Ring and Side Chain Alkylation of Toluene with Methanol over Modified Zeolite Beta

A

Dissertation submitted

In the partial fulfillment of the requirement for the degree of

M.Sc. (Chemistry)

Submitted by

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July 2016

CERTIFICATE

This is to certify that the dissertation entitled **"Ring and Side Chain Alkylation of Toluene with Methanol over Modified Zeolite Beta"** being submitted by **Ms. Yashika Raparia** in partial fulfillment of requirements for the award of degree of **M.Sc. Chemistry** and being submitted to the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafied work carried out by her under our supervision. The work has reached the standard necessary for submission. The contents of this dissertation has not been submitted for the award of any other degree or diploma.

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CANDIDATE'S DECLARATION

I, hereby declare that the work presented in the thesis entitled "**Ring and Side Chain Alkylation of Toluene with Methanol over Modified Zeolite Beta**", 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 2016 to July 2016 under the supervision of Dr. Sanghamitra Barman, Associate Professor, Department of Chemical Engineering, Thapar University, Patiala, Punjab and Dr. Kamaldeep Paul, Associate Professor, School of Chemistry and Biochemistry, 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.

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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

Kinetic study for toluene alkylation with methanol over Fe and K modified beta zeolite has been investigated in the present study. The reaction has been carried out in a fixed bed down-flow reactor. The influences of various process parameters such as temperature (613K - 673K) and space-time (0.009 - 0.057 kgh/kmol) on methanol conversion and xylene selectivity were studied. Maximum methanol conversion of 99.86% was achieved at a temperature 673K, reactant ratio 5:1, space time 0.023 kgh/kmol. However maximum toluene conversion of 32.63% was found at temperature 673K, reactant ratio 5:1, space time 0.057 kgh/kmol. The kinetic runs have been carried out to choose the zone in which the mass transfer effects are negligible. Based on product distribution, a mechanism for the formation of xylene over the Fe modified catalyst was proposed along with a rate expression. The kinetic and adsorption constants of the rate equations were estimated by non-linear regression. The activation energy was found to be 10.36 kJ/mol. Highest xylene selectivity of 58.58% at 0.0231 kgh/kmol space-time was noted.

The second investigation has also been carried out to determine the catalytic performance of Fe and K exchanged zeolite beta for the synthesis of styrene. A series of K modified zeolite beta was prepared. The experimental runs were taken to optimize the different parameters like temperature, reactant mole-ratio, and space-time. The catalyst is characterized by XRD, SEM and EDS.

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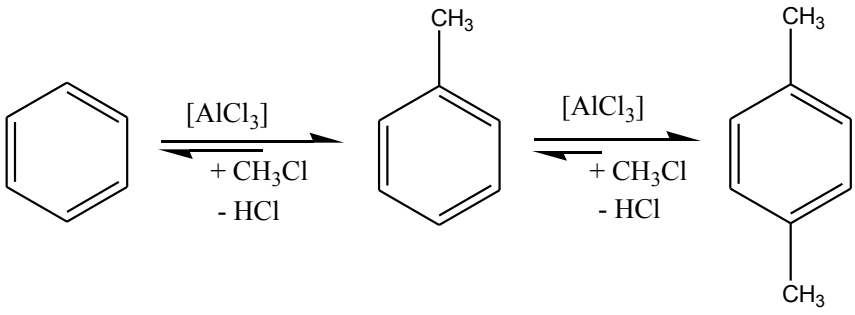
CHAPTER-1 INTRODUCTION

1.1 Alkylation

Alkylation is the introduction of an alkyl (or aromatic alkyl) group by substitution or addition into an organic compound. While the number of possible different alkyl groups is very large, the groups containing C_1–C_6 are mostly preferred due to the commercial importance of the respective alkyl aromatics. The alkylating agent originally used in the Friedel-Crafts reaction was alkyl halide (Friedel et al. 1877). 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 Alkylation reaction is used in a many industrial applications like in production of plastics, synthetic fibers, high octane gasoline, synthetic rubber etc. In this reaction the acylating or alkylating agent like $AlCl_3$ and the catalyst such as HCl, react to form either acylium ion or carbonium ion or complex. The formed ion or complex attacks the aromatic ring. So when alkylation of toluene is carried out in the presence of $AlCl_3$ and CH_3Cl is taken as a catalyst we get the following reaction:



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.

1.1.1 Alkylation of toluene with methanol

Toluene alkylation with methanol over zeolites is a good synthetic route to form either styrene or ethyl benzene or xylenes when compared with the Friedel–Crafts alkylation (Aboul-Gheit et al. 1999). The distribution of products depends on whether ring alkylation is occuring or side chain alkylation is preferred. When ring alkylation is favoured then Xylenes are formed, while side-chain alkylation gives styrene and ethylbenzene as the main products (Bokade et al. 2007).

The products formed (styrene, ethyl benzene, and xylenes) depends on the pore size of the molecular sieve and catalyst's acidity. Side- chain alkylation is favored by while large-pore basic zeolites, such as K-X, favor but ring alkylation is favored by medium-pore acidic zeolites, such as H-ZSM-5.

With acid catalysts ring alkylation favours (path B) but side chain alkylation (path A) takes place when basic catalysts are used. Path B favoures the formation of Xylenes, while Path A leads to the formation of styrene, cumene, TMB as product (Bokade et al. 1999; Yashima et al. 1974).

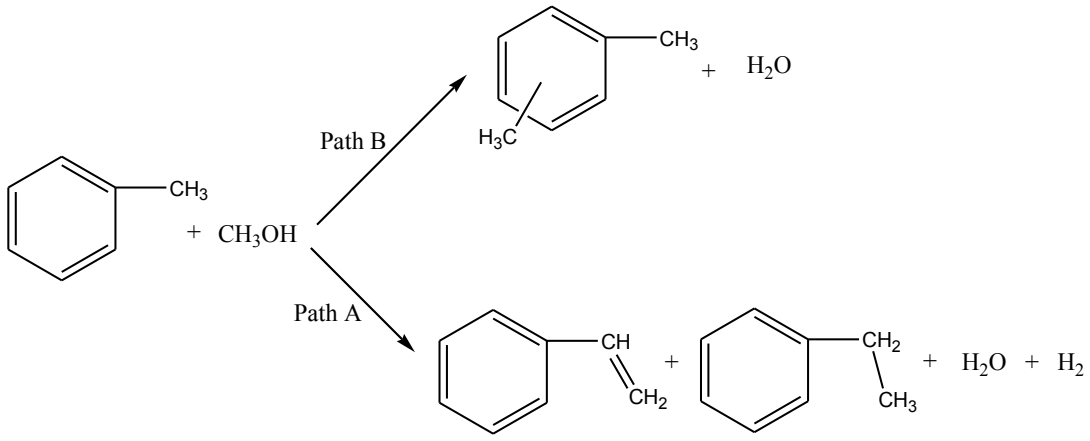


Figure 1.1 Reaction Scheme

1.1.2 Ring Alkylation (formation of Xylene)

There is large industrial need for p-xylene because it is used as important raw material for manufacture of dimethyl terephthalate and terephthalic acid. It is also used for the production of vitamins and other pharmaceutical medicines. Conventionally xylene isomers were separated by Parex process of adsorption or by toluene disproportionation. But now selective preparation of p-xylene through alkylation of toluene with methanol is used as an alternate route. ZSM-5 type zeolites are used for selective formation of p-Xylene by alkylation of toluene. ZSM-5 is used because of its shape selectivity. Its shape selectivity can be improved by modification with other agents (Bowes et al.1996; Yashima et al. 1974)

Many researchers has studied the selective formation of p-xylene by toluene alkylation with methanol in presence of modified zeolite catalyst because p-xylene it is important raw material for purified terephthalic acid and dimethyl terephthalate. Mostly ZSM-5-type zeolites have been studied because these zeolites are effective for alkylation because of their good activity and shape selectivity. On adjusting the diffusion parameters, acid activity and reaction parameters, good p-xylene yield in alkylation of toluene was obtained. The selective formation of p-xylene over modified ZSM-5 structure has been presented (Borade et al. 1986).

Toluene methylation was first examined over different cationic forms of Y-zeolite. Later, mostly ZSM-5 zeolites structure of medium-pore with silicon, isomorphously exchanged by trivalent cations such as B, Fe, and Al were used (Čejka et al. 2002). Due to the greater shape-selectivity properties, ZSM-5 was used. Eventhough there are many papers on mechanism of methylation of toluene but still full details of the mechanism of reaction are not yet known. Currently it is believed that alkylation occurs when methanol is chemisorbed on the acid sites and then formation of surface-active species occurs like methoxonium ions or methoxy groups, which are supposed to further react with toluene which is weakly adsorbed.

1.1.3 Side Chain Alkylation (formation of Styrene)

The side-chain methylation of toluene and other methylbenzenes by methanol is an industrially important alkylation reaction particularly for its product styrene. Basic zeolites favoured the side chain reaction, the most common choice being a NaX zeolite exchanged

with one or two heavy alkali metals like cesium, rubidium, or potassium (Itoh et al. 1983). Often such basic catalysts were modified by addition of B and Cu or Ag (Lacroix et al. 1984); B, P, Cu; KOH or CsOH (Engelhardt et al. 1987); or cesium acetate (Hathaway et al. 1989). Recently, an association of X and ZSM-5 zeolites, exchanged with B and modified K and alkali metal hydroxides, was suggested.

Styrene and ethyl benzene are vital resources for the petrochemical industry. Presently, the catalytic alkylation of benzene with ethylene, followed by the catalytic dehydrogenation of ethyl benzene is used to produce them. But for economic advantages, the side-chain alkylation of toluene with methanol is considered for their production.

Certain catalysts, have been used to test toluene side-chain alkylation, like LDHs (Leonard et al. 1927), alkali ion-exchanged X or Y zeolites, CaO, MgO encapsulated silicalite (Itoh et al. 1983) and cesium-containing microporous carbon. Out of these catalysts, high activities for the side-chain alkylation are shown by K and Cs-exchanged X zeolites (KX, CsX).

Lacroix et al. 1984 reported that copper contributes to dehydrogenation of reaction intermediates. When zinc is compared with copper, former possesses a resembling electronic structure and thus is used in the reaction of methanol dehydrogenation to formaldehyde. However, the effects of Zn addition on side-chain alkylation are not much studied.

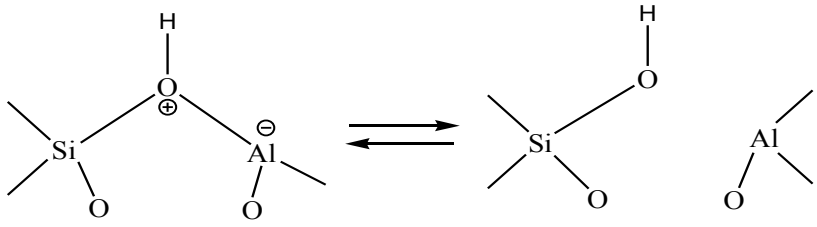
1.2 Zeolites

Zeolite are molecular sieves which are crystalline, hydrated microporous aluminosilicates. They have a 3-D framework of tetrahedral blocks of SiO_4 and AlO_4. These tetrahedral blocks are the building blocks in which Al and Si are tetrahedral atoms (T atoms) and each oxygen is shared with an adjacent T atom. The general formula of the crystallographic unit cell of zeolites may be represented by:

$$M_{x/n}\,[(AlO_2)_x(SiO_2)_y]_zH_2O$$

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^+, $NH4^+$ 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. They're solids with a relatively open, three-dimensional

crystal structure built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-Earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them. 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 (Haag et al. 1984). Classical Brönsted and Lewis acid models have been used 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. They also resist high pressures, don't disssolve in water or other inorganic solvents, and don't oxidize in the air.



