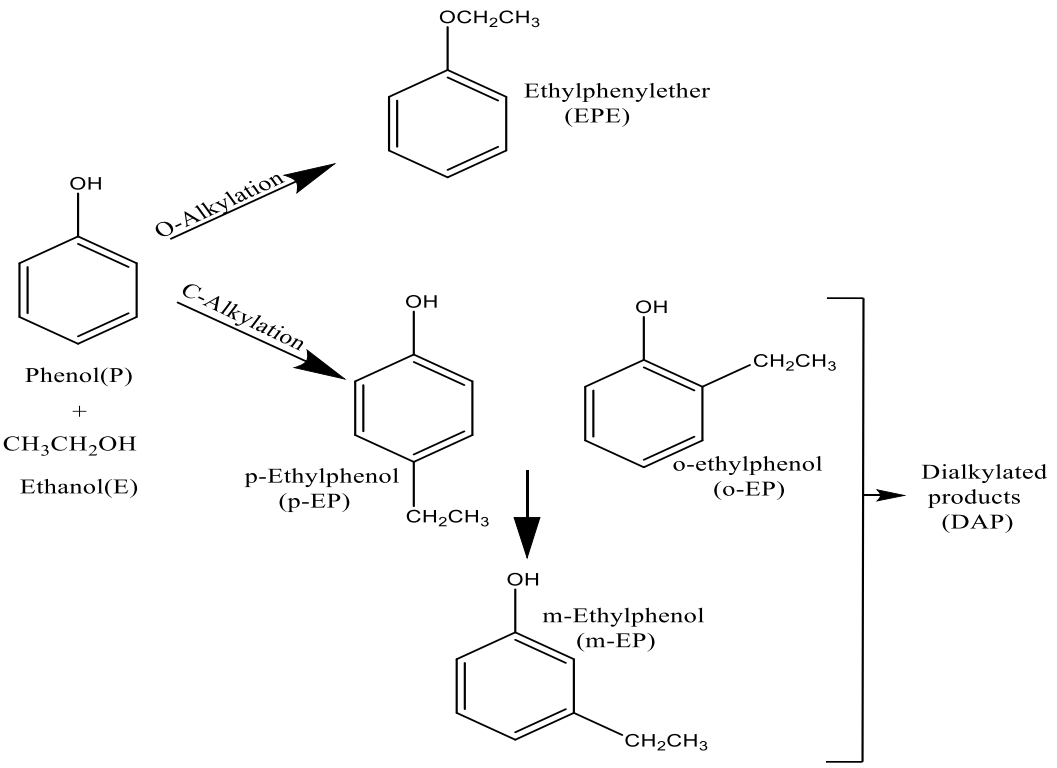
Friedel Crafts reactions are complex because the attacking reagents re-arranges. In some cases a carbonium ion formed during the reaction rearrange to form a more stable secondary or tertiary carbonium ion. Friedel Crafts reaction is catalyzed by acids. Bronsted and Lewis acids can be used to catalyse this. Mostly anhydrous $AlCl_3$ is used as catalyst for the liquid phase alkylation reaction along with HCl. Hydrochloride helps to improve efficiency. Many other catalysts are used for alkylation of aromatic compounds. Some of them includes protonic acids like HF, BF_3, polyphosphoric acid and inorganic oxides such as P_2O_5 on alumina; weak acidic metal halides like as $FeCl_3$, BF_3 and $ZnCl_2$. These catalysts need to be used in liquid state, which results in problems like toxicity, corrosion and pollution. Hence we replace homogenous catalysts with heterogenous ones. Solid catalysts like zeolites are free from corrosion and environmental problems. Also, in zeolites, the combination of shape

selectivity and acidity make them potential catalysts for diverse Friedel Crafts Alkylation. The present work is concerned with the alkylation of phenol and ethanol over cerium modified HZSM-5. The modification of HZSM5 was done with exchanging of H+ ion by Ce^{3+} ions, thereby changing its catalytic properties. The superior catalytic performance of the modified catalysts has been explained in the study. Scarce literature is available on the use of rare earth metal ions modified ZSM5 on this particular reaction system The process of Alkylation of phenol undergoes a complex reaction scheme due to C- alkyalation and o-alkylation[3].

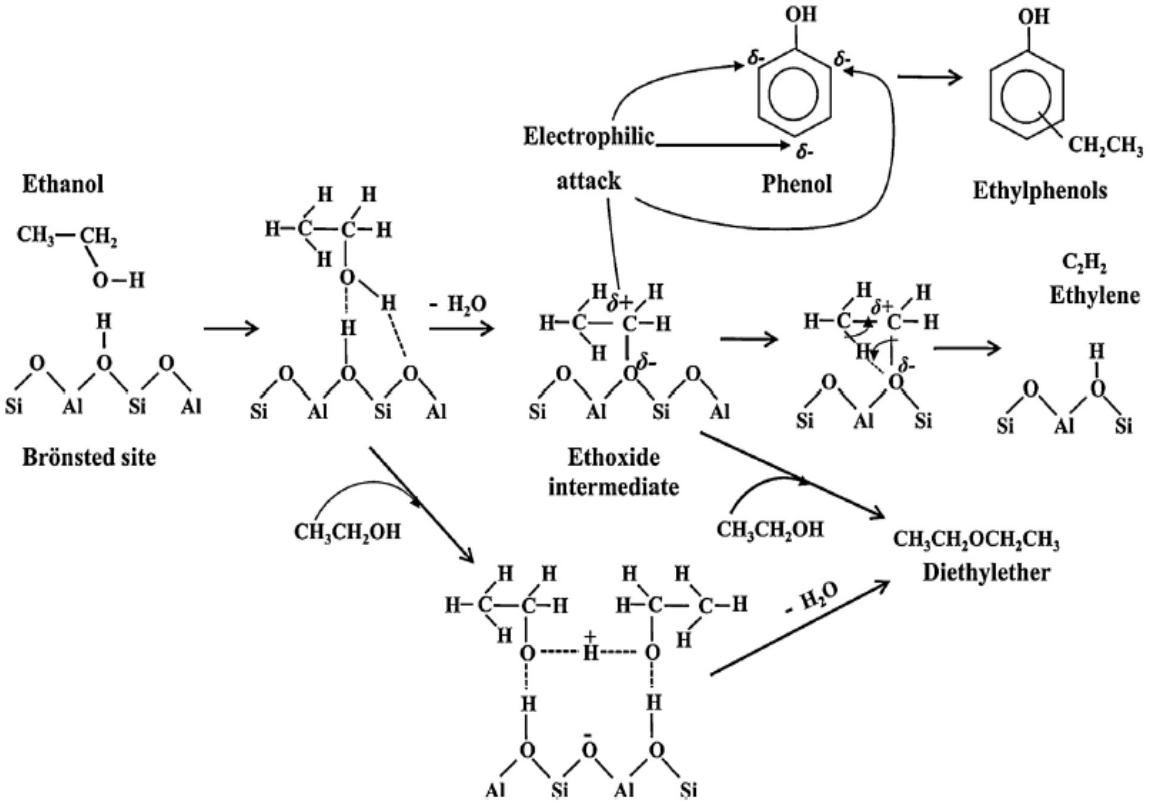
1.1.1 Alkylation of Phenol with Ethanol

Phenol alkylation with ethanol over zeolites is a good synthetic route to form either para, meta and ortho ethyl phenol and also ethyl phenyl ether or diethylether. In alkylation of phenol both C-alkylated (Electrophilic aromatic substitution) and O-alkylated (Nucleophilic acyl substitution) products are formed. Para-ethylphenol, meta-ethylphenol and ortho-ethylphenol are formed through C-alkylation while O-alkylation gives ethylphenylether and dialkylate as side products [4].

The alkylation of aromatic compounds with ethanol on zeolites occurs through an electrophilic substitution on the aromatic ring by the alkylating agent formed from ethanol dehydration on zeo-lite acid sites [5]. Scheme 1 shows Phenol can initially react with ethanol via two parallel alkylation reactions to form primaryproducts: by O-alkylation phenol is transformed to EPE and by C-alkylation yields directly o-EP and p-EP. Then EPE may be converted to ethylphenols while isomerization of o-EP and p-EP leads to the formation of m-EP. Finally, ethylphenols can react with ethanol to produce dialkylated products. In the present investigation, ethanol is dehydrated on zeolitic OH groups forming surface-bound ethoxide species that can alky-late phenol or produce ethylene (by intramolecular dehydration) and diethylether (by dehydration/condensation) [6]. Scheme 2 presents surface-bound ethox-ide intermediates are formed during ethanol conversion on Bronsted acid sites which produce ethylphenols, ethylene or diethylether. The alkylating agent attacks the phenol ring by electrophilic substitution in ortho and para positions because of the electron donor effect of phenol OH group that increases the electronic density of positions 2, 4, and 6 in the ring [7].



