

Alkylation of Benzene with Ethanol over HZSM-5 Zeolite Catalyst

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ABSTRACT: Alkylation of benzene with ethanol was analysed using shape selective HZSM-5 (Si/Al = 90) zeolite catalyst. The reaction was carried out in a continuous fixed bed flow reactor in the temperature range of 300-500°C at atmospheric pressure to investigate the activity of this catalyst for the selectivity and yield of ethylbenzene (the desired product). The alkylation of benzene with ethanol (2:1 and 4:1 by volume) produces ethylbenzene as primary product and others like 1, 2-Diethylbenzene, 1, 4-Diethylbenzene and xylene mixtures as secondary products. The physicochemical properties of catalyst were characterised by XRD, BET, TGA, FTIR, NH₃-TPD and SEM. The feed and products were analysed by gas chromatography and mass spectroscopy. The conversion of benzene was found to be better for benzene to ethanol ratio 4:1. The HZSM-5 (SAR=90) catalyst gave good selectivity (63.84%) and yield (45.03%) of ethylbenzene.

KEYWORDS: Alkylation, HZSM-5, Benzene, Ethanol, Ethylbenzene

I. INTRODUCTION

Porous solids with pores of the size of molecular dimensions, 0.3 – 2.0 nm in diameter are called molecular sieves. Examples include zeolites, carbons, glasses and oxides. Some are crystalline with a uniform pore size and more described in detail by their crystal structure, for example, zeolites [1].

Zeolites are so special when compared to other crystalline inorganic oxide materials due to a combination of the following properties: the microporous character with uniform pore dimensions, allowing certain hydrocarbon molecules to enter the crystals while rejecting others based on too large a molecular size, the ion-exchange properties which allow to perform all sorts of ion exchange reactions, the ability to develop internal acidity which makes the zeolites interesting materials for catalysing organic reactions and the high thermal stability of the zeolites [2].

According to International Zeolite Association (2014), until now, there are 218 zeolite framework type codes that have been discovered. Worldwide consumption of zeolites (natural and synthetic) is estimated to be about 5 million tons per year. The annual market for synthetic zeolites and molecular sieves was developed vastly to 1,800,000 ton worldwide in 2008 [3].

Alkylation of benzene is a vital reaction in the petrochemical industry. Benzene alkylation technologies offer improvements in octane number and gasoline volume. Ethylbenzene, diethylbenzene, toluene and xylenes are important raw materials for many intermediates of commodity petrochemicals and valuable fine chemicals.

Ethylbenzene (EB), which is one of the most important products used as the chemical intermediate, is the main feedstock for the synthesis of styrene which is then polymerised into polystyrene, a common plastic material [4]. Ethylbenzene is also used in the chemical industry in the manufacture of acetophenone, cellulose acetate, diethylbenzene (DEB), ethyl anthraquinone, ethylbenzene sulfonic acids, propylene oxide, and α -methylbenzyl alcohol [5]. Additionally it is used as a solvent, a constituent of asphalt and of naphtha, and in fuels. Ethylbenzene and xylene mixture are used in the paint industry and in the production of pesticides in agriculture [5].

Several researchers have proposed the alternative catalytic reaction pathways for the production of ethylbenzene. The catalytic reaction which uses ethanol for benzene alkylation, instead of ethene, would eliminate the ethene production

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step and, therefore, leading to the commercial and environmental benefits in the ethylbenzene manufacturing [6]. In addition to the intrinsic scientific interest, the direct use of ethanol (instead of ethene) in the manufacture of ethylbenzene also has economic significance in those countries like Brazil and India, where biomass-derived alcohol is an additional feedstock for the manufacture of chemicals (see Fig.1).