Bronsted 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. The most interesting thing about zeolites is their open, cage-like, "framework" structure and the way it can trap other molecules inside it. This is how water molecules and alkali or alkaline-Earth metal ions (positively charged atoms with too few electrons, sometimes called cations) become a part of zeolite crystals—although they don't necessarily remain there permanently. Zeolites can exchange other positively charged ions for the metal ions originally trapped inside them (technically this is known as **cation exchange**) and they can gain or lose their water molecules very easily too (this is called **reversible dehydration**). The particular zeolites are of a fixed size and shape, zeolite catalysts can work selectively on certain molecules, which is why they're sometimes referred to as **shape-selective catalysts**.

The use of zeolite as catalysts in the Petroleum and Petrochemical Industry is their most vital application. The “Parex Process” of M/s UOP uses FAU framework zeolites to separate p-xylene from a mixture of other xylene isomers and ethyl benzene. Also, Lindox and Unox processes use low silica zeolites in their pressure swing adsorption. Other petrochemical

processes using these catalysts are Mobil-Badger ethylbenzene process (from benzene and ethyl alcohol), ALBENE one step ethylbenzene process also from benzene ethyl alcohol, Mobil's methanol to gasoline (MTG) process, selective alkylation of toluene with methanol to *p*-xylene, etc.

1.2.1 Application of zeolites for alkylation of toluene

Alkylation of toluene with methanol over zeolite catalysts can produce ethylbenzene, styrene, and/or xylenes depending upon the acidity of the catalyst and the pore size of the molecular sieve. Medium-pore acidic zeolites, e.g. H-ZSM-5, favor ring alkylation 8-I0 while large-pore basic zeolites, e.g. K-X, favor side-chain alkylation.

Methylation of toluene over ZSM-5 zeolites modified by the introduction of Sr of 2.5%, 5%, and 10% by weight was studied (El et al. 2014). Their work deals with the effect of added N-octyl-N-benzyl-N-methylglyene emulsifier on the alkyla- tion of toluene by methanol to investigate the performance of Sr/ZSM-5 catalyst of different (Sr) ratios, through the alkylation of toluene by methanol.

Different modifications of zeolite catalysts has resulted in high p-xylene selectivity. The higher p-xylene selectivity over the modified zeolite, used in Faramawy is attributed to the removal of external surface acid sites and smaller pore openings size (Faramawy et al. 1999). Methylation of toluene, in addition to some other side reactions such as xylene isomerization, occurs inside the pores of the zeolite catalyst. Palomares et al. 1997 have reported that diffusion plays an important role in the transport of xylenes from the pores inside out, and that the diffusion coefficient of p-xylene can be about 100 times that of o-xylene and about 1000 times that of m-xylene above 250°C.

Borgna et al. 2005 found that formation of styrene and ethylbenzene was significant only on CsNaY zeolites of exchange degree higher than about 40%. Cesium ion-exchanged zeolite X or Y has been accepted to be the most effective solid base catalyst for producing styrene from toluene and methanol. According to Unland and Baker and Lin and Sphon, cesium ion-exchanged zeolite X or Y further modified with boron or phosphorus could favor the formation of styrene. Palomares et al. indicated that cesium ions bonded on the framework could not only improve the catalyst base strength but also stabilize adsorbed toluene.

1.3 Objectives of present investigation

1) Synthesis and characterization of Fe modified beta zeolite and K modified beta zeolite.

2) Evaluation of the catalytic performance of the modified catalysts for the production of xylene and styrene by alkylation of toluene with methanol

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.

To the best of our knowledge, some other modified basic zeolites such as CsX, RbX, KX and LiX are obtained from NaX by ion-exchanged technology and their surface acid–base properties can be modified by varying the ionic exchange degree. Therefore, it is reasonably established that the exchange degree of K can affect on the direction to ring or side-chain alkylation of toluene with methanol.

CHAPTER-2 LITERATURE REVIEW

2.1 Zeolite

The history of zeolites began in 1756 when the Swedish mineralogist Cronstedt discovered the first zeolite mineral, stilbite (Cronstedt et al. 1756). He recognized zeolites as a new class of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths. Because the crystals exhibited intumescence when heated in a blowpipe flame, Cronstedt called the mineral a "zeolite" (derived from two Greek words, zeo and lithos, meaning "to boil" and "a stone"). From 1777 through about the 1800s various authors described the properties of zeolite minerals, including adsorption properties and reversible cation exchange and dehydration.

Leonard et al. (1927) 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. The early synthetic work remains unsubstantiated because of incomplete characterization and the difficulty of experimental reproducibility.

Barrer began his pioneering work in zeolite adsorption and synthesis in the mid-1930s to 1940s. He presented 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.

Flanigen et al. (1987) 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 0.3 nm to 0.8 nm encompassing small, intermediate and large pore structures. The new molecular sieves are synthesized by hydrothermal crystallization of reactive alumino-phosphate gels containing the additional framework elements and an organic template.

Bedard et al. (1989) 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) 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 (1997) 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.

Bu et al. (1998) 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) 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.

Bowes et al. (1999) 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) 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.

Kim et al. (2004) 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 et al. (2005) 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.

Mintova et al. (2006) 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.

Kantam et al. (2006) 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. (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 et al. (2008) carefully designed a multistep templating procedure allowing the alignment of silicalite nanoparticles in a porous carbon replica.

Odedairo et al. (2012) 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 Toluene alkyation

Itoh et al. (1983) describe the cooperation of Lewis acid/base pairs in the mechanism of toluene alkylation. A base site activates the methyl group of toluene, whereas the acid site interacts with the aromatic ring. Consistent with the proposed synergism between acid and base sites, small amounts of Li added to RbX catalysts significantly promoted the alkylation re- action.

Lacroix et al. (1984) prepared catalysts from Cs-exchanged X zeolites by addition of Cu and Ag. The presence of those metals (and boron) on CsX substantially improved the alkylation yield over an unpromoted catalyst. However, most of their experiments used H_2 as the carrier gas.

Engelhardt et al. (1987) found that washing KX zeolites with water resulted in materials that catalyzed formation of styrene, ethylbenzene and xylenes. Additional washes caused xylene formation to increase at the expense of side-chain alkylation. Washing alkali-exchanged zeolites with water apparently introduces some acidity into the catalysts. In contrast, post-exchange treatment of KX zeolite with KOH solution completely suppressed xylene formation and promoted side-chain alkylation. Occluded KOH appears to play an important role in the base-catalyzed reaction.

Hathaway and Davis (1989) showed that occlusion of cesium oxide into the pores of Cs-exchanged X and Y zeolites, via acetate impregnation and decomposition, promoted the reaction of toluene and methanol. Unfortunately, substantial amounts of methanol decompose

to carbon monoxide over such strongly basic materials.

Xiangsheng et al. (1991) found that a mixture of KX and KZSM-5 zeolites was more active than the separate components. They proposed that the strong base sites of the KX component activate the side-chain of toluene and that the weak base sites of the smaller pore KZSM-5 catalyze methanol conversion to formaldehyde.

Bibby et al. (1992) studied methylation of toluene over ZSM-5 zeolites modified by the introduction of Sr of 2.5%, 5%, and 10% by weight. Experiments were performed in a fixed bed under the conditions of reaction temperatures between 300°C - 500°C, liquid hour space velocity of 4 g toluene/hg catalyst, methanol to toluene ratio 4:1, and 0.01% of N-Octyl-N-benzyl-N-methylglycine as emulsifier. Data for conversion of toluene and selectivity towards xylene isomers showed that 2.5% Sr/ZSM-5 catalyst has the highest conversion of toluene at 500℃, and the lowest p-xylene selectivity, while 10% Sr/ZSM-5 catalyst has the highest selectivity for p-xylene production. Nevertheless, the catalyst 2.5% Sr/ZSM-5 has the highest selectivity for m-xylene. The two catalysts 2.5% and 5% Sr/ZSM-5 give nearly the same selectivity for the three xylene isomers at all conversions obtained at the reaction conditions under study.

Vasiliev et. al. (1993) investigated the catalytic properties of NaX-type zeolites modified by alkali metal cations under hydrothermal conditions. The highest process efficiency is obtained for CsNaX catalysts. The effect of operation conditions on the process results was examined. In addition, the effects of adding Group IIIA elements (B, Al, Ga, In) to the catalysts were examined. At 680 K and atmospheric pressure, the major reaction products were styrene, ethylbenzene, and carbon monoxide. Cesium-exchanged zeolite X was the most effective alkali-containing catalyst for the alkylation reaction. Of the Group IIIA additives that were tested, only boron promoted the alkylation reaction. The primary effect of adding boron was to reduce the decomposition of methanol to carbon m0onoxide. Apparently, boron selectively modifies the sites associated with methanol decomposition without inhibiting the sites active for alkylation.

Zhao et al. (1993) synthesized molecular sieves SAPO-11, SAPO-31 and SAPO-41 have been synthesized using di-n-propylamine as the organic template. synthesized molecular sieves SAPO-11, SAPO-31 and SAPO-41 have been synthesized using di-n-propylamine as the organic template. They have characterized by various methods such as X-ray powder

diffraction, solid state MAS NMR spectroscopy, thermal analysis, chemical analysis and temperature programmed desorption (TPD) of ammonia. Catalytic activities of these materials in the alkylation of toluene with methanol have been studied. While SAPO-11 and SAPO-31 showed moderate activity, very high catalytic activity was shown by SAPO-41. All the catalysts showed varying degrees of shape selectivity towards p-xylene. SAPO-41 gave a large amount of 1,2,4-trimethylbenzene in addition to the xylenes.

Sotelo et al. (1993) developed a novel process for the production of p-xylenes by the catalytic methylation of toluene followed by reactive distillation for the separation of p-xylene (instead of the more costly conventional technique of separation based on crystallization and adsorption) and a complete process flow diagram is simulated using Aspen Plus. Using the built-in optimization tool in Aspen Plus, we optimized reactor parameters for a maximum p-xylene selectivity of 97.7%. After separation, a p-xylene product stream purity of 99.7% is achieved. High p-xylene selectivity in the reactor and use of reactive distillation reduces the separation cost and renders the new process economically competitive.

Palomares et al. (1997) found that the sorption strength of toluene increased with increasing cation size, presumably due to a better steric match of the π orbitals of toluene to the alkali.

Vos et al. (2001) used ZSM-5 for toluene methylation because it has greater shape-selectivity properties. Eventhough there are many papers on mechanism of methylation of toluene but still full details of the mechanism of reaction are not yet known.