Scheme 1. Reaction Scheme



Scheme 2 : Reaction Mechanism

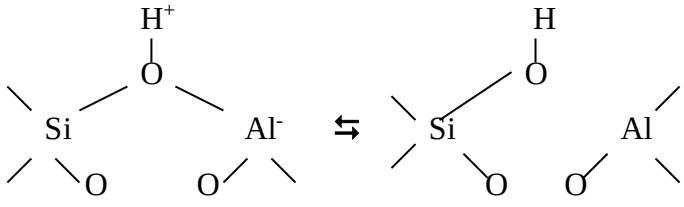
1.2 Zeolites

Zeolite molecular sieves are hydrated, crystalline, microporous aluminosilicates with a framework based on extensive three dimensional network of SiO_4 and AlO_4 tetrahedral building blocks where in Si and Al are the tetrahedral atoms (T atoms) and each apical oxygen is shared with an adjacent tetrahedra. The crystallographic unit cell of the zeolites may be represented by the general formula.

$$M_{x/n}\,[(AlO_2)_x(SiO_2)_y]\,zH_2O$$

The net negative charge of the framework is same as the number of aluminium atoms and is balanced by exchangeable charge compensating cations M of valency n, typically Na^+, NH_4^+ or H^+. z is the number of water molecules, and x + y represents total number of tetrahedra in the unit cell of zeolite. In general, the ratio y/x>1, and controls the acidity, and to a lesser extent, the morphology of zeolites. All zeolites that are significant for catalytic and adsorbent applications can be classified by the number of T-atoms (i.e., Si or Al) that define the pore openings. There are only three types of pore openings known to date in the aluminosilicate zeolite system; they are descriptively referred to as the 8-membered ring (small-pore), 10-membered ring (medium pore) and 12-membered ring (large pore) zeolites. The size and shape of the pore opening is determined by factors such as (a) configuration of the T and O atoms relative to each other, (b) silica to alumina ratio, (c) size and location of the cation, (d) temperature and (e) framework structure of the zeolites [8].

The reactivity of zeolites is determined by the active sites provided by the imbalance in the charge between the silicon and aluminium ions in the framework. Thus, each aluminium atom present within the framework constitutes an active site . Classical Brönsted and Lewis acid models have been defined to classify active sites in zeolites. Brönsted acidity arises in the zeolite when the cation balancing the anionic framework charge is a proton (H^+). Differences in the acidic strength between different zeolites is often related to T-O-T bond angles and lengths, and crystal resonance energy [9].



Brönsted acidity

A trigonally co-ordinated aluminium atom, which acts as an electron acceptor, behaves as a Lewis acid. Higher temperature (>773 K) can result in the conversion of the Brönsted acid sites to Lewis acid sites by dehydroxylation . Dealumination by hydrothermal treatment of zeolites has also been found to produce a variety of cations and neutral species which function as Lewis acids These cations also induce activity on nearby Brönsted acid sites.

1.2. Zeolite HZSM-5

ZSM-5 is a shape-selective zeolite is an industrially important catalyst. HZSM-5 zeolite is hydrogen form of ZSM-5 zeolite. The sodium form of the zeolite is converted to the acid form using $(NH_4)_2SO_4$ solution. The ZSM-5 structure contains two intersecting channel systems of specific size and shape that restrict molecular diffusion into and through the framework. Figure 1.1 shows a pentasil unit of ZSM-5. The porous material is therefore useful for catalytic reactions inside the nanopores of the material. The ZSM-5 structure is a commonly occurring framework topology, where the chemical composition of the metal centers varies. MFI type ZSM-5 zeolite is an alumino (silicate) zeolite belongs to the pentagon family of zeolite. Its formula is $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ ($0<n<27$). It is extensively used in the industry of petroleum as catalyst for petrochemical reactions [11]. Ion-exchange can be performed to render the sodium form of ZSM-5 (Na-ZSM-5).

Figure 1.1 Pentasi unit of ZSM-5 zeolite

1.3 Objective of present investigation

1) Modification and characterization of HZSM-5.

2) Evaluation of the catalytic performance of the modified catalysts for the production of p-ethylhenol .

3) Studying the influences of process variables such as temperature, reactant mole ratio and space velocity on the conversion of the limiting reactants and on the selectivities of the main alkylation products of the above mentioned alkylation reactions with the most promising catalysts.

4) Kinetic studies for the reactions on the modified catalyst.

5) Kinetic modeling of the above mentioned commercially important alkylation reactions and estimation of model parameters.

CHAPTER-2 LITERATURE REVIEW

2.1 Zeolite

In 1756 the Swedish mineralogist Cronstedt [33] discovered the first zeolite mineral, stilbite. He established zeolites as a new class of minerals made of hydrated aluminosilicates of the alkali and alkaline earths. From 1777 to 1800 years various authors described the properties of zeolite minerals, including adsorption properties, non corrosiveness, reversible cation exchange and dehydration.

Leonard and meloni D. et.al. 2001[12] described the first use of X-ray diffraction for identification in mineral synthesis. By the mid-1930s the literature described the ion exchange, adsorption, molecular sieving and structural properties of zeolite minerals as well as a number of reported syntheses of zeolites. Due to incomplete characterization and the difficulty of experimental reproducibility the early synthetic work remains unsubstantiated

Barrer el al. 1945 [13] started his work in zeolite adsorption and synthesis in the mid-1930s to 1940s. He investigated the first classification of the then-known zeolites based on molecular size considerations in 1945 and in 1948 reported the first definitive synthesis of zeolites, including the synthetic analog of the zeolite mineral mordenite and a novel synthetic zeolite much later identified as the KFI framework.

Edith M.F. et al. (1987) [34] incorporated elements such as Li, Be, B, Mg, Si, Ga, Ge, As, Ti, Mn, Fe, Co, and Zn, spanning monovalent through pentavalent framework cationic species. Pore sizes range from 0.3nm to 0.8nm encompassing small, intermediate and large pore structures. The new molecular sieves were synthesized by hydrothermal crystallization of reactive alumino-phosphate gels containing the additional framework elements and an organic template.

Bedard et al.(1989) [14] reported the discovery of microporous metal sulfides, based on germanium (IV) and Sn (IV) sulfide frameworks. The microporous sulfides are synthesized hydrothermally in the presence of alkylammonium templating agents. The GeS_4-based compositions include one or more framework-incorporated metals: Mn, Fe, Co, Ni, Cu, Zn, Cd and Ga. Gier et al. 1991[15] reported zinc and beryllium phosphates and arsenates with the X (FAU), ABW and SOD structures reminiscent of the early aluminum-rich synthetic

zeolite chemistry. The synthesis of $ZnPO_4$-X (FAU) is especially spectacular. Crystallization occurs almost instantaneously at 0°C. Concurrent with ease of synthesis, the structure is thermally unstable.

Camblor M.A. et al. 1997 [16] studied the effects of variation in Si/Al ratio (25 and 100) and crystallization temperature (80°C to 180°C, at an interval of 20 K) on crystal size of zeolite beta were studied. Products obtained at different synthesis parameters were characterized by powder X-ray diffraction, IR spectroscopy, thermal analysis, scanning electron microscopy and nitrogen adsorption. Increase in crystal size with crystallization temperature and Si/Al molar ratio was observed. Crystal morphology at 140°C was spherical whereas at 180°C it was of irregular shape.

Stucky et al. 1998 [35] discovered a generalized method for preparing a large number of metallo-aluminophosphate and metallo-gallophosphate frameworks containing transition metals. The method utilizes amine SDAs and high concentrations of transition metal and phosphate in mixed solvents, typically alcohol and water. Two of the novel structures (UCSB-6, UCSB-10) have multi-dimensional 12-ring channels connecting large cages. In addition numerous zeolite structure analogs were also observed. Unfortunately, the high framework charge reduces structural stability when template removal is attempted.

Takewaki et al. 1999 [17] framework of zinc silicates with Zn include CIT-6. Incorporation of B, Be, Ge and Zn in metallosilicate compositions can yield novel structures difficult or impossible to obtain with Al. To date only B, Be, Ga, Ge, Fe, Ti and Zn have been sufficiently characterized to confirm structural incorporation. The titanium-silicalite composition, TS-1, has achieved commercialization in selective oxidation processes and iron-silicalite in ethylbenzene synthesis.

Ozin et al. 1999 [36] have extended this work to a large number of microporous sulfides and selenides. It should be noted that the microporous sulfides and selenides are prone to structure collapse upon calcination to remove the template species.