In the reaction of converting benzene to ethylbenzene, HZSM-5 zeolite has been used as a catalyst. It is well-known that the alkylation reaction of benzene in the presence of an acid catalyst belongs to a carbenium ion type mechanism. The alkylation of benzene with ethanol produces ethyl benzene as primary product and others like diethylbenzene and xylene mixtures as secondary products (see Fig. 2). This research focused on to study HZSM-5 catalyst of silicon to aluminium ratio = 90 for benzene alkylation with ethanol into ethylbenzene.

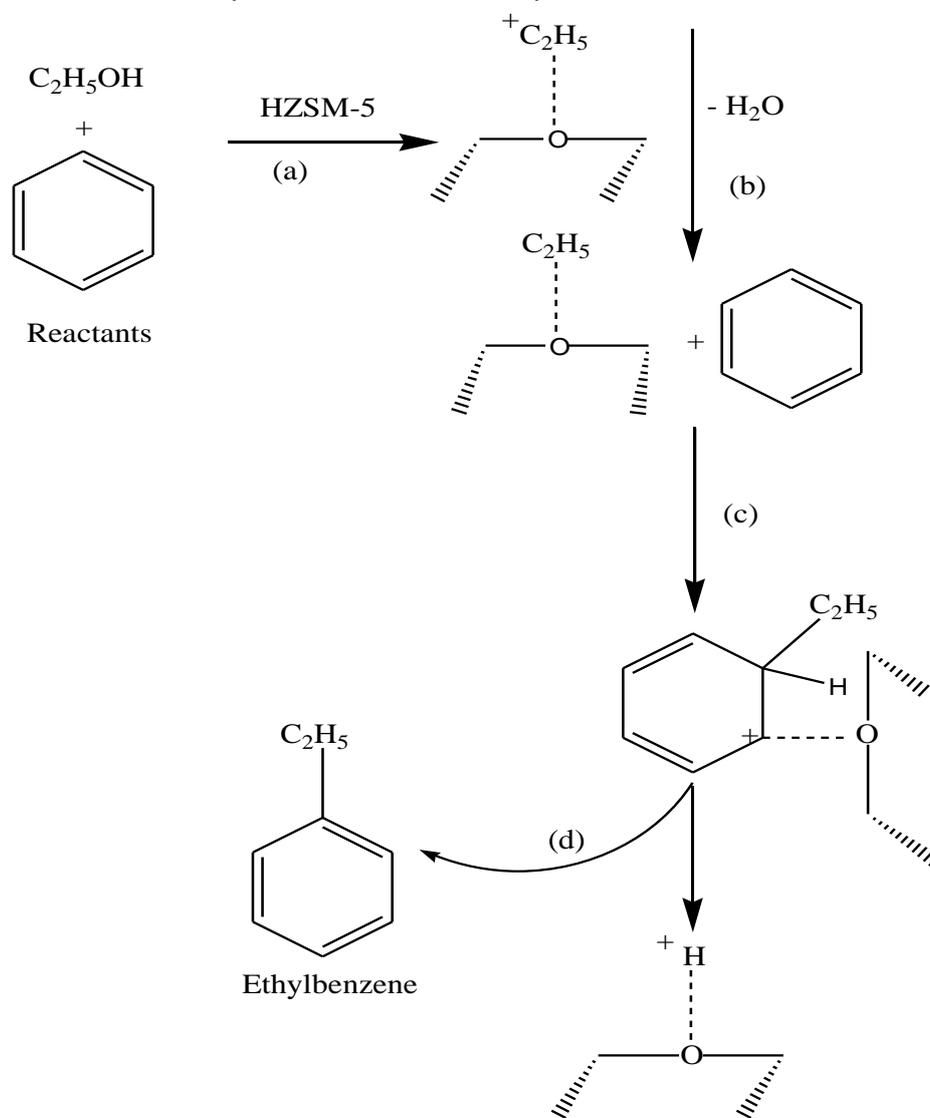


Figure 1: Possible mechanism for benzene alkylation with ethanol to form ethylbenzene