Borgna et al. (2005) found that formation of styrene and ethylbenzene was significant only on CsNaY zeolites of exchange degree higher than about 40%. Cesium ion-exchanged zeolite X or Y has been accepted to be the most effective solid base catalyst for producing styrene from toluene and methanol.

Walton et al. (2006) prepared a set of K-exchanged X zeolites with different exchange degree were and investigated in the alkylation of toluene with methanol. The chemical composition, textural properties, crystalline phase and acid– base properties of catalysts were analyzed by ICP, N_2 physisorption, XRD, NH_3-TPD and XPS. Experimental results demonstrated that the direction to ring or side-chain alkylation depended on the K exchange degree (K_{ED}) greatly.

Bokade et al. (2007) said that the products formed (styrene, ethyl benzene, and xylenes) depends on the pore size of the molecular sieve and catalyst's acidity. Side- chain alkylation

is favored by while large-pore basic zeolites, such as K-X, favor but ring alkylation is favored by medium-pore acidic zeolites, such as H-ZSM-5.

Manivannan et al. (2009) used LDHs as catalyst to test toluene side-chain alkylation for the production of styrene. But is showed less acivity when compared to K- exchanged X zeolite.

Jiang et al. (2010) studied the effect of MgO encapsulated silicalite zeolite for side chain alkylation of toluene with methanol for the production of styrene. Cs and K-exchanged X zeolites (KX, CsX). shows high activities for the side-chain alkylation than MgO encapsulated silicalite zeolite.

El et al. (2014) studied methylation of toluene over ZSM-5 zeolites modified by the introduction of Sr of 2.5%, 5%, and 10% by weight. Their work deals with the effect of added N- octyl-N-benzyl-N-methylglyene emulsifier on the alkyla- tion of toluene by methanol to investigate the performance of Sr/ZSM-5 catalyst of different (Sr) ratios, through the alkylation of toluene by methanol.

Han et al. (2016) examined cesium ion-exchanged zeolite X with different precursors; in addition, their work focuses on investigating the different performances of cesium hydroxide modified zeolite X by ion-exchange and impregnation.

CHAPTER-3 EXPERIMENTAL METHODOLGY

3.1 Synthesis of Beta Zeolite

Reagents- LUDOX TM-40 Colloidal Silica (40 wt%) was purchased from Sigma-Aldrich, Tetra-Ethyl Ammonium Hydroxide (TEAOH, 35 wt% in water) was procured from TCI Chemicals (India) Pvt. Ltd., Sodium Hydroxide (Pellets, AR) was obtained from Merc, India and Aluminium Sulphate (Purified LR, $Al_2(SO_4)_3.16H_2O$) was purchased from SDFCL Ltd. (India). All chemicals were used as such.

Synthesis Procedure- Colloidal Silica (6.54 g) was added to a mixture of comprising of 10.98 g aqueous solution of TEAOH and 0.52 g NaOH pellets with vigorous stirring for 30 minute to form a clear gel. An aqueous solution containing 0.54 g $Al_2(SO_4)_3$ was added to the mixture. Ethanol formed during hydrolysis was evaporated resulting into a viscous gel, which was aged under stirring at room temperature for 24 h. Hydrothermal treatment of nucleated gel was carried out by refluxing 80°C to 130°C for 48 hrs. The resulting gel was washed and centrifuged to obtain product. It was, then, dried at 110°C for 12 h to obtain zeolite in powder form. Bentonite was used to make the pellets of the zeolite powder.

3.2 Modification of Beta Zeolite

Procedure- The catalyst was modified by exchanging the prepared pellets of beta zeolite with ferric chloride. Ion exchange was carried out at 24°C, at 1 atm. pressure. A $50cm^3$ aqueous solution (with concentration of 2.67g/l) of $FeCl_3$ was made and 20g of zeolite pellets were mixed with the solution and stirred for about 15 minutes. The sample was then placed in stirrer at 24°C for about a day. It was then dried at 70-75°C in an oven. The Fe modified catalyst was named as $Fe\beta_{0.26}$

For zeolite modification with potassium ions, 0.26%, 0.5%, 1% and 1.5% potassium sulphate solution were made. Zeolite pellets were mixed with the solution and stirred at 24°C for about a day. It was then dried at 70-75°C in an oven. After exchange with potassium, $K\beta_{0.26}$, $K\beta_{0.5}$, $K\beta_1$ and $K\beta_{1.5}$ zeolite were prepared.

3.3 Characterization of Catalyst

3.3.1 Powder X-ray Diffraction

Crystallinity of the synthesized and modified catalyst were determined using XRD using Cu-Kα as a source. Zeolite Beta gives three characteristics peaks at Bragg angles of 7.5, 21.3 and 22.4. XRD graph of potassium-exchanged zeolite (K-β) showed that there has been no much structural change during potassium modification in figure 3.1. Potassium appears at the 2θ value of 22.51^o, 33.3^o, 43.5^o, 55.8^o that exactly matched with the values obtained from JCPDS. The particle size was found to be 500 nm.

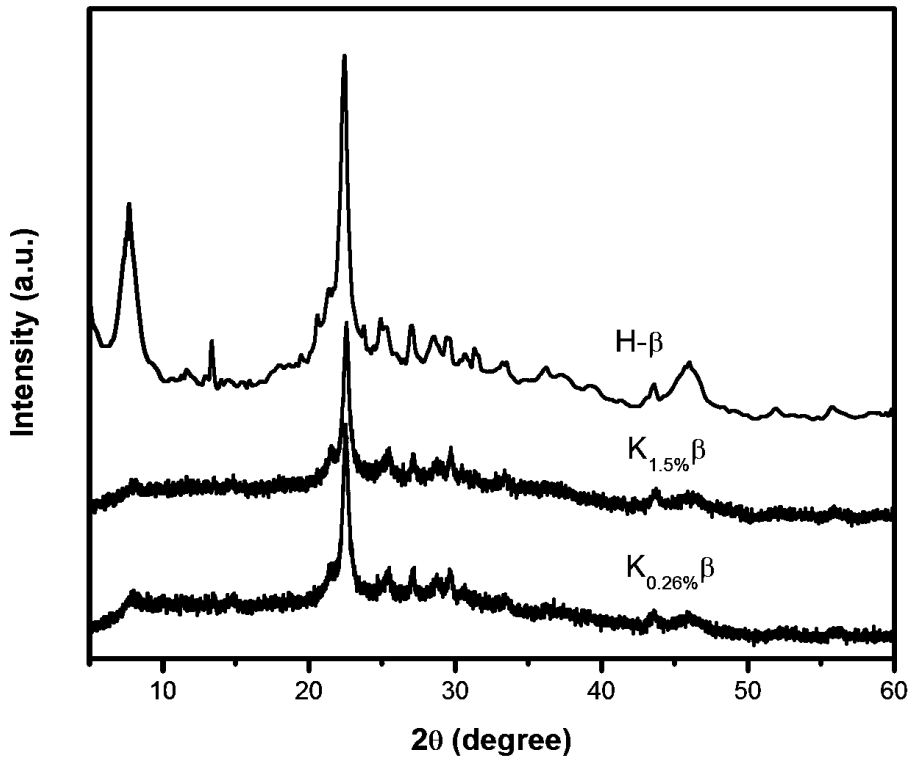


Figure 3.1 XRD of zeolite beta

3.3.2 Scanning Electron Microscopy

The zeolites modified with different ions are designated as Fe-β and K-β. The structural composition of modified beta zeolite was confirmed using SEM. The SEM of Fe modified beta and K modified beta has been shown in figure 3.2 and 3.3 respectively. The micrographs show that there is no change in the typical morphology of the support after ion exchange.

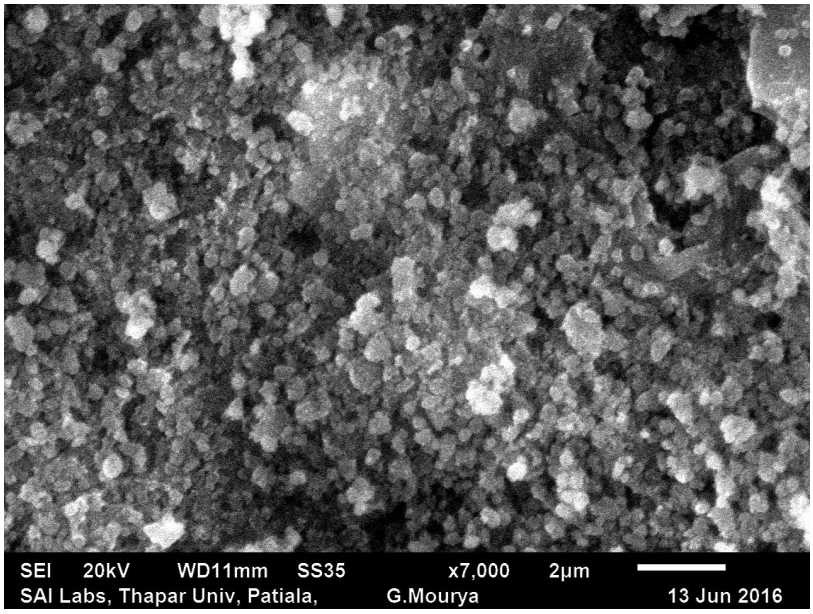


Figure 3.2 SEM of Fe$\beta_{0.26}$

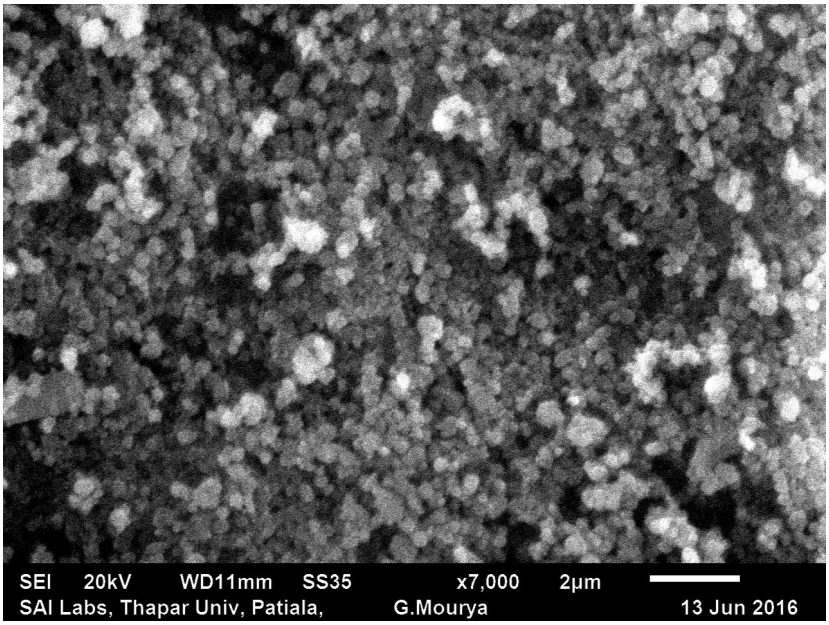


Figure 3.3 SEM of K$\beta_{0.26}$

3.3.3 EDS Analysis

EDS can also quantify the elements in the zeolite. 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 iron and potassium contained zeolite are given below in figure 3.4 and figure 3.5 and the composition are given in the table

3.1 and table 3.2.It shows that the Fe-β zeolite which is modified with 2.67gm/dm^3 solution of ferric chloride contains 4.07 wt% of iron and K$\beta_{0.26}$ zeolite contains 1.89 wt% of potassium.