Petersen et al.2002 [18] reported crystalline framework with compositions of beryllosilicate (nabesite). Other includes silicates containing incorporated tetrahedral iron, boron, chromium, arsenic, gallium, germanium and titanium. Most of the earlier work has been reported with structures of the MFI type. Also metallosilicate analogs of ZSM-11, -12, THETA-1, ZSM-34 and beta are formed.

D. S. Kim et al.2004 [19] obtained beta zeolite as nano-crystallite at 150 °C under microwave irradiation with different crystallization duration. Usually, zeolite beta is synthesized by hydrothermal treatment using colloidal silica solution, amorphous silica or tetraethylorthosilicate as silica source and tetraethylammonium hydroxide as structure directing agent.

Tosheva L. et.al. 2005 [20] describes a method for preparing nano- zeolites in a solution consisting of a surfactant, organic solvent, and water (called the emulsion method). The nano-zeolite is a promising material for increasing external surface area as well as decreasing diffusion resistance of the organic reactant within the micropores, thereby improving catalytic activity and lifetime. In addition, deactivation of acid sites of the zeolite using an organic silane compound improves the zeolitic properties when applying nano-zeolites to heterogeneous catalytic reactions. A new method based on catalytic cracking of silane (called the CCS method) is also described. Finally, light olefin synthesis via n-hexane cracking and acetone-to-olefin reaction over nano-zeolites, which successfully produce high yields of the light olefin with long catalyst life, is outlined.

S. Mintova et.al. 2006 [21] developed an efficient synthesis methodology to obtain crystalline zeolite beta with Si/Al of ratio of 25 to infinity in nanometer size at 100°C. These nanosized Beta zeolites show better catalytic behavior towards the industrially relevant alkylation of benzene with propylene to obtain cumene compared with other commercially available nanosized beta zeolites.

M. Lakshmi Kantam et al. 2006 [37] synthesized zeolite beta with crystal size of 40 – 90 nm (Si/Al ratio of 12.5 to 50) by employing two temperature stages.Choi et al.[26] (2006) showed that with new bifunctional soft templates, containing micro-pore directing diquaternary ammonium structures as well as mesopore directing organic partitions, it is possible to synthesize highly ordered multilamellar nanosheets of MFI.

Fan W. et al. 2008 [22] carefully designed a multistep templating procedure allowing the alignment of silicalite nanoparticles in a porous carbon replica.

T. Odedairo et.al. 2012 [23] investigated catalytic behavior of micro/mesoporous ZSM-5/MCM-41 composites in the transformation of 1,2,4-trimethylbenzene (TMB), meta-xylene transformation and in the cracking of 1,3,5-triisopropylbenzene (TIPB). The composite

materials exhibited exceptional catalytic performance compared with the microporous ZSM-5 in the transformation of 1,2,4-trimethylbenzene and m-xylene. In the cracking of 1,3,5-triisopropylbenzene, the composite materials showed higher activity as compared with the conventional Y-zeolite. The distinctive catalytic performance of these micro/mesoporous composite materials in the reactions studied was attributed to the excellent accessibility of the active sites provided by the mesopores for both reactant and product molecules. In the transformation of m-xylene, selectivity towards para-xylene over all catalysts is more.

2.2 Phenol alkyation

Grabowska H., et.al. 1992 [24] carried out alkylation of phenol with ethanol, n- and iso-propyl alcohols in gas phase in presence of iron catalyst. C_2 and C_3 alcohols exhibited high selectivity towards ortho-alkylation.

Bezouhanova C., et.al. 1992 [25] studied alkylation of phenol with ethanol in the presence of Ti-HZSM-5 and H-ZSM-5 zeolites. The selectivity of formation of the isomeric ethylphenols depends on the concentration of the acid sites of the catalyst, estimated by cyclohexanol dehydration. titanium introduction into pentasil structure improved the selectivity ~ phenol alkylation due to the lowered acidity of the zeolites.

Das J., et.al. 2000 [26] studied alkylation of phenol with ethanol to obtain *para*-ethylphenol, over ZSM-5 zeolite. Fine control of pore openings of ZSM-5 was achieved by chemical vapour deposition of silica employing tetra-ethyl orthosilicate. Selectivity for *para*-ethylphenol increased with the extent of silica deposition and under a comparable phenol conversion level, pore size controlled ZSM-5 exhibited about 88% selectivity for *para*-ethylphenol, as compared to only 37% with unmodified ZSM-5.

Bal R et.al. 2002 [27] studied vapour phase selective O-alkylation of phenol with methanol, ethanol, n-propanol and n-butanol in the temperature range 573–673K over alkali loaded (Li, Na, K and Cs) fumed silica. Fumed silica has negligible alkylation activity, but on impregnation with alkali metal oxides (Li, Na, K and Cs) becomes active for O-alkylation producing arylalkyl ethers. Activities of the catalysts increase with metal loading and with basicity of the metal ions (Cs > K > Na > Li). Very high conversion (approx. 90%) and 100%

selectivity of o-alkylated product was obtained over Cs loaded silica with methanol as the alkylating agent. Conversion decreased with increase in carbon chain of the alkylating agent. Catalyst deactivation rate and the reaction rates at various reaction parameters like contact time, temperature, mole ratio, were also investigated.

Vinu A., et.al. 2005 [28] used CoAl-MCM-41 (*X*) catalyst to study ethylation of phenol with ethanol in vapor-phase in the temperatures range (250-450)◦C. The products obtained were *O*-alkylated product (ethyl phenyl ether), *C*-alkylated products (2-ethylphenol and 4-ethylphenol), and *C*-/*O*-alkylated products (ethyl ethylphenyl ether). The phenol conversion increased significantly with reaction temperature over all the catalysts. The activity of the catalysts followed the order CoAl-MCM-41 (20) > CoAl-MCM-41 (50) > CoAl-MCM-41 (80). Selectivity between the *C*-alkylation and the *O*-alkylation depended on the factors such as acidity of the catalyst and the reaction temperature. CoAl-MCM-41 (20) catalyst displayed a phenol conversion of 40% and a selectivity of more than 80% for 2-ethylphenol under the optimized reaction condition.

Barman S. et.al. 2006 [29] investigated vapor phase alkylation of phenol with methanol over a series of cerium-exchanged NaX zeolite with Ce loadings ranging from 0 to 10.43 wt%. The catalyst containing 8.86 wt% cerium was found to be the best one with total cresols selectivity of 72% at a temperature of 573 K and MeOH to phenol mole ratio of 4:1. The catalyst was also found to be quite stable in the operating range investigated. It was established that the stronger acid sites are required for C-alkylation compared to O-alkylation. From the study of the effects of various parameters, the optimum operating condition for highest cresols selectivity were determined as: MeOH to phenol mole ratio, 4:1; temperature, 623 K; space-time, 10.2 kg h/kmol under atmospheric pressure. From the kinetic analysis of the experimental data, the apparent activation energy for the reaction was determined as 57.2 kJ/mol.

Sad M.E. et al., 2008 [30] studied selective synthesis of p-cresol by gas-phase alkylation of phenol with methanol on SiO_2–Al_2O_3 and zeolites HBEA, HZSM5 and HMCM22. Cresols were formed from phenol alkylation of methanol via two parallel pathways: the direct C-alkylation of phenol and the conversion of anisole intermediate obtained by O-alkylation of phenol. Methylation of o- and p-cresol led to the formation of 2,6- and 2,4-xylenols while

anisole produced methylanisoles either by alkylation with methanol or by disproportionation. Regarding the cresol isomers distribution, p- and o-cresol were the major products on all the samples while m-cresol formation remained always lower than 6%. In contrast, p-cresol was the predominant product on HMCM22 because the narrow sinusoidal 10-membered ring channels of this zeolite were particularly suitable for improving the selectivity of p-cresol. Thus, the p-cresol yields of 55% and p-cresol:o-cresol ratios of 4 were obtained on HMCM22 by gas-phase alkylation of phenol with methanol at 473 K, atmospheric pressure and contact time of 350 g h/mol phenol.

Sad M.E. et al., 2010 [31] studied the mechanism of gas-phase alkylation of phenol with methanol on zeolites HBEA, HZSM5 and HMCM22. The nature, density and strength of the acid sites were determined by temperature programmed desorption of NH_3 and FTIR spectroscopy of adsorbed pyridine. In all the cases, anisole, o-cresol and p-cresol were the primary products, but the initial product distribution greatly depended on the zeolite pore structure and surface acid properties. The complete reaction network was established by investigating the formation of secondary products (xylenols, methylanisoles, m-cresol) via the reactions of primary products with phenol and methanol.