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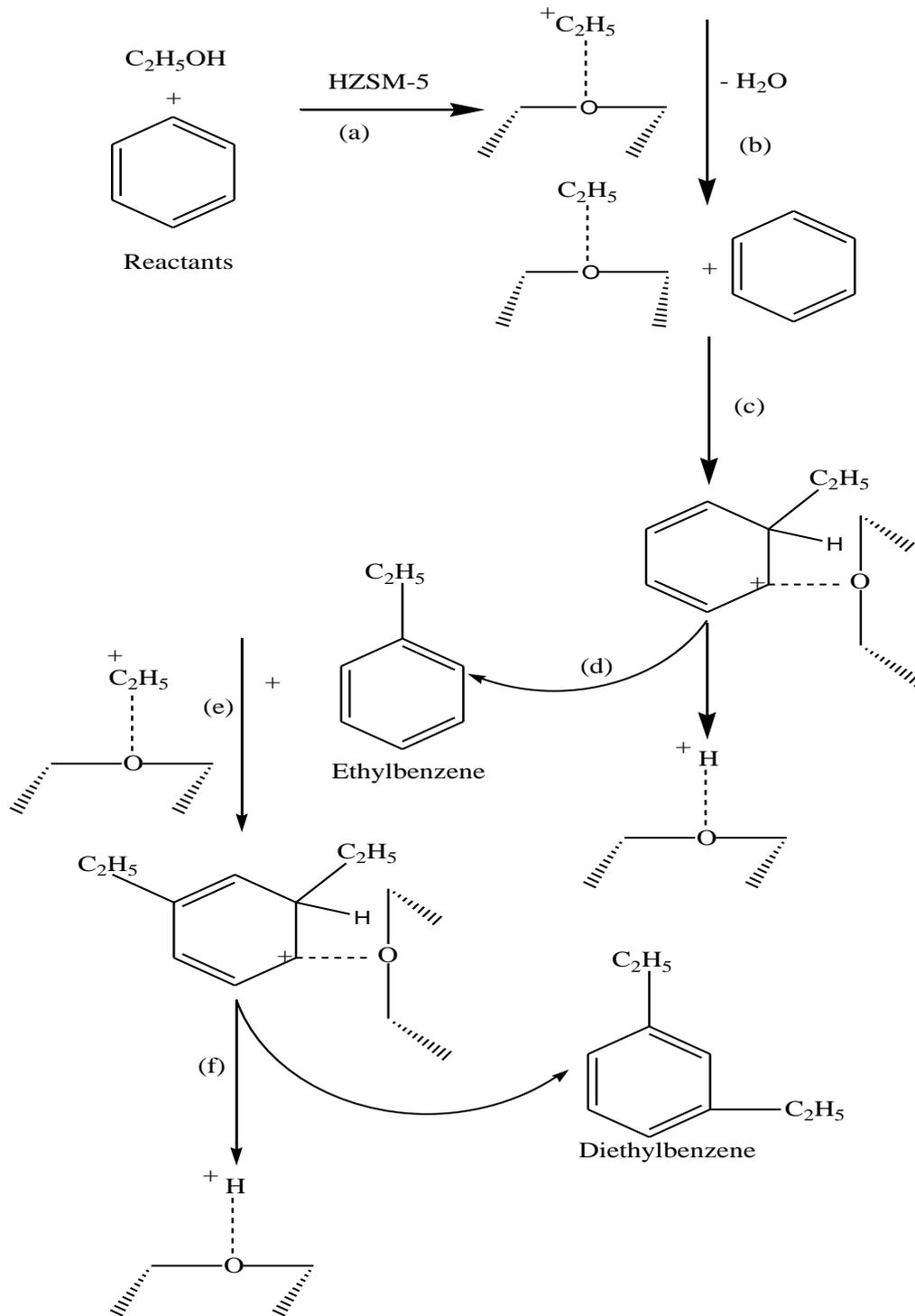


Figure 2: Possible mechanism for benzene alkylation with ethanol to form Diethylbenzene