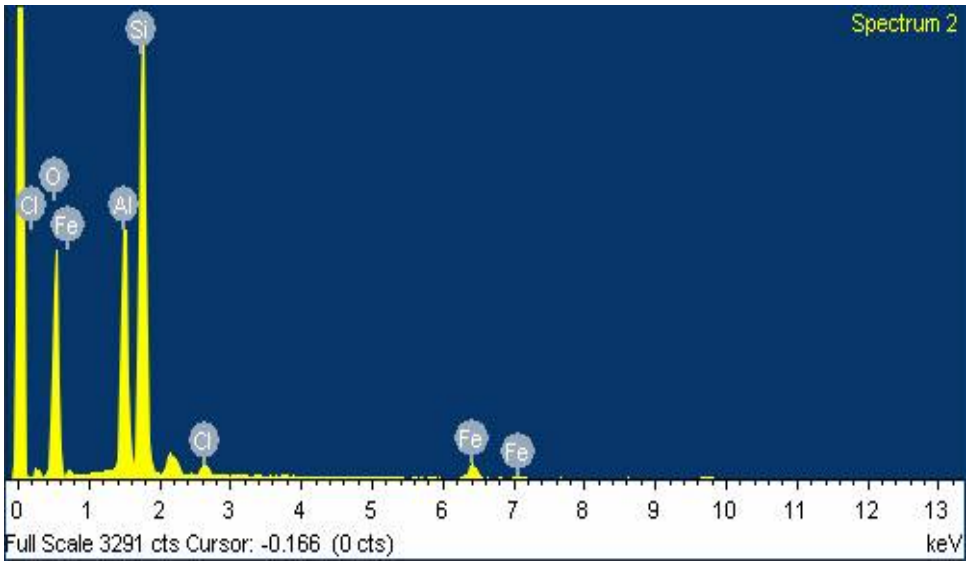


Figure 3.4 EDS spectra of Fe$\beta_{0.26}$

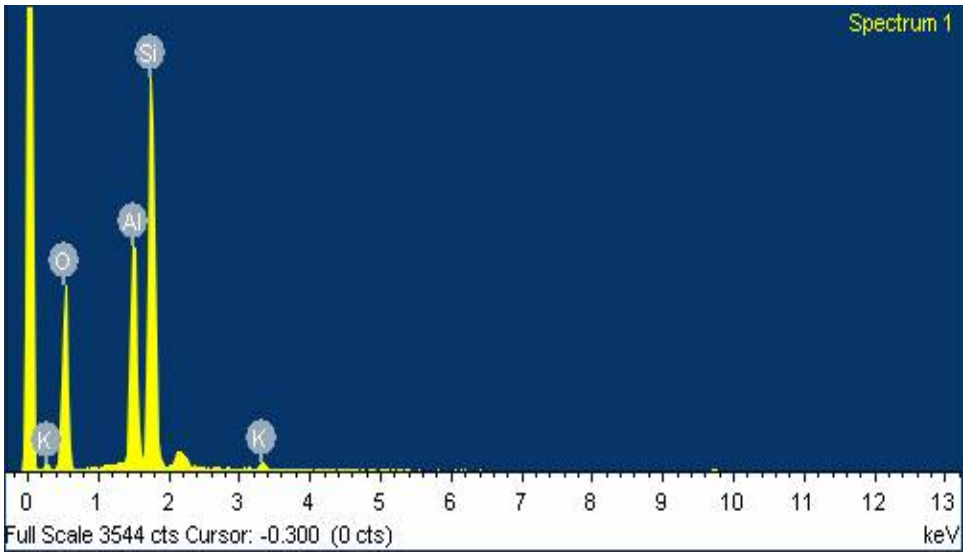


Figure 3.5 EDS spectra of K$\beta_{0.26}$

Table 3.1 Composition of Feβ $_{0.26}$

Element	Weight %	Atomic %
O	50.79	65.20
Al	13.81	10.51
Si	30.54	22.34
Cl	0.79	0.46
Fe	4.07	1.50
Totals	100.00	

Table 3.2 Composition of Kβ$_{0.26}$

Element	Weight %	Atomic %
O	52.55	65.87
Al	14.63	10.88
Si	30.93	22.80
K	1.89	0.46
Totals	100.00	

3.4 Alkylation Reaction in Flow Reactor

Alkylation reaction was carried out in fixed-bed, continuous down-flow and stainless-steel (SS-316) reactor. In figure 3.6 and 3.7 it is seen that the reactor was fitted with a preheater in the upstream and a condenser in the downstream. The zeolite catalyst (2g) was loaded into the reactor, which was supported on a wire mesh at the center of reactor. The catalyst was activated for 3h in nitrogen atmosphere before the experimental runs were started. The reaction temperature was measured using a thermocouple placed in a thermowell extending from the top of the reactor to the center. All experimental runs were carried out at atmospheric pressure. Toluene-Methanol feed mixture was introduced into the reactor using a metering pump through the preheater. The product vapors along with unreacted reactants were condensed in condenser and the liquid samples collected were analyzed in a Gas Chromatograph (Bruker) using a flame ionization detector (FID).

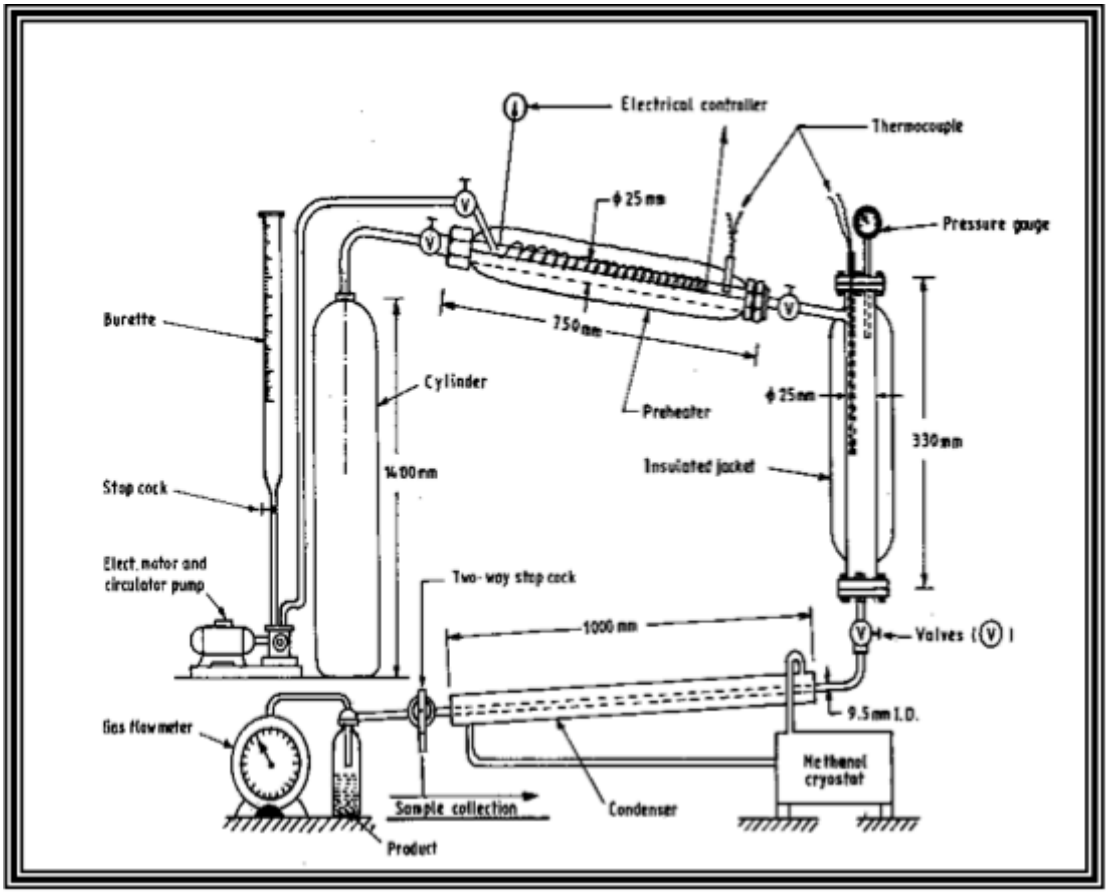


Figure 3.6 Schematic diagram of reactor set-up (Karan et al. 2016)

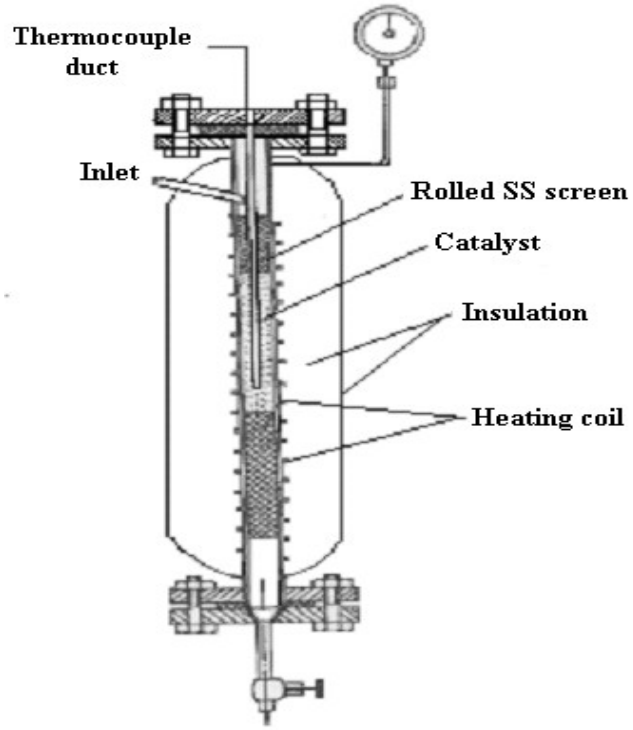


Figure 3.7 Schematic diagram of a single flow reactor (Karan et al. 2016)

The conversion of any reactant and selectivity of any product were calculated according to following formula:

$$Reactant\ Conversion(\%) = \frac{(Reactant\ in\ feed - Reactant\ in\ product)}{Reactant\ in\ feed} \times 100$$

$$Product\ Selectivity(\%) = \frac{y_{i,o}}{\sum y_{i,o}} \times 100$$

$$Product\ Yield(\%) = \frac{y_{i,o}}{y_{met,o} + \sum y_{i,o}} \times 100$$

where $\sum y_{i,o}$ and $y_{met,o}$ are the molar fractions of aromatic products and the outlet molar fraction of methanol, respectively.

4.1 Alkylation of toluene with methanol (Ring Alkylation)- A kinetic study

Karan et al. 2016 studied effect of temperature and mole ratio on reactant conversion and product selectivity in alkylation of toluene with methanol over $Fe\beta_{0.26}$. Optimum temperature (673K) and reactant ratio (5:1) were selected for kinetic study from the data reported. In present investigation, effect of space-time on conversion of methanol was studied to find the kinetic and adsorption constant.