Sad M.E. et al., 2014 [32] studied the selective synthesis of p-ethylphenol from gas-phase alkylation of phenol with ethanol was studied onzeolites HZSM5 and HMCM22 at 523 K. Phenol reacted directly with ethanol to form ethylphenylether by O-alkylation, and p- and o-ethylphenol isomers by C-alkylation; secondary products were m-ethylphenol and dialkylated compounds. Both zeolites presented similar activity and formed low amounts of ethylphenylether and dialkylated products, but exhibited different ethylphenol isomers distribution. Infact, for a contact time of 99.3 g h/mol the selectivity to p-ethylphenol was 51.4% on HMCM22 and only14.2% on HZSM5. The superior performance of zeolite HMCM22 for selectively producing p-ethylphenol was due to its narrower pore channels that suppressed the formation of dialkylated products and ham-pered by diffusional constraints the formation of o-ethylphenol.

2.3 Summary

The selective synthesis of p-ethylphenol from vapor phase alkylation of phenol with ethanol was investigated in a fixed bed reactor on cerium modified zeolite CeZSM5. A series of CeZSM-5 were prepared by modifying with 4%, 6%, 8% and 10% ceric ammonium nitrate solution. ZSM-5 exchanged with 10% cerium nitrate solution was proved to be the best of all the catalyst used. The modified catalyst were further characterized by SEM, XRD. Phenol reacted with ethanol to form ethylphenyl ether by O-alkylation, and p- and o-ethylphenol isomers by C-alkylation; secondary products were m-ethylphenol and dialkylated compounds. From the study of the effects of various parameters, the optimum operating condition for maximum selectivity of p-ethyl phenol were Pressure, 1 atm; temperature, 693 K; PhOH to EtOH mole ratio,1:3; nitrogen to feed mole ratio, 0.16, space time-0.0384kgh/kmol. A systematic and detailed kinetic study was carried out for the alkylation reaction. From the product distribution pattern, a kinetic model for the reactions was proposed following Langmuir–Hinshelwood approach. The kinetic and adsorption parameters of the rate equation were determined by non-linear regression analysis From the kinetic analysis of the experimental data, the apparent activation energy for the reaction was found to be 43.27kJ/mol.

CHAPTER-3 EXPERIMENTAL METHDOLOGY

3.1 Materials

1.5 mm extrudates HZSM-5 was procured from sub chemie, Vadodara ,India. Cerium ammonium nitrate was purchased from CDH chemicals, Chandigarh. Nitrogen gas was supplied from Lalit gas (99.99% pure) Patiala, Punjab. Phenol and ethanol were purchased from sigma Aldrich company.

3.2 Modification of HZSM-5 by cerium

The commercial HZSM-5 zeolite was modified using cerium ammonium nitrate solution to increase their activity by cerium exchange. At first, the zeolite was calcined at 623K for 2 hour then it get refluxed with required concentration of cerium ammonium nitrate solution for 24 hour using 100 rpm magnetic stirrer. After filtration washing of zeolite was done for three times by distilled water for removing extra ions and then dried it in an oven. After that it is calcined at 623K in a furnace for 3 hours. Similarly we prepared zeolite of different cerium content. After exchange HZSM-5 is transformed into Ce-ZSM-5.

3.3 Characterization of Catalyst

Zeolite sample was characterized through X-ray diffraction (XRD) analysis, Scanning electron microscopic (SEM), Energy dispersive spectroscopy (EDS)

3.3.1 Powder X-ray Diffraction

Crystallinity of the virgin and modified catalysts were determined using XRD (Bruker AXS, Diffractrometer D8, Germany) using Cu-Kα as a source. The XRD pattern of parent and cerium exchanged ZSM5 shows that there is no major structural change during cerium modification as shown in Figure 3.1 Crystallinity of all the modified zeolite was found to be approximately around 90 Crystallinity . The sample was analyzed on a PANalytical X'Pert Pro Diffractometric between the range $5° \leq 2 \text{ theta} \geq 60°$ using Cu-k-alpha radiation. ZSM-5 zeolite shows xrd peak at 2θ value of 23° which remains perfect in modified zeolite. And the peaks which is defined in cerium modified zeolite at 28.67°, 47.61° and 56.37° peaks (Figure 3.1) represent the presence of cerium in modified zeolite.

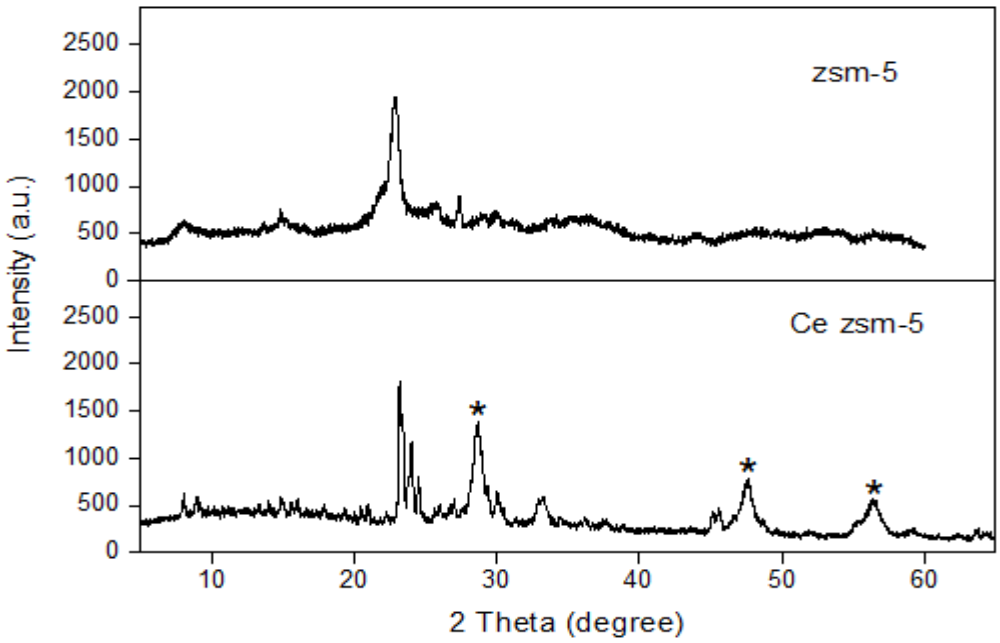


Figure 3.1 (XRD of ZSM-5 and modified CeZSM-5)

3.3.2 Scanning Electron Microscopy of HZSM-5

The SEM images of HZSM-5 and CeZSM-5 as shown in the **Fig. 3.3(a) and Fig. 3.3(b)** respectively. These show that the zeolite contain wide range of crystal sizes from 0.5 µm-1 µm and consisted of non uniform particles of spherical shape. It is seen from the graph that there is no morphological changes occur after exchange.

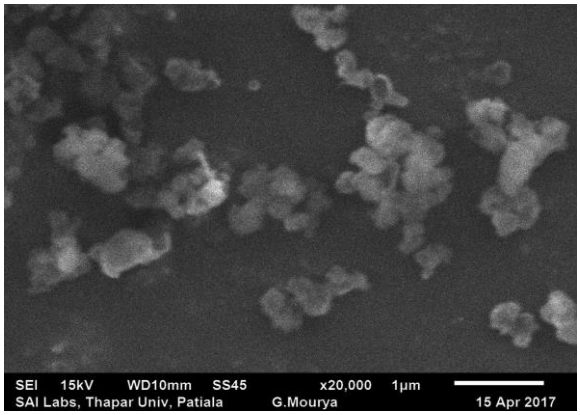


Figure 3.2 (a) SEM images of HZSM-5 Zeolite

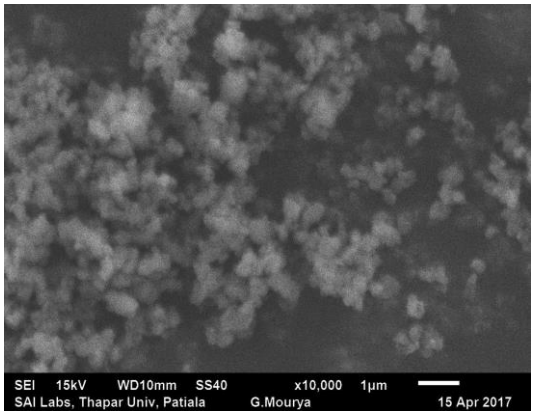


Figure 3.2(b)-SEM images of modified CeZSM-5 Zeolite

3.3.3 EDS Analysis

EDS shows the elemental composition of the zeolites. A quantitative analysis was performed. An analysis quantifies the elements by calculating the area under the peak of each identified element and after taking account for the accelerating voltage of the beam to produce the spectrum, performs calculations to create sensitivity factors that will convert the area under the peak into weight or atomic percent. The EDS spectra of CeZSM-5 is shown in Fig 3.3(a) and Fig 3.3(b) and compositions of catalysts are shown in tables 3.1(a) and table 3.1(b).