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II. RELATED WORK

Several studies have been reported regarding benzene alkylation using unmodified zeolites like HZSM-5, Beta, HY, mordenite, TNU-9, SSZ-33, ZSM-12, MCM-22 and ITQ-22 [7-12] as well as HZSM-5 modified with phosphorous and boron [6]. Venuto et al. [9] had shown that although Linde type X and Y zeolites exchanged with rare earth ions catalyse the alkylation of benzene with ethanol, the catalyst aging was severe leading to catalyst deactivation in a few hours. Junhui Li et al. [13] had performed alkylation of benzene with ethanol for synthesis of ethylbenzene over parent zeolites and zeolites modified with La_2O_3 , such as HMCM-22, HBeta and nano HZSM-5.

III. EXPERIMENTAL

3.1 Materials

HZSM-5 with SAR = 90 were obtained from Sud-Chemie India Pvt. Ltd. Benzene used for the experiments was 99% pure. Benzene (99.5% pure) for the present studies was obtained from RFCL limited, A-3, Okhla Industrial Area, Phase-I, New Delhi, India. Pure ethanol (99.9%) was supplied by Merck KGaA, 64271 Darmstadt, Germany.

3.2 Catalyst Preparation

HZSM-5 SAR = 90 obtained from Sud-Chemie India Pvt. Ltd was in protonic form so that no further transformation activities were done except catalyst was calcined at 550°C for 5 hour to be activated. The zeolite powder so obtained was pelletized at 10 tonne / cm^2 pressure and broken into small pieces in the size range 0.3 - 0.5 mm. The fraction in this size range was used in the reactor for the activity test runs.

3.3 Experimental setup

The catalytic experiments were carried out in a fixed bed; continuous down flow tubular quartz (0.6 cm I.D and 66 cm long) reactor placed inside a microprocessor controlled furnace (Metrex Scientific Instruments Pvt.Ltd, New Delhi) which was preceded by a preheater and followed by a condenser. The same reactor tube was used in all the experiments. In a typical run, about 0.7g of catalyst (which occupied 6 cm height of the reactor) was charged into the reactor and the reaction was carried out at atmospheric pressure using HZSM-5 catalyst. The catalyst was activated for one hour in an atmosphere of nitrogen before the experimental runs were started. The benzene ethanol mixture of 2:1 and 4:1 ratio introduced with the help of a metering pump at rate of 0.4 ml/min and vaporized in the pre-heater before contacting the catalyst. The reactant vapours along with nitrogen entered the reactor, which was electrically heated. The flow rate of the nitrogen carrier gas was 0.5 litres per minutes. The products vapours, along with unreacted reactants, were condensed in the condenser and the liquid samples collected were analyzed in a gas chromatograph and mass spectroscopy with a 30 m x 0.32 mm (0.25 μm film thickness) Elite-1 capillary column (Perkin Elmer) using a flame ionization detector (FID). The program used was as follows. Initial oven temperature was 70°C then held for 2 min. After that the temperature was increased to 200°C with a ramp rate of $10^\circ\text{C}/\text{min}$. Again it stayed at 200°C for 1 min. The Detector and Injection temperature was 250°C . Flow rate of air, hydrogen and nitrogen were 450, 45 and 45 ml/min respectively. Nitrogen was used as carrier gas and the split ratio was 1:50. From gas chromatography results, the selectivity and yield of ethylbenzene in the product was calculated. The conversion of benzene was also noted for HZSM-5 catalyst.

3.4 Catalyst Characterization

3.4.1 BET Analysis

The BET surface area and the pore volume of the catalyst samples were determined by liquid nitrogen adsorption at -196°C using Micromeritics ASAP 2020 instrument. Degassing was done for 8 hour under vacuum at 250°C . The BET surface area of HZSM-5 SAR = 90 was $347 \text{ m}^2/\text{g}$.