4.1.1 Effect of space-time on methanol conversion and xylene yield

The effect of space-time was studied in the range of 0.009-0.057 kgh/kmol. The methanol conversion increased with increase in space-time as shown in Figure 4.1. Maximum methanol conversion of 99.86% at 0.0231kgh/kmol space-time was observed. This may be due to a higher contact time between the reactant and the catalyst. Initially, xylene selectivity increased with space-time, however, at much higher space-time, xylene selectivity decreased due to the formation of undesired products. Highest xylene selectivity of 58.58% at 0.0231 kgh/kmol space-time was noted.

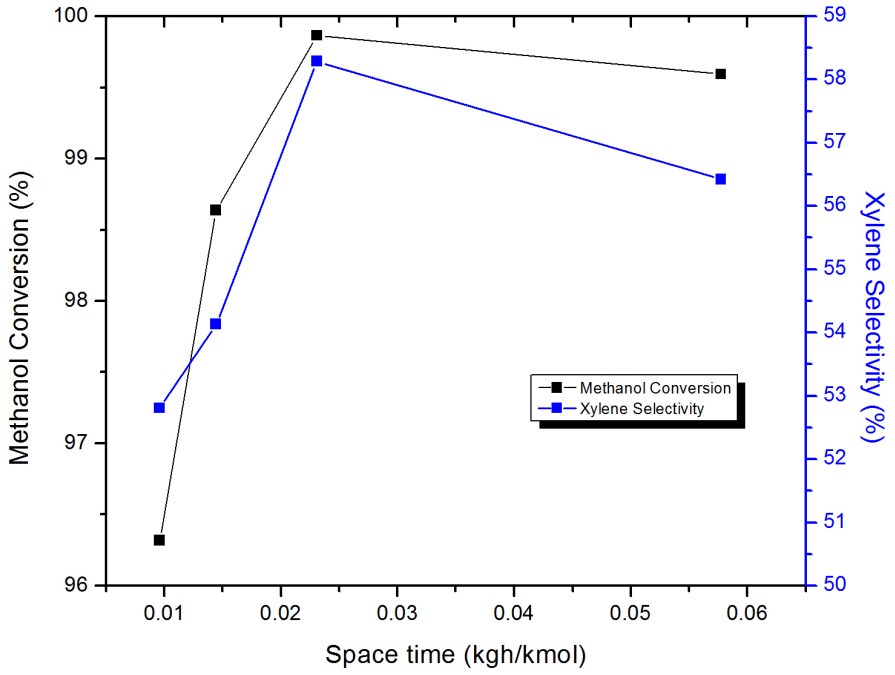


Figure 4.1 Effect of space-time on methanol conversion and xylene selectivity. Temperature-673K, Toluene to methanol ratio- 5:1

4.2 Kinetic Study

4.2.1 Mass Transfer Consideration

Any kinetic study must be done in the presence of negligible mass transfer resistance during reaction. To investigate the external diffusion effects, experiments were performed with same catalyst size but different space-time (varying different feed rates). The results in table 4.1, indicates that conversion of toluene is almost same at all four values of W/F. Hence, we can say that external diffusional resistance was found to be negligible.

Table 4.1 Effect of external diffusion on conversion of toluene over Feβ$_{0.26}$ zeolite catalyst

Space-time (kgh/kmol)	**Conversion of Toluene (%)**	
	Catalyst weight = 0.002 kg	Catalyst weight =0.004 kg
0.057	32.63	32.55
0.023	25.82	25.79
0.014	22.15	22.09
0.009	20.01	19.87

4.2.2 Kinetic Modeling

The kinetic runs were carried out at four different temperatures (613K, 633K, 653K, and 673 K). The experiments were carried out to choose the zone in which the mass transfer effects are negligible. Figure 4.2 presents the effect of space-time on methanol conversion at four different temperatures.

The system can be described by the following reaction:

Primary Reaction:

$$Toluene + Methanol \overset{k_1}{\rightarrow} Xylene + H_2O$$

Secondary Reactions:

$$Xylene + Methanol \overset{k_2}{\rightarrow} TMB + H_2O$$

$$2Toluene \overset{k_3}{\rightarrow} Benzene + Xylene$$

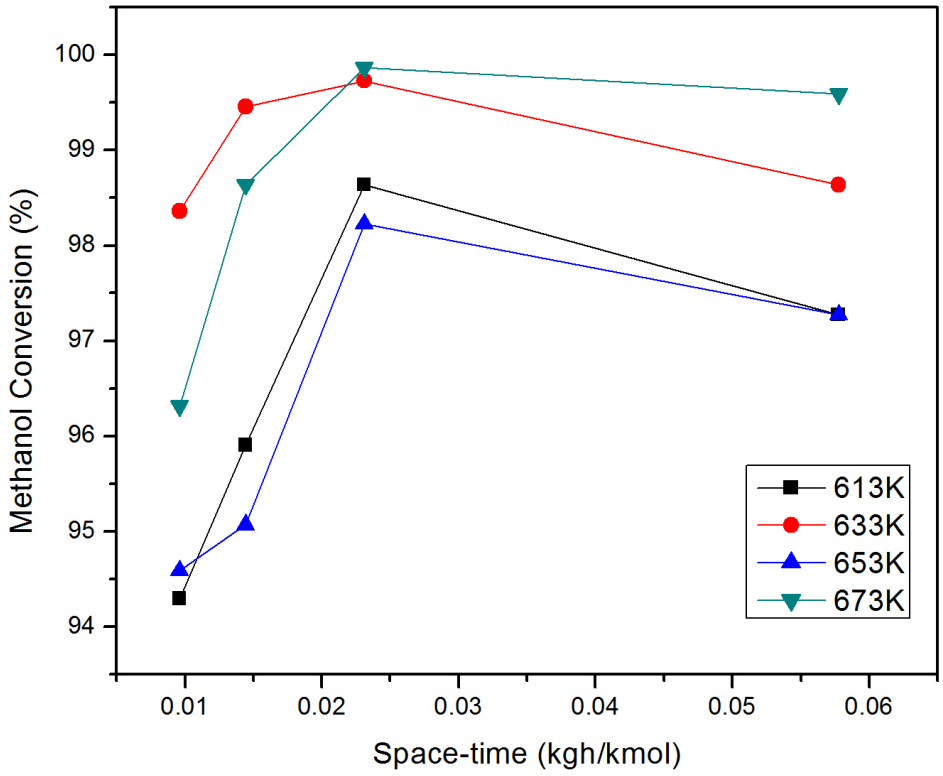


Figure 4.2 Effect of space-time on methanol conversion at various temperatures. Conditions: pressure- 1atm; catalyst- Feβ$_{0.26}$; toluene/methanol mole ratio- 5:1; N_2 to feed ratio- 0.16.

Langmuir-Hinshelwood-Hougen-Watson (L-H-W-W) Model

For the rate of disappearance of methanol, L-H-H-W model was attempted to evaluate various rate constants of the reaction scheme. The following rate expression using L-H-H-W model with surface reaction as a rate controlling step and dual site (both reactant adsorbed on catalyst) mechanism was found to fit the kinetic data significantly better than the other models derived from single site and Elei-Rideal mechanism. For the rate of disappearance of methanol, the rate expressions for dual site mechanism is:

$$-r_M = dX_M/d\tau = (k_1 K_T K_M p_M p_T + k_2 K_M K_X p_M p_X)/Z^2 \quad (1)$$

where, $$Z = 1 + K_T p_T + K_M p_M \quad (2)$$

k_1 and k_2 are the reaction rate constants; K_T, K_M and K_X are adsorption coefficients; p_M, p_T and p_X are partial pressures of methanol, toluene and p-xylene respectively. The partial pressures in the above equations were calculated using the fractional conversions and total

pressure, P, as given below,

$$p_M = (1 - X_M)P/6.96 \quad (3)$$

$$p_T = (5 - X_T)P/6.96 \quad (4)$$

$$p_X = (X_{xylene})P/6.96 \quad (5)$$

In the reaction system, the total number of moles of different components was found to be 6.69. 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:

$$f = \sum_{i=1}^{n}[(Rate\ predicted)i - (Rate\ experimental)i]^2 \quad (6)$$

Model Selection

The kinetic and adsorption constants evaluated by non-linear regression are tabulated in Table 4.2 for dual site model. The experimental and the predicted methanol conversions for this model, at different temperatures, are plotted in Figure 4.3. The plot shows a good correlation between the experimental and predicted rates having an R^2 value of **0.98**.

Table 4.2 Kinetic and adsorption parameters for dual site mechanism for toluene-methanol alkylation over Feβ$_{0.26}$ zeolite catalyst

Kinetic and adsorption parameters	Temperature			
	613K	**633K**	**653K**	**673K**
k_1 (kmol/kgh)	0.25	0.30	0.35	0.40
k_2 (kmol/kgh)	0.012	0.025	0.084	0.01
K_M (atm^{-1})	0.05	0.04	0.03	0.02
K_T (atm^{-1})	0.03	0.02	0.015	0.01
K_X (atm^{-1})	0.01	0.009	0.007	0.0005

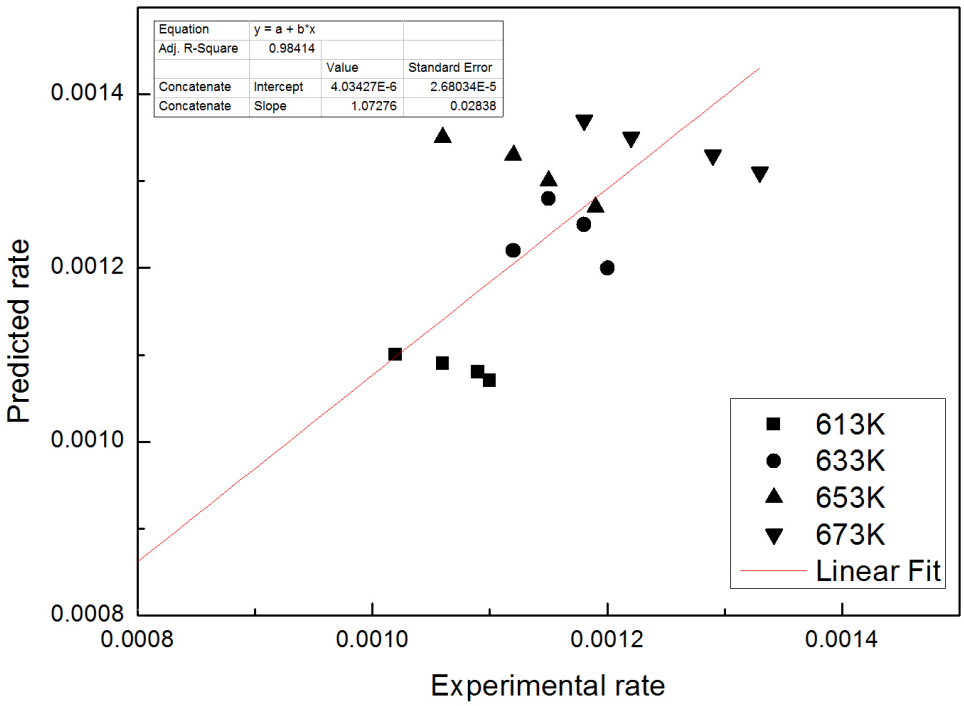


Figure 4.3 Experimental versus predicted rate of toluene conversion to xylene over Feβ$_{0.26}$ zeolite catalyst

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

$$lnK = lnA - E_a/RT \tag{7}$$

Activation energy for alkylation reaction was estimated from the graph plotted, figure 4.4. It was found to be be **10.36 kJ/mol**. Apparent activation energy of 14 kJ/mol for toluene methylation with ZM13 was reported (Perego et al. 1996). The value of frequency factor (A) was found to be **7.98**. Activation energy and pre-exponential factors of different reactions are reported in Table 4.3.