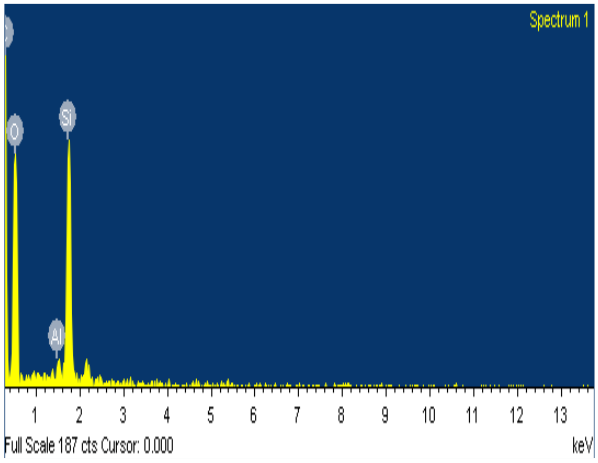


Figure 3.3(a) EDS spectra of HZSM-5

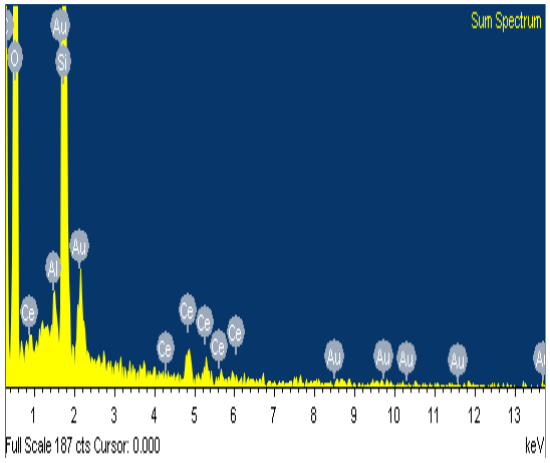


Figure 3.3(b) EDS spectra of CeZSM-5

Table 3.1(a)Composition of HZSM-5

Element	Weight %	Atomic %
C	61.13	69.35
O	32.13	27.37
Al	0.44	0.22
Si	6.30	3.06

Table 3.1(b) Composition of CeZSM-5

Element	Weight %	Atomic %
C	45.61	57.86
O	37.52	35.74
Al	0.50	0.28
Si	10.19	5.53
Ce	3.52	0.38
Fe	2.65	0.20

3.4 Determination of acidity of different zeolite:

Brönsted acidity [Mendham et al., 2000] [38] and Lewis acidity of various catalysts were estimated by the following procedures.

Protonic/Brönsted acidity: 20 mL each of KI (0.025 M), KIO3 (0.025 M) and sodium thiosulphate (0.025 M) were added to 0.5 g of catalyst sample in a conical flask. The catalyst was allowed for soaking in the mixture for 48 h. The excess of thiosulphate was then titrated against (0.008 M) I2 solution using starch indicator. At the end point the pale yellow solution turned to blue color. The protonic acidity of the catalyst was calculated from the volume of standard thiosulphate solution consumed by the liberated iodine. The thiosulphate solution was earlier standardized against a standard potassium dichromate solution. Protonic acidity was expressed as meq/g of catalyst.

Lewis acidity: For the determination of Lewis acidity, 0.5 g of catalyst sample was soaked in 25 mL of (0.025 M) n-butyl amine for 24 h. A 10 mL of supernatant liquid was pipetted out and titrated against trichloroacetic acid using 0.1% neutral red as indicator. Trichloroacetic acid was standardized earlier using standard n-butyl amine solution using neutral red as indicator. All the solutions were prepared in benzene. At the end point, the green color solution turned pink red color. The acidity of various catalysts are reported in Table 3.1. It is evident from this table that the acidity of the catalysts increases with increase in cerium content in the zeolite framework.

Table 3.2 – Pysiochemical properties of various catalysts

Catalyst	Metal (wt%)	Crystallinity (%)	Acidity (mmol/gm)	BET Surface area (m2/g)	Pore volume c.c/g	Mean pore dia
HZSM-5	Nil	95	0.65	424	0.694	6.5 nm
Ce-ZSM5	3.50	93	1.85	178	0.519	11.4nm

3.5 Alkylation Reaction in Flow Reactor

Alkylation reaction of phenol with ethanol was carried out in stainless-steel (SS-316) fixed-bed flow reactor shown in Fig.3.4. 2g of zeolite was loaded in the reactor. Before each experimental run the zeolite was activated for 3 hour in presence of nitrogen at temperature 573K. The temperature was recorded through a thermocouple which was inserted in a thermowell from the top to the centre of the fixed bed reactor. Phenol-Ethanol feed mixture was vaporized in a preheater and entered into the fixed reactor through a syringe pump. The vapour product and the unreacted reactant passes through a condenser where the vapour product get condensed to liquid and analyzed by gas chromatograph (Bruker GC) using FID (flame ionization detector).

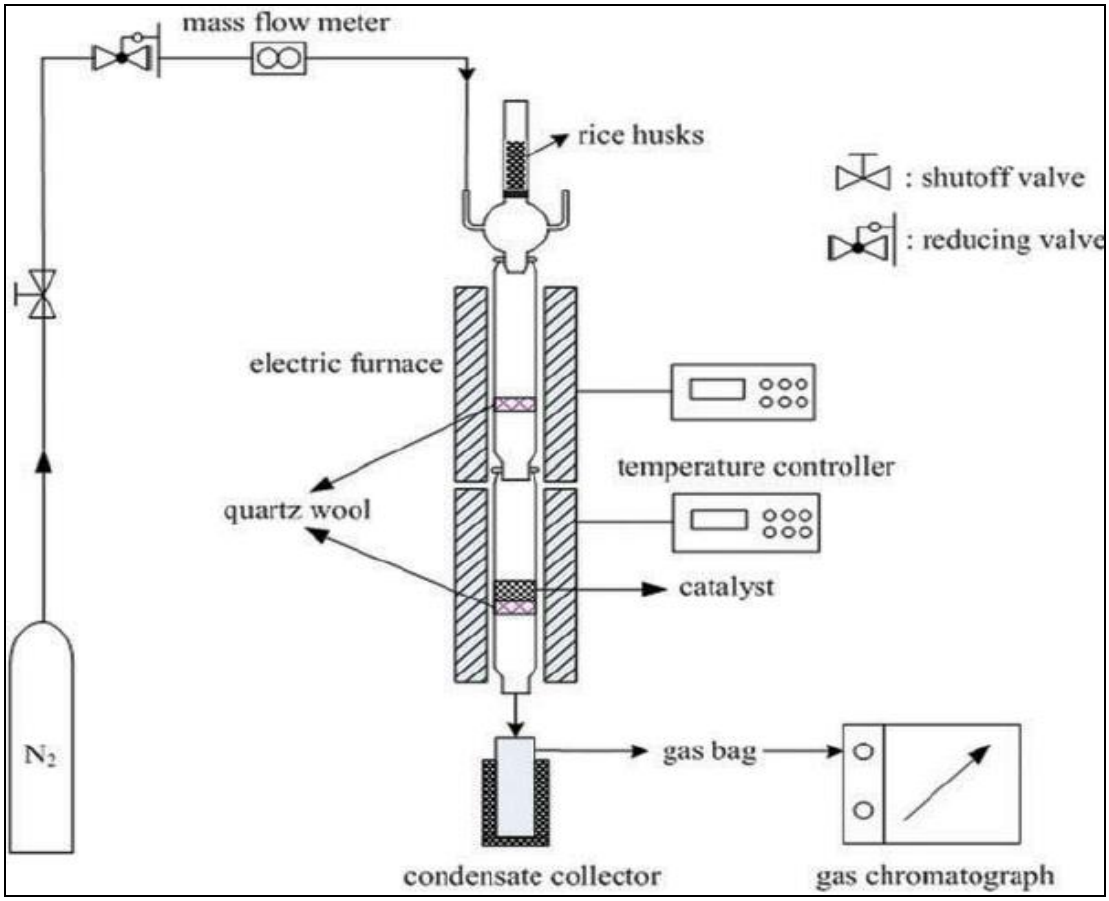


Figure 3.4 Schematic diagram of reactor set up

The ethanol conversion and selectivity of different product were estimated using the equations:

$$reactant\ conversion = \frac{(reactant \text{ in } feed) - (reactant \text{ in } product)}{reactant \text{ in } feed} \times 100$$

$$\text{Pr}oduct\ selectivity(\%) = \frac{y_{i,o}}{\sum y_{i,o}} \times 100$$

$$\text{Pr}oduct\ yield(\%) = \frac{y_{i,o}}{y_{eth,o} + \sum y_{i,o}} \times 100$$

Where $y_{i,o}$and $y_{eth,o}$ are the molar fractions of aromatic products and the outlet molar fraction of ethanol, respectively.