3.4.2 XRD Analysis

XRD analysis was carried out using powder diffractometer (Bruker D8) at Institute Instrumentation Centre (IIC), Indian Institute of Technology Roorkee. Cu-K α ($\lambda=1.5417 \text{ \AA}$, 40kv and 30mA) was used as anode material and the range of scanning angle (2θ) was kept between 5° to 50° with scan speed of $2\theta= 1^\circ/\text{min}$. The powder XRD patterns (Fig. 3) of HZSM-5 sample exhibited well-resolved diffraction peaks, which was characteristic of the MFI framework structure. The high intensity of peaks in the XRD patterns indicate that the zeolite sample was highly crystalline materials and the highest diffraction peaks was seen at $2\theta = 23^\circ$. By using X'Pert High Score Plus software, this zeolite belongs to Ref. Code = 00-033-1161 material.

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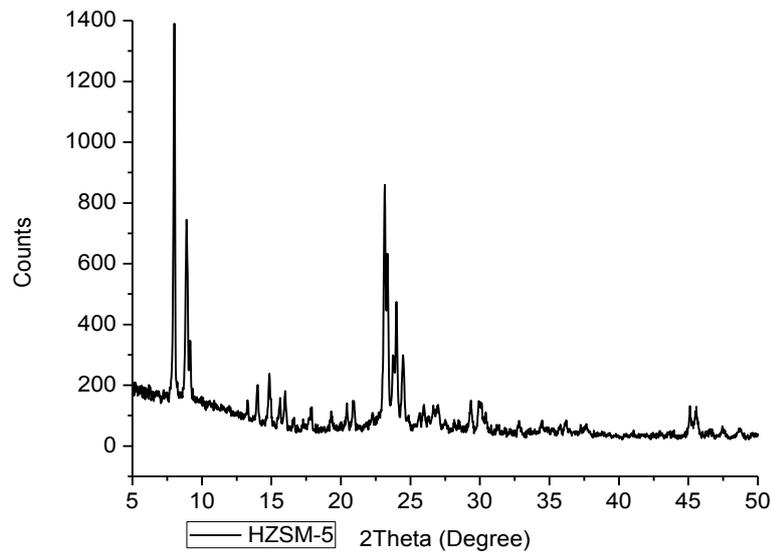


Figure 3: X-ray diffraction pattern of HZSM-5

3.4.3 FE-SEM and TEM

The morphology of the zeolite sample was evaluated by Field Emission- Scanning Electron Microscope (FE-SEM) using ULTRA plus. FE-SEM image of the sample was shown in Fig. 4.

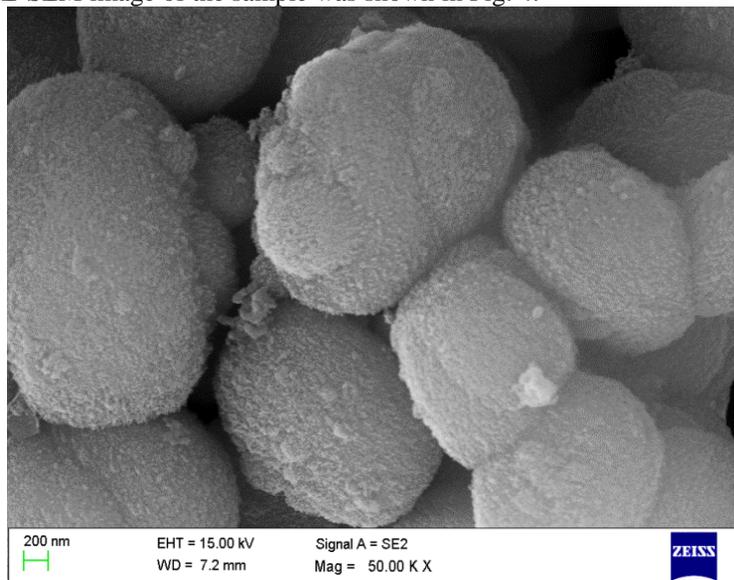


Figure 4: FE-SEM result of HZSM-5 SAR= 90

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3.4.4 Thermo- gravimetric Analysis