Table 4.3 Activation energy and pre-exponential factor

Reaction	E_a (kJ/mol)	Pre-exponential factor
Alkylation Reaction	10.36	7.98

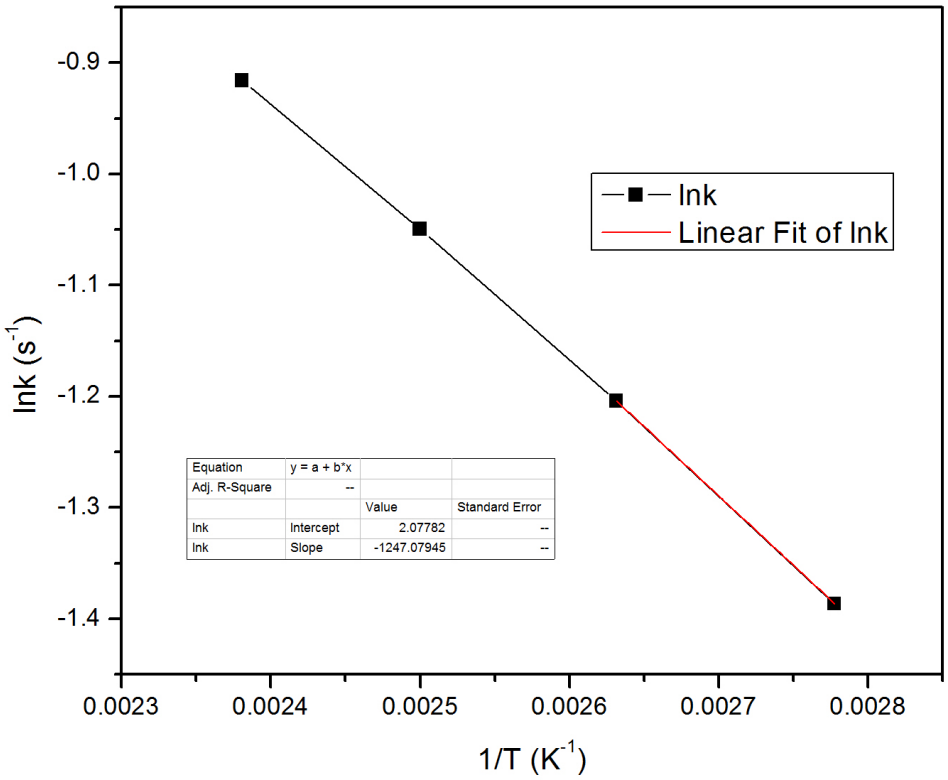


Figure 4.4 Plot of lnk versus 1/T

4.3 Side Chain Alkylation by K modified zeolite beta

In toluene alkylation with methanol over K-beta zeolite ring chain and side chain alkylation both may takes place. A series of K modified beta zeolite were prepared namely $K\beta_{0.26}$, $K\beta_{0.5}$, $K\beta_{1}$, $K\beta_{1.5}$ (modified with 0.26%, 0.5%, 1%, 1.5% of potassium sulphate solution).

4.3.1 Effect of time on stream

The activity and stability of both parent and K modified zeolites were tested by time on stream study. It was observed that modification of H-beta zeolite with K ions leads to a very significant change in activity of zeolite as with increase in potassium content in the zeolite, conversion of toluene increases. But Conversion of toluene in 60 minutes time on stream shows that the catalyst is not stable in long run due to the deactivation of catalyst and also the diffusional resistance may come into play.

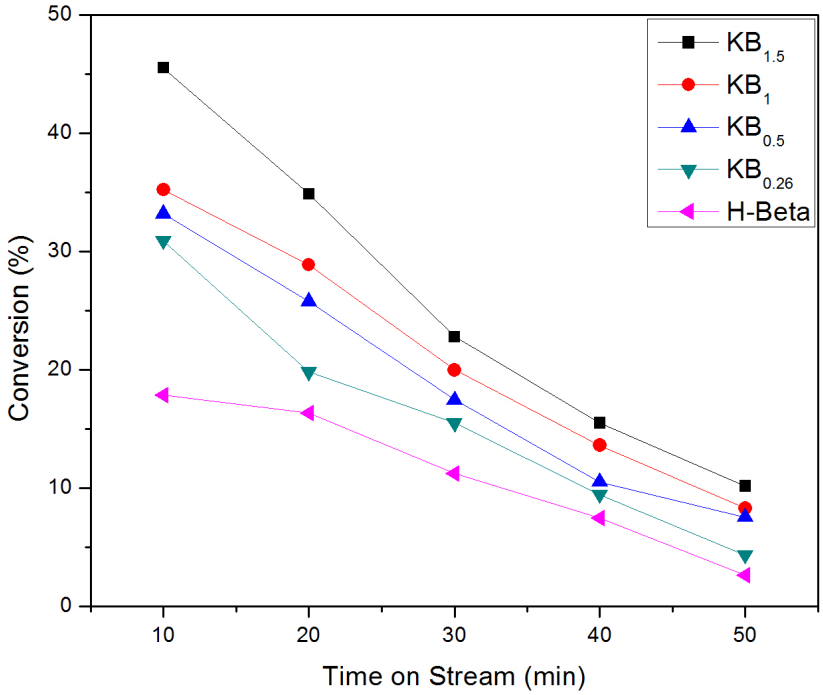


Figure 4.5 Effect of time on stream on toluene conversion. Conditions: pressure- 1atm; temperature- 773K; toluene/methanol mole ratio- 2.5:1; N_2 to feed ratio- 0.16.

Table 4.4 Product distribution for different concentration of potassium modified zeolite beta

Catalyst	Hβ	$K\beta_{0.26}$	$K\beta_{0.5}$	$K\beta_{1}$	$K\beta_{1.5}$
Product Distribution wt%					
Methanol	0.08	0.11	0.08	0.05	0.07
Formaldehyde	1.46	3.3	3.39	3.62	6.09
Toluene	76.14	64.03	61.9	60.03	50.48
Xylene	11.86	17.56	18.5	19.47	23.08
Styrene	5.19	6.45	6.7	6.83	8
Cumene	1.44	2.28	2.63	2.92	3.75
TMB	3.84	6.26	6.81	7.08	8.53
Conversion of Toluene	17.82	30.89	33.19	35.21	45.52
Selectivity of Styrene	21.81	17.99	17.61	17.10	16.17
Selectivity of Xylene	49.85	48.98	48.64	48.77	46.67
Selectivity of Formaldehyde	6.13	8.91	9.06	9.20	12.31
Selectivity of Cumene	6.05	6.35	6.91	7.31	7.58
Selectivity of TMB	16.14	17.24	17.46	17.73	17.9

From table 4.4 it was noted that conversion of toluene increases with increase in

concentration of potassium in solution. Also it can be seen that selectivity of styrene and xylene decreases but of formaldehyde, cumene and TMB increases with increase in potassium concentration.

4.3.2 Effect of temperature on conversion and selectivity

Reactions were carried out to see the effect of temperature on reactants conversion and product distribution, in the temperature range 733K- 793K. It can be seen from the graph that reaction temperature has a significant effect on the reactant conversion. Methanol being the limiting reactant has higher conversion than toluene. A maximum of 99.63% methanol conversion was obtained at 773K and maximum of toluene conversion of 24.91% was obtained at 773K. However, at higher temperature methanol is completely exhausted. This may be due to the fact that at higher temperatures, excessive vaporization of methanol occurs and hence, it is not available in the vicinity of active sites. This is also reflected from toluene conversion, which shows decrease at higher temperature.

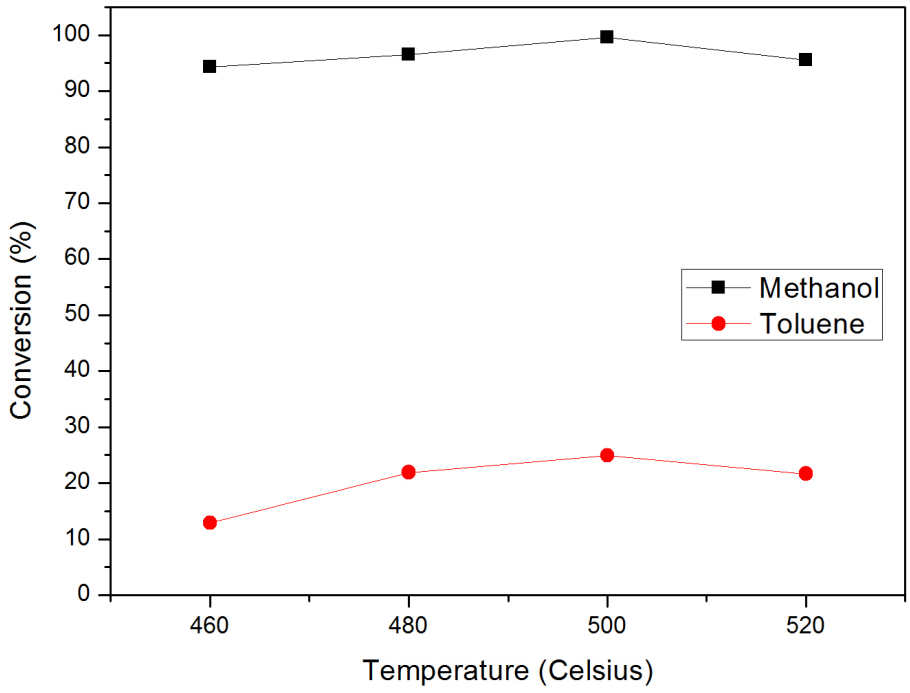


Figure 4.6 Effect of temperature on reactant conversion. Conditions: pressure- 1atm; catalyst- $K\beta_{0.26}$; toluene/methanol mole ratio- 5:1; N_2 to feed ratio- 0.16.

From the product distribution it can be seen that among the various products formed, xylene has maximum yield and selectivity. However, styrene formed is less in yield because potassium exchanged beta zeolite is weakly basic. The selectivity of styrene increases from 15.15% at 733K and is maximum (16.97%) at 773K. Xylene is selectively formed more than any other product. Selectivity of formaldehyde is maximum (25.61%) at 793K. At this temperature, selectivity of xylene is least (48.84%).