CHAPTER-4 RESULT AND DISCUSSION

4.1 Alkylation of Phenol with Ethanol Over CeZSM5-A kinetic study

In alkylation of phenol with ethanol effect of temperature, mole ratio, space time on reactant conversion and product selectivity were investigated over Ce-ZSM-5

4.1.1 Time on stream study of phenol conversion and Effect of Cerium on Product selectivity

The activity and stability of both parent and Ce modified zeolites were tested by 1 h time on stream and is shown in Figure 4.1(a), It was observed that modification of HZSM5 zeolite with Ce ions leads to a significant change in activity of zeolite as with increase in Ce content in the zeolite conversion of phenol increases due to strong acidity generated by cerium exchange. CeZSM5 modified with 10% cerium nitrate solution was proved to be the most active catalyst as it leads to highest phenol conversion 86.38%. where as over Ce-ZSM-5 modified with 8%, 6%, 4% cerium nitrate solution lead to phenol conversion of 75.25%, 54.58% and 46.02% respectively. But in 1 hour time on stream activity of all the catalysts are in decreasing trends. Ce-ZSM-5 modified with 10%, 8%, 6% and 4% cerium nitrate solutions lead to the decrease of phenol conversion to 81.25%, 68.25%, 49.02% and 41.21% respectively. The drop in conversion may occur due to deactivation of catalyst or dealkylation of product. .

The effect of cerium loading on product selectivity is shown in Figure 4.2. It is evident from this figure that with increase in cerium content of the modified ZSM-5 the selectivities of C-alkylated products increases and that of O-alkylated product decreases. The increase in C-alkylation is due to generation of stronger acid sites in the catalysts with more and more cerium exchange and the decrease in O-alkylation product require low acid strength as compared to C-alkylation. The selectivity of p-ethylphenol is 28.25% over zeolite exchanged with 4% cerium nitrate solution and maximum 46.12% ZSM5 zeolite with 10% Cerium nitrate solution.

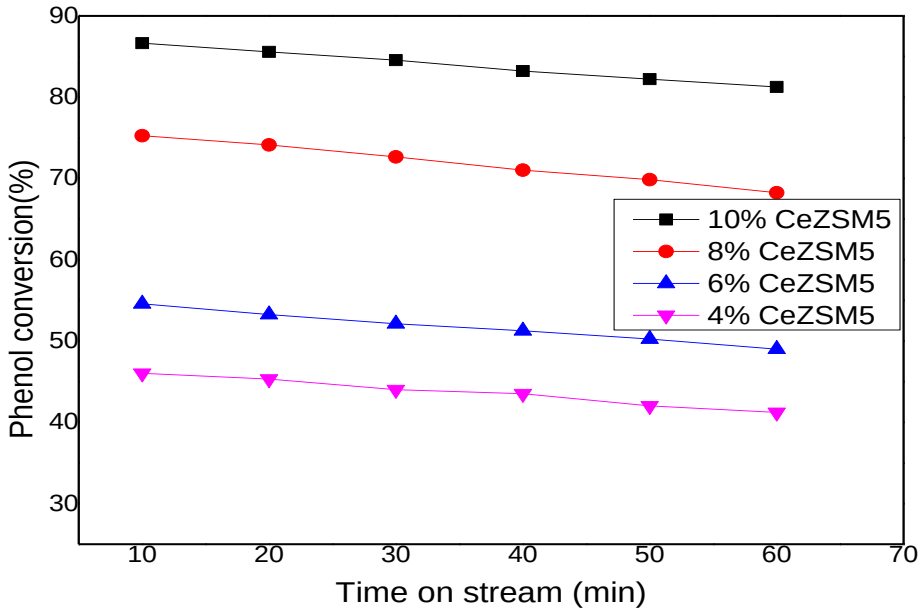


Figure 4.1 Effect of time on stream on phenol conversion: Pressure, 1 atm; temperature, 693 K; PhOH to EtOH mole ratio,1:3; space time-0.0384kgh/kmol, nitrogen to feed mole ratio, 0.16.

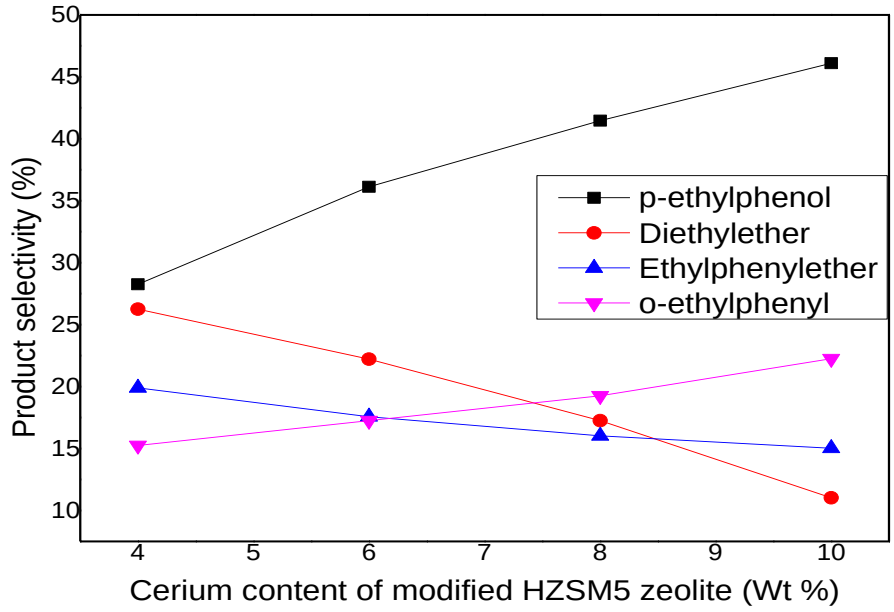


Figure 4.2 Effect of cerium content of catalysts on products selectivities; Condition: Pressure, 1 atm; temperature, 693 K; PhOH to EtOH mole ratio,1:3; space time-0.0384kgh/kmol, nitrogen to feed mole ratio, 0.16.

4.1.2 Effect of temperature on selectivity

Reactions were carried out to see the effect of temperature on reactants conversion and product distribution, in the temperature range 633K- 693K and using CeZSM5. it can be seen that among the various products formed, p-ethylphenol has maximum selectivity. The selectivity of o-ethylphenol increases from 12.65% at 633K and is maximum (18.46%) at 693K. p-ethylphenol is selectively (46.12%) formed more than any other product. Selectivity of ethylphenylether is maximum (23.42%) at 633K. At this temperature, selectivity of p-ethylphenol is least (40.25%) as shown in figure 4.3.

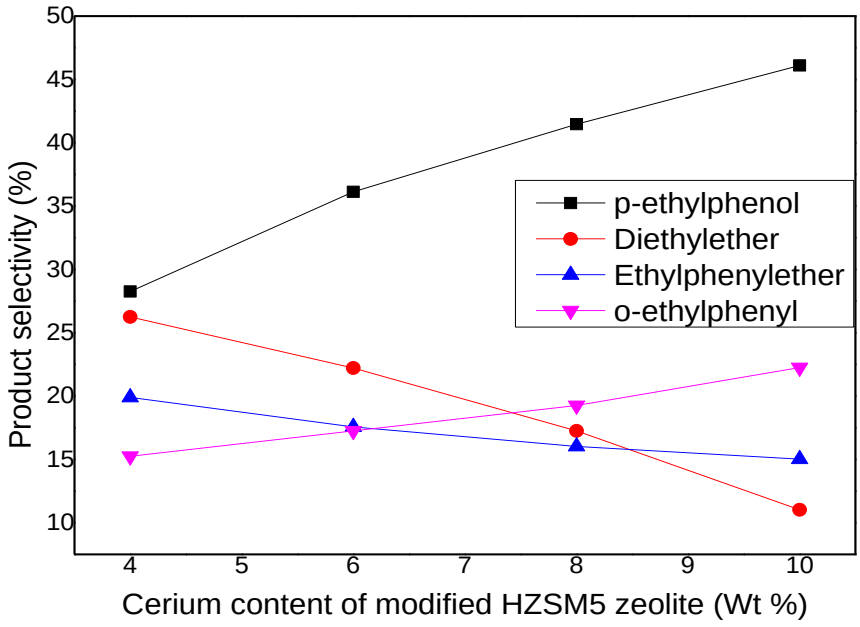


Fig.4.3 Effect of temperature on product selectivity; Conditions: pressure- 1atm; catalyst- CeZSM-5; Space time-0.0384kgh/kmol phenol/ethanol mole ratio- 1:3; N_2 to feed ratio- 0.16

4.1.3 Effect of reactant mole ratio on phenol conversion and selectivity of product

To check the effect of reactant ratio on product distribution, the reactant ratio of phenol : ethanol was varied form 1:1-1:10. Phenol was taken as limiting reactant. Initially with increase in mole ratio Both the reactant show maximum conversion at phenol to ethanol reactant ratio of 1:3. Phenol shows maximum conversion of 86.38% at reactant ratio 1:3. Above this reactant ratio, both phenol and ethanol conversion decreases which shows that

phenol to ethanol ratio of 1:3 is optimum for achieving maximum conversion of reactants. At reactant ratio 1:3 the selectivity of p-ethylphenol was 46.12%. With increase in reactant mole ratio phenol conversion increases upto a mole ratio of 0.33. At much higher reactant ratio, due to less availability of phenol, conversion drops. However, p-ethylphenol and m-ethylphenol selectivity is high at higher mole ratios. this indicate the formation of C-alkylated alkylated product is dependent upon the availability of excess ethylating agent as shown in Figure 4.4.

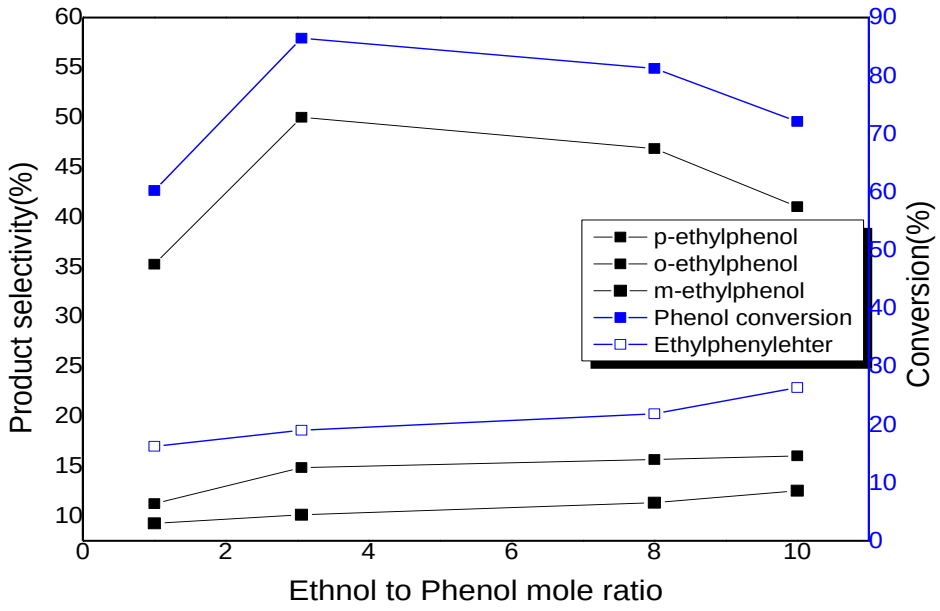


Fig 4.4 Effect of mole ratio on product selectivity and phenol conversion. Conditions: pressure- 1atm; Space time-0.0384kgh/kmol, Catalyst; CeZSM5, Temperature -693K, N_2 feed ratio; 0.16.

4.1.4 Effect of space time on phenol conversion and p-ethylphenol selectivity

The effect of space-time was studied in the range of 0.023-0.047 kgh/kmol. The phenol conversion increased with increase in space-time as shown in Figure 4.4. This may be due to higher contact time between the reactant and catalysts. The active sites in the catalyst are come in contact with reactants for longer time. Maximum phenol conversion of 86.38% was observed over CeZSM5 catalyst at 0.0384 kg h/kmol space-time . Initially, p-ethyl phenol selectivity increased with space-time, however, at much higher space-time, selectivity of p-

ethyl phenol decreased due to the formation of undesired products. P-ethylphenol selectivity reaches a maximum of 46.12% over CeZSM5 at 0.0384 kgh/kmol space-time. Effect of Space time on Selectivity is shown in the Figure 4.5.

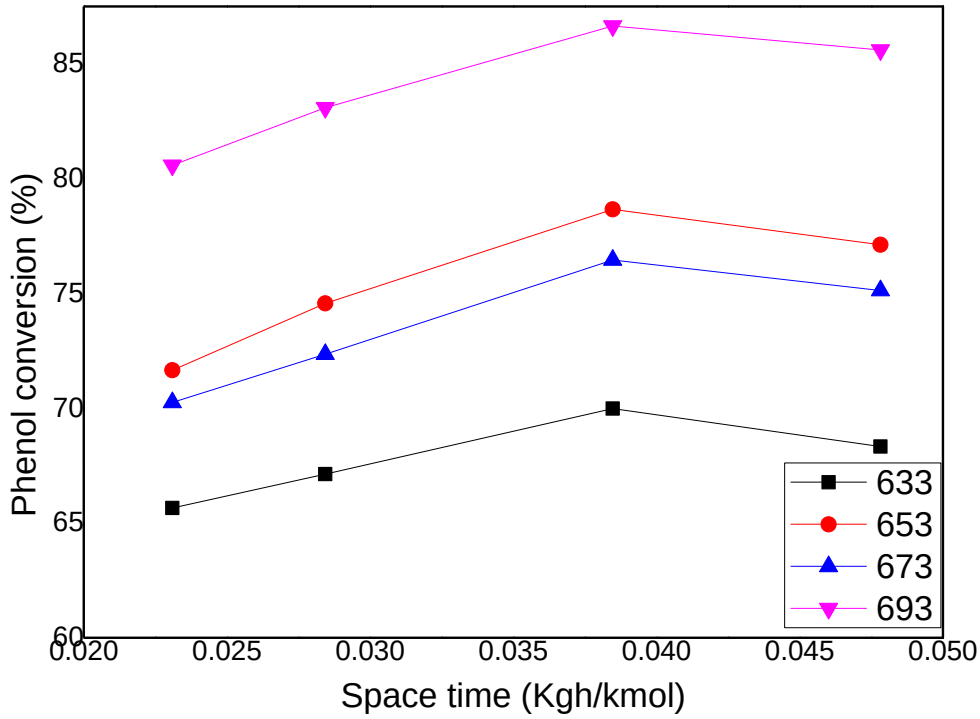


Figure 4.5 Effect of Space time on product selectivity and phenol conversion. Conditions: pressure- 1atm; Catalyst; CeZSM5, Temperature -693K,N_2 feed ratio;0.16.

4.2 Kinetic modeling

The kinetic runs were carried out at four different temperatures (633K, 653K, 673K, and 693K).. With the help of the reaction scheme described in Scheme 1, various reaction rate models (adsorption, desorption, and surface reaction controlling) were formulated following Langmuir-Hinshelwood approach. The models were tested with the help of the experimental data. All models, except the surface reaction controlling one, gave negative constants. Hence they were not considered. The following surface reaction-controlling model was found to fit the experimental data better with proper trend of various constants. Alkylation of phenol with ethanol is a complex reaction which is accompanied by the following reactions such as:

$$Phenol + Ethanol \xrightarrow{K1} Ethylphenylether + water$$

$$Phenol + Ethanol \xrightarrow{K2} p-Ethylphenol$$

Secondary reaction

$$2Ethanol \xrightarrow{K3} diethylether$$

k_1, k_2, k_3 are reaction rate constants. k_{ads} is adsorption constant. C_{site} is concentration of active sites available for adsorption. *P* is the partial Pressure.