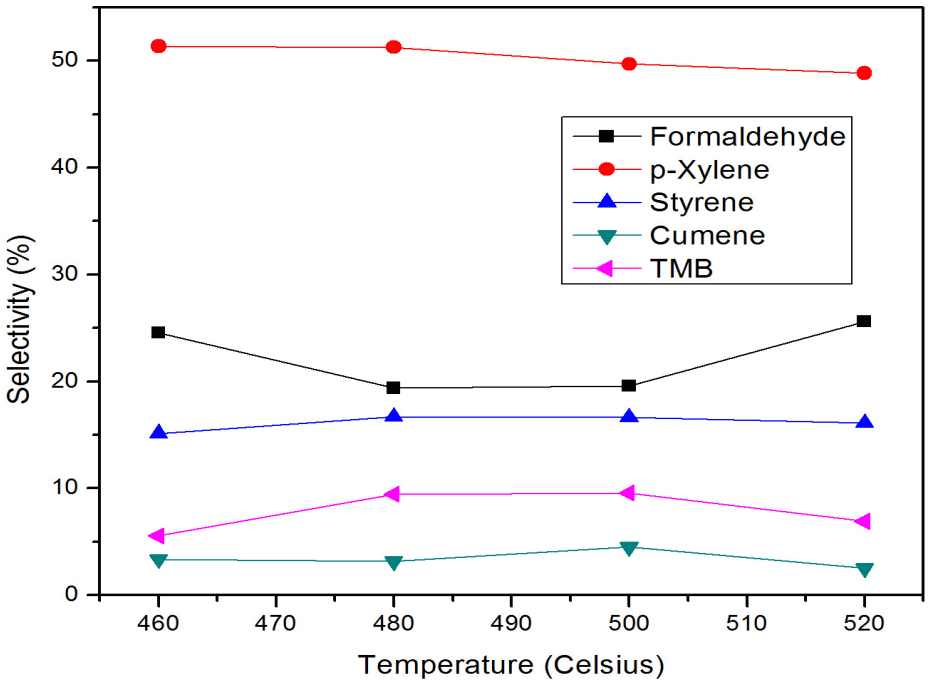


Figure 4.7 Effect of temperature on product selectivity. Conditions: pressure- 1atm; catalyst- $K\beta_{0.26}$; toluene/methanol mole ratio- 5:1; N_2 to feed ratio- 0.16

4.3.3 Effect of reactant mole ratio on conversion and product selectivity

To check the effect of reactant ratio on product distribution, the reactant ratio was varied form 2.5-7. Methanol was taken as limiting reactant. Both the reactant show maximum conversion at toluene to methanol reactant ratio of 2.5. Methanol and toluene shows maximum conversion of 99.81% and 36.33%, respectively, at reactant ratio 2.5:1. Above this reactant ratio, both methanol and toluene conversion decreases which shows that toluene to methanol ratio of 2.5 is optimum for achieving maximum conversion of reactants. Methanol shows much higher conversion than toluene. This may be explained by the fact that methanol being limiting reactant is present in small amount. This small amount is completely converted to products whereas, toluene is present in excess amount. The excess molecules are not able to come at active site. At lower reactant ratio, due to less availability of alcohol, conversion

drops. However, formaldehyde and p-xylene selectivity is high at higher mole ratios.

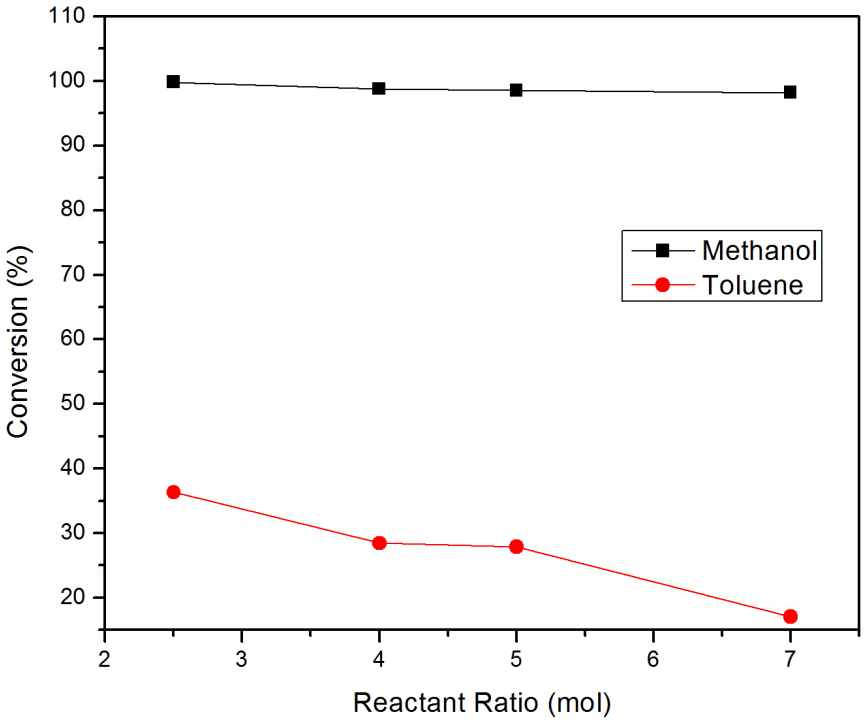


Figure 4.8 Effect of mole ratio on reactant conversion. Conditions: pressure- 1atm; catalyst- $K\beta_{0.26}$; temperature- 773K; N_2 to feed ratio- 0.16

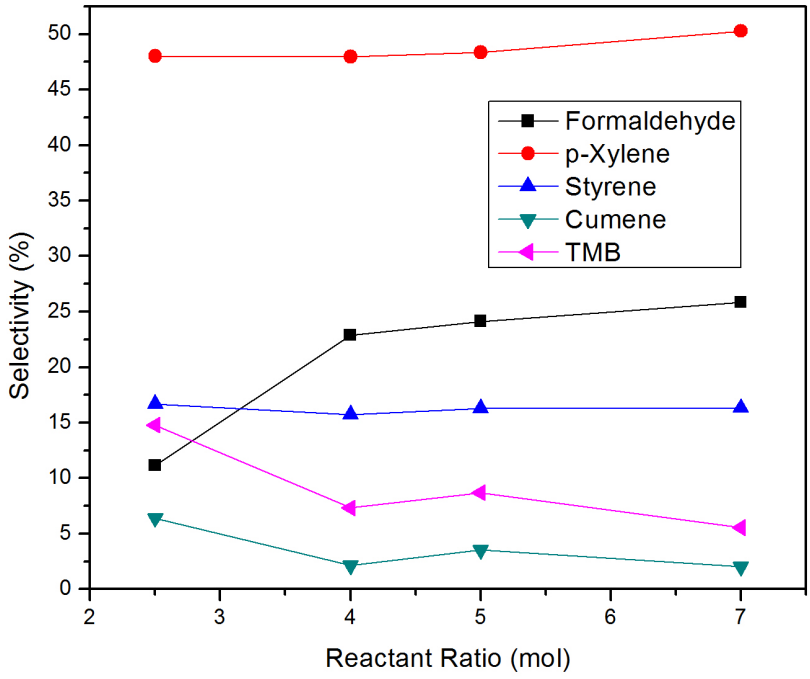


Figure 4.9 Effect of mole ratio on product selectivity. Conditions: pressure- 1atm; catalyst- $K\beta_{0.26}$; temperature- 773K; N_2 to feed ratio- 0.16

4.3.4 Effect of space-time on conversion and selectivity

The weight of catalyst was kept constant at 2g for each reaction and effect of flow rate on reactant conversion was checked. With increase in flow rate (or decrease in space-time) the conversion of both reactants initially increases but then gets decreased. Space- time range was taken from 0.009-0.0231 kgh/kmol. Methanol and toluene shows maximum conversion of 99.54% and 27.89% respectively at 0.0144 kgh/kmol space-time. However, it was noticeable that toluene conversion was much lower than methanol, which was taken as limiting reactant. Moreover, methanol conversion remains almost constant over a quiet wide range of flow rate whereas, toluene conversion show a sharp decrease in conversion. The reason of such trends lies in the amount of the reactant taken. Methanol being limiting reactant does not suffer a drastic change in conversion with increase in flow rate.

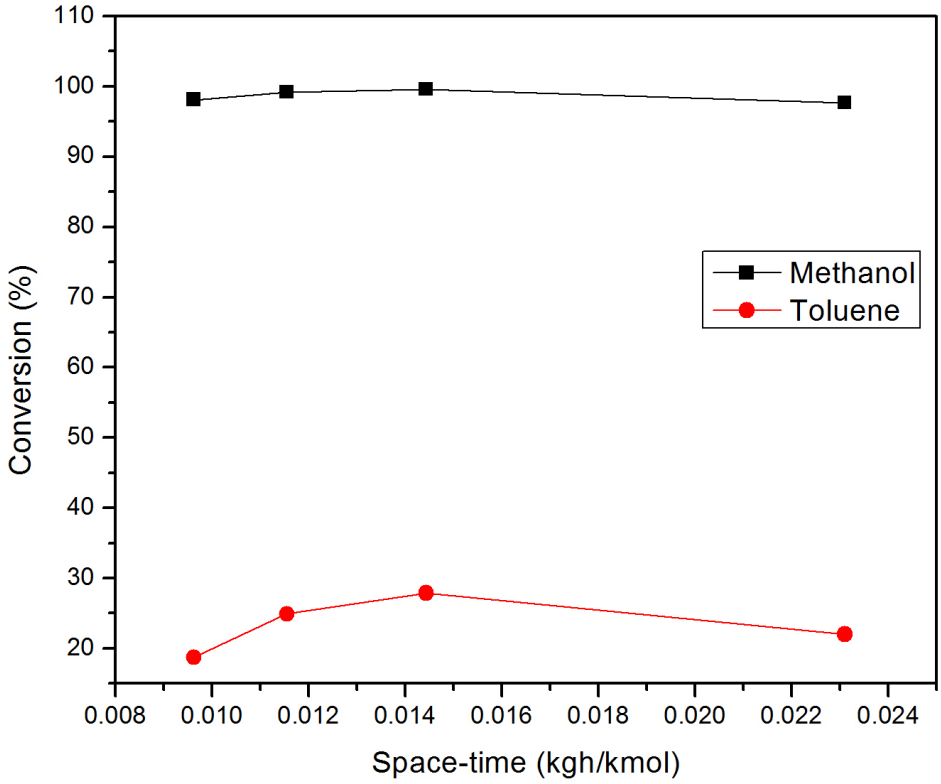


Figure 4.10 Effect of space-time on reactant conversion. Conditions: pressure- 1atm; catalyst- $K\beta_{0.26}$; toluene/methanol mole ratio- 2.5:1; temperature- 773K; N_2 to feed ratio- 0.16

From the product distribution, it can be seen that styrene selectivity decreases with increase in flow rate (decrease in space-time). Maximum selectivity of 17.48% for styrene was reported at 0.009 kgh/kmol space-time. This may be explained on the fact that with increase in flow rate the reactants do not get sufficient time for side reactions. At lower flow rate the reactants get enough time to undergo side reactions like disproponate, de-alkylate. Therefore, the selectivity of side products like formaldehyde was more at lower flow rate which decreases with increase in flow rate. Selectivity of formaldehyde decreases from 33.2% to 19.45% with increase in flow rate. Selectivity of xylene increases from 44.80% to 52.008%. Similarly, selectivity of cumene and TMB ranges from 2.12% to 4.51% and 5.2% to 9.5% respectively.

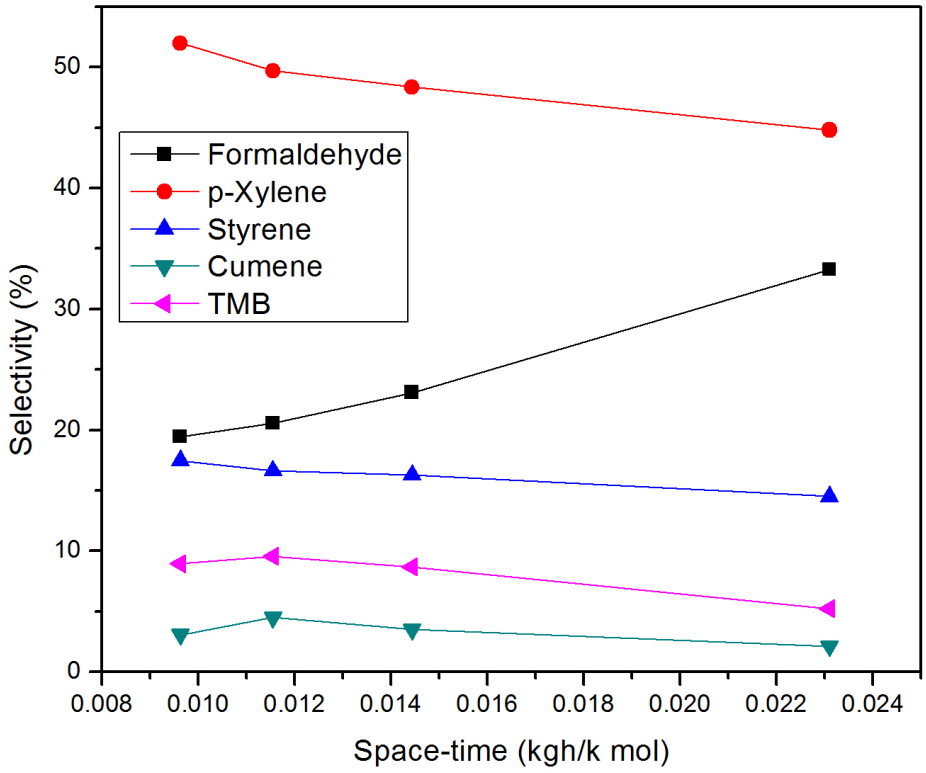


Figure 4.11 Effect of space-time on product selectivity. Conditions: pressure- 1atm; catalyst- $K\beta_{0.26}$; toluene/methanol mole ratio- 2.5:1; temperature- 773K; N_2 to feed ratio- 0.16

CHAPTER- 5 CONCLUSION AND FUTURE WORK

5.1 Conclusion

Nano zeolite beta was synthesized, characterized and modified with Fe and K. Alkylation of toluene with methanol is carried out over Fe-beta ($Fe_{0.26}$) and K-beta ($K_{0.26}$) zeolite catalysts. Modification of zeolite with these metals brought significant increase in the activity of catalyst and selectivity of the product.

$Fe\beta_{0.26}$ catalyst shows maximum methanol conversion of 99.86%, at a temperature 673K, reactant-ratio 5:1, space time 0.023 kgh/kmol. However maximum toluene conversion of 32.63% was found at temperature 673K, reactant ratio 5:1, space time 0.057 kgh/kmol. Based on the product distribution, a reaction mechanism is proposed together with a rate expression for the disappearance of methanol. The kinetic and the adsorption constants of the rate equation are estimated. The activation energy for alkylation reaction is determined to be 10.36 kJ/mol, which is comparable with the data reported in the literature for alkylation reactions. Highest xylene selectivity of 58.58% at 0.0231 kgh/kmol space-time was noted.

On the other hand potassium modified zeolite contributes for ring chain alkylation (xylene) as well as side chain alkylation (styrene). When exchanged with potassium ($K_{0.26}$), catalyst showed maximum methanol conversion of 99.81% at a temperature 773K, reactant ratio 2.5:1 and space-time 0.0144 kgh/kmol. However maximum toluene conversion of 36.33% was found at temperature 773K, reactant ratio 2.5:1, space time 0.0144 kgh/kmol. Maximum selectivity of 17.48% and 52.008% for styrene and xylene, respectively, was reported at 0.009 kgh/kmol space-time at temperature 773K and reactant ratio 2.5:1. K modified beta zeolite being a basic catalyst does not have much potential for side chain alkylation so it has a intermediate activity for side chain alkylation where as Fe modified beta is very active for formation of ring chain product xylene.

5.2 Future Work

Kinetic study and modeling of side chain alkylation reaction of toluene with methanol over KB 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.

REFERENCES

1. A. Gheit, K .Ahmed, M. Sohair, H. Abdel, and A. Emam. *Appl Catal.* 1999, **179**, 107-115.
2. R.M. Barrer. *J. Soc Chem Ind.* 1945, **64**, 130. (b) R.M. Barrer, *J. Chem Soc*. 1948, **2158**. (c) Barrer,. *J.Chem.Soc.*1948, **33**, 127-132.
3. R.L. Bedard, S.T. Wilson, L.D. Vail, J.M. Bennett, and E.M. Flanigen. *Stud. Surf. Sci.* 1989, **49**, 375-387.
4. M. David, F.H. Russell, and G.D. McLellan. *Appl Catal.*1992, **93,** 1-34.
5. V.V. Bokad, S.S. Deshpande, R. Patil, S. Jain, and G.D. Yadav. *J. natural gas chem*. 2007, **16**, 42-45.
6. R.B. Borade, A.B. Halgeri, and T.P. Rao. *Stud Surf Sci.* 1986, **28,** 851-858.
7. A. Borgna, S. Magni, J. Sepulveda, C.L. Padró, and C.R. Apesteguía. *Catal Let.* 2005, **102,** 15-21.
8. L. Carol, and A.O. Geoffrey. *Adv Mater*. 1996, **8,** 13-28.
9. (a) B. Xianhui, P. Feng, and G.D. Stucky. *Science*. 1997, **278,** 2080-2085. (b) P. Feng, X. Bu, T.E. Gier, and G.D. Stucky. *Micropor Mesopor Mater.* 1998, **23,** 221-229.
10. M.A. Camblor, A. Corma, A. Mifsud, J.P. Pariente, and S. Valencia. *Surf Sci Cat*. 1997, **105,** 341.
11. B. Wichterlová. *Catal reviews* 2002, **44,** 375-421.
12. M. Choi, H.S. Cho, R. Srivastava, C. Venkatesan, D.H. Choi, and R. Ryoo. *Nature mater*. 2006, **5,** 718-723.
13. C.A. Fredric, *R.beskrifning. Zeolites*. 1756.
14. E. Morsi, A.M. Omar, and N.Y. Almehbad. *J. Surf Eng Mater Adv Tech*. 2014, **4**, 41.
15. J. Engelhardt, J. Szanyi, and J. Valyon. *J. Catal*. 1987, **107,** 296-306.
16. W. Fan, M.A. Snyder, S. Kumar, P.S. Lee, W.C. Yoo, A.V. McCormick, R.L. Penn, A. Stein, and M. Tsapatsis. *Nature Mater*. 2008, **7**, 984-991.
17. S. Faramawy. *Pet Sci Tech.* 1999, **17,** 249-271.
18. E.N. Flanigen, B.M. Lok, R.L. Patton, and S.T. Wilson. *Pure Appl Chem.* 1986, **58**, 1351-1358.
19. F. Crafts and J.M. Crafts. *Compt. Rend.* 1877, **84**, 1392.
20. E. Thurman, and D.G. Stucky. *Nature*. 1991, **349**, 508-510.
21. N. Giordano, L. Pino, S. Cavallaro, P. Vitarelli, and B.S. Rao. *Zeolites* 1987**, 7**, 131-134.

22. W.O. Haag, R.M. Lago, and P.B. Weisz. *Nature*. 1984, **309**, 589-591.
23. H. Han, M. Liu, F. Ding, Y. Wang, X. Guo, and C. Song. *Ind Eng Chem Res*. 2016, **55**, 1849-1858.
24. E. Paul and M.E. Davis. *J. Catal*. 1989, **119**, 497-507.
25. H. Itoh, T. Hattori, K. Suzuki, and Y. Murakami. *J. Catal*. 1983, **79,** 21-33.
26. N. Jiang, H. Jin, E.Y. Jeong, and S.E. Park. *J. Nanosci Nanotech.* 2010, **10,** 227-232.
27. M.L. Kantam, B.P. Rao, B.M. Choudary, K.K. Rao, B. Sreedhar, Y. Iwasawa, and T. Sasaki. *J. Mol Catal.* 2006, **252,** 76-84.
28. D.S. Kim, J.S. Chang, J.S. Hwang, S.E. Park, and J.M. Kim. *Micropor Mesopor Mater.* 2004, **68,** 77-82.
29. C. Lacroix, A. Deluzarche, A. Kiennemann, and A. Boyer. *Zeolites*. 1984, **4**, 109-111.
30. J. Raymond. *Econ Geol*. 1927, **22,** 18-43.
31. R. Manivannan, and A. Pandurangan. *Appl Clay Sci.* 2009, **44**, 137-143.
32. S. Mintova, V. Valtchev, T. Onfroy, C. Marichal, H. Knözinger, and T. Bein. *Micropor Mesopor Mater*. 2006, **90**, 237-245.
33. T. Odedairo, R.J. Balasamy, and S.A. Khattaf. *Catal Sci Tech*. 2012, **2**, 1275-1286.
34. G. E. Mirth, and J. A. Lercher. *J. Catal.* 19971, **68**, 442-449.
35. C. Perego, S. Amarilli, R. Millini, G. Bellussi, G. Girotti, and G. Terzoni. *Micropor Mater.* 1996, **6**, 395-404.
36. O.V. Petersen, G. Giester, F. Brandstätter and G. Niedermayr. *The Canadian Miner*. 2002, **40**, 173-181
37. J.L. Sotelo, M.A. Uguina, J.L Valverde and D.P. Serrano. *Ind Eng Chem Res*. 1993, **32**, 2548-2554..
38. T. Takahiko, L.W. Beck, and M.E. Davis. *J. Phy Chem.* 1999, **103**, 2674-2679.
39. L. Tosheva, and V.P. Valtchev. *Chem Mater*. 2005, **17**, 2494-2513.
40. M.A. Uguina, J.L. Sotelo, D.P. Serrano, and R.G. Van. *Ind Eng Chem Res*. 1992, **31**, 1875-1880.
41. A.N. Vasiliev, and A. A. Galinsky. *React Kinet Catal L.* 1993, **51**, 253-259.
42. A.M. Vos, X. Rozanska, R.A. Schoonheydt, R.A. Santen, F. Utschka, and J. Hafner, *J. Amer. Chem. Soc*. 2001, **123**, 2799-2809.
43. Walton, S.K. Morgan, B. Abney, and M.D. LeVan. *Micropor Mesopor Mater*. 2006, **91**, 78-84.
44. W. Xiangsheng, W. Guiru, S. Dongmin, F. Chengbi, and W. Ming, *Zeolites*. 1991, **11**, 254-257.

45. T. Yashima, H. Suzuki, and N. Hara. J. *Catal*. 1974, **33**, 486-492.

46. Z. Zhao and R. Zhao. *Zeolites.*1993, **13**, 634-639.