Considering Dual Site mechanism,
For the rate of disappearance of phenol,
Net rate of disappearance of phenol = rate1 + rate2
Rate=k k_{ads} $k_{reactant}$ C_{site}

$$-r_{Ph} = [k_1 K_{Ph} K_{Et} C_{Ph} C_{Et} C_v^2 + k_2 K_{Pt} K_{Et} C_{Ph} C_{Et} C_v^2]$$

$$-r_{Ph} = \frac{dx_{Ph}}{d\tau} = [k_1 K_{Ph} K_{Et} C_{Ph} C_{Et} + k_2 K_{Ph} K_{Et} C_{Ph} C_{Et}] / Z^2 \quad (1)$$

$$r_{diethylether} = k_3 K_{Et}^2 C_{Et}^2 C_v^2 \quad (2)$$

$$Z = 1 + K_{Ph} C_{Ph} + K_{Et} C_{Et} + K_{EPE} C_{EPE} + K_{p-EP} C_{p-Ep} + K_{DiEtE} C_{DiEtE} + K_{H_2O} C_{H_2O} \quad (3)$$

The partial pressures in the vapor phase were calculated using the fractional conversion and total pressure P as shown below:

$$p_{Ph} = (1 - X_{Ph})P / 4.64 \quad (4)$$

$$p_{Et} = (3 - X_{Et})P / 4.64 \quad (5)$$

$$p_{p-EP} = (X_{p-EP})P / 4.64 \quad (6)$$

$$p_{m-EP} = (X_{m-EP})P / 4.64 \quad (5)$$

$$p_{0-EP} = (X_{o-EP})P / 4.64 \quad (6)$$

$$p_{EPE} = (X_{EPE})P / 4.64 \quad (7)$$

$$p_{Diethylether} = (X_{Diethylether})P / 4.64 \quad (8)$$

$$p_{Ethylene} = (X_{Ethylene})P / 4.64 \quad (9)$$

In this reaction total no of moles can be calculated by

Moles of nitrogen = N_2 / (Ph+Et) = N_2 feed flow rate (0.16)

N_2/(1+3) = 0.16

N_2 = 0.64 moles

In the reaction system, the total number of moles of different components was found to be 4.64. A non-linear regression algorithm was used for parameter estimation. The optimum value of the parameters was estimated by minimizing the objective function given by the following equation:

$$f = \sum_{i=1}^{n} [(Rate\ predicted)i - (Rate\ experimental)i]^2$$

The kinetic and adsorption constants evaluated by non-linear regression are tabulated in Table 4.1 for dual site model. The standard error of estimate ease found to be 3.82×10^{-4}. The experimental and the predicted ethanol conversions for this model, at different temperatures, are plotted in Figure 4.6. The plot shows a good correlation between the experimental and predicted rates having an R^2

Table 4.1: Kinetic and adsorption parameters for dual site mechanism for phenol – ethanol alkylation over CeZSM5 zeolite

Kinetic and adsorption parameters	Temperature(K)			
	633 K	653 K	673 k	693 K
k_1(kmol/kgh)	0.22	0.30	0.32	0.50
k_2(kmol/kgh)	0.12	0.22	0.35	0.44
k_3(kmol/kgh)	0.02	0.04	0.06	0.10
K_a(atm^{-1})	0.02	0.04	0.007	0.02
K_b(atm^{-1})	0.04	0.03	0.02	0.01
K_c(atm^{-1})	0.03	0.04	0.05	0.06

The kinetic constants derived from equation (1), were used to find the activation energy (E_a) for ring alkylation using the Arrhenius equation,

$$Lnk = \ln A - E_a / RT$$

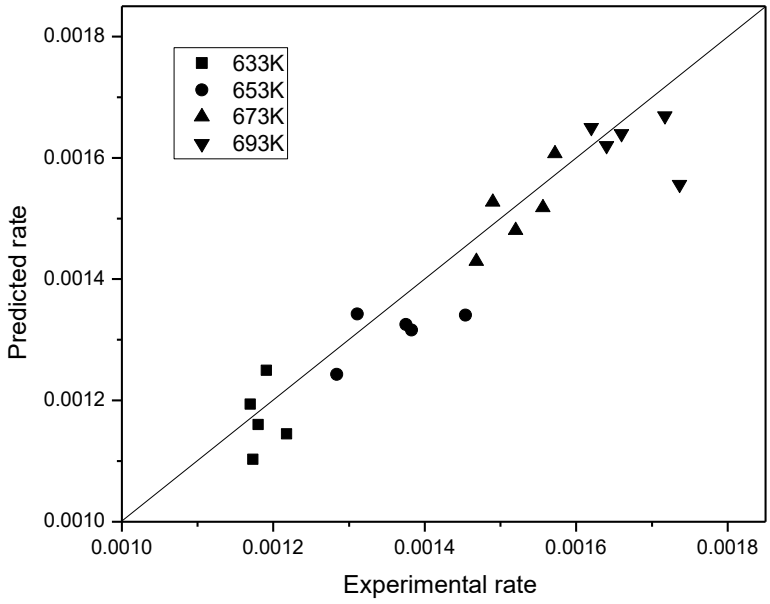


Figure 4.6 Experimental vs predicted rate of phenol conversion over CeZSM5

Activation energy for alkylation reaction was estimated from the graph plotted, Figure 4.7. It was found to be be 43.27 kJ/mol for CeZSM5 zeolite. Apparent activation energy of 57.2kJ/mol for phenol alkyaltion with NaX zeolite was reported (Barman et al. 2006). The value of frequency factor (A) was found to be 3.06×10^5 for CeZSM5 used catalyst.

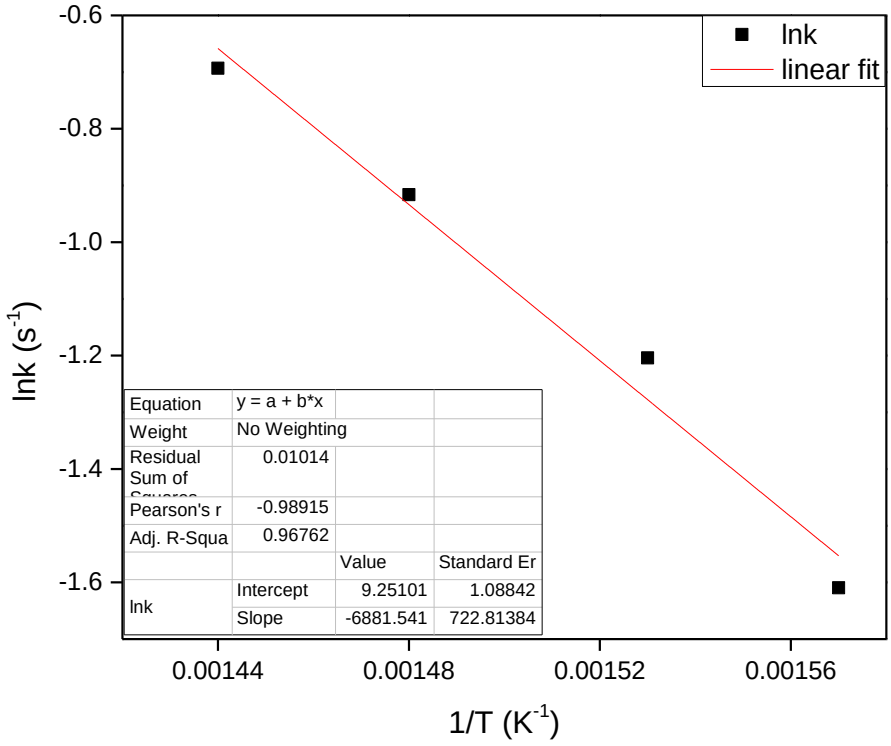


Figure 4.7 Plot of lnk vs 1/T

CHAPTER-5 CONCLUSION AND FUTURE WORK

5.1 Conclusion

HZSM-5 was characterized and modified with cerium. Alkylation of phenol with ethanol was carried out over Ce-ZSM-5 zeolite catalysts. Modification of zeolite with this metal brought significant increase in selectivity of the product of catalyst due to increased acidity by cerium exchange.

CeZSM5 shows maximum phenol conversion of 86.38% was found at temperature 693K, reactant ratio 1:3, space time 0.03849 kgh/kmol. Based on the product distribution, a reaction mechanism is proposed together with a rate expression for the disappearance of ethanol. The kinetic and the adsorption constants of the rate equation are estimated. The activation energy for alkylation reaction over CeZSM5 was determined to be 43.27 kJ/mol, which is comparable with the data reported in the literature for alkylation reactions. Highest p-ethylphenol selectivity of 46.12% at 0.0384 kgh/kmol space-time was observed.

It is observed that cerium modified zeolite contributes for C-alkylation (ethylphenol isomers) as well as O-alkylation (Ethylphenylether). When exchanged with cerium (10%Ce), catalytic performance was improved. However maximum phenol conversion of 86.04% was found at temperature 693K, reactant ratio1:3, space time 0.03849 kgh/kmol. Maximum selectivity of 46.12% for p-ethylphenol, respectively, was reported at 0.0384 kgh/kmol space-time at temperature 693K and reactant ratio 1:3.

5.2 Future Work

Kinetic and modeling of C-alkylation reaction of phenol with ethanol over faujasite beta, X and Y zeolite can be carried out. A suitable model can be developed for predicting the conversion. By finding reaction constants proper reactor can be designed for pilot scale.

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