Thermo- gravimetric analysis technique was conducted in order to determine the thermal stability of the zeolite framework and weight loss occurring from zeolite lattice during heating. TGA was conducted on SII 6300 EXSTAR using air as carrier gas at 200 ml/min on a 10 mg of sample. Figure (5) presents the TGA of HZSM-5 (Si/AL ratio = 90) heated from ambient temperature to 1000°C in temperature progression of 10°C/min. The portion of the curve up to 200°C is normally linked with the weight loss due to moisture content of the catalyst, whereas, the portion of the curve from 200 to 1000°C is assigned to the weight loss due to removal of hydrocarbon, moisture contained inside the pores and coke formation. Percent weight loss of HZSM-5 zeolite catalyst from ambient temperature to 1000°C was 5.1%.

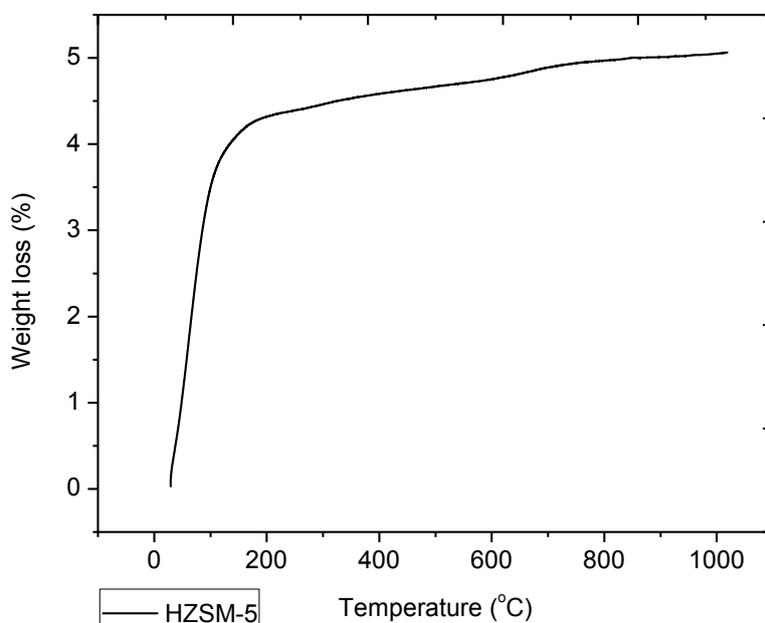


Figure 5: TGA graph of HZSM-5 Zeolite

3.4.5 FTIR Analysis

Infrared spectra were obtained at 4 cm⁻¹ resolution on Nicolet 6700 series FTIR Spectrometer. The infrared cell used was fitted with KBr windows. A sample of the zeolite powder was accurately weighed and mixed with around 300 mg KBr and then passed into a 10mm diameter wafer at 15 tonnes/cm² pressure. This wafer was placed in the IR cell. The IR cell spectra were recorded at room temperature in air. Background IR correction for air was also made.

The IR structural studies of zeolite have been carried out in the infrared region of wave number 400 to 4000 cm⁻¹, because fundamental vibrations of SiO₄, AlO₄ or TO₄ units are contained in this region. In the KBr pellet technique a small amount of the solid sample was mixed with powdered KBr and pressed into pellet. In the pelletizing process the KBr crystalline boundaries flow together and around the sample particles sufficiently so that they do not scatter much light and the whole pellet looks more or less clear.

The band at (i) 545 cm⁻¹ is assigned to the highly distorted double five membered rings present in the ZSM-5 structure, (ii) 3739, 3660 and 3490 cm⁻¹ are assigned to weak, medium and strong Brønsted acid sites, respectively, (iii) 1700 cm⁻¹ to water bond, (iv) 800 cm⁻¹ to Al-O bond and (v) 1350 cm⁻¹ to Si-O-Si bond, etc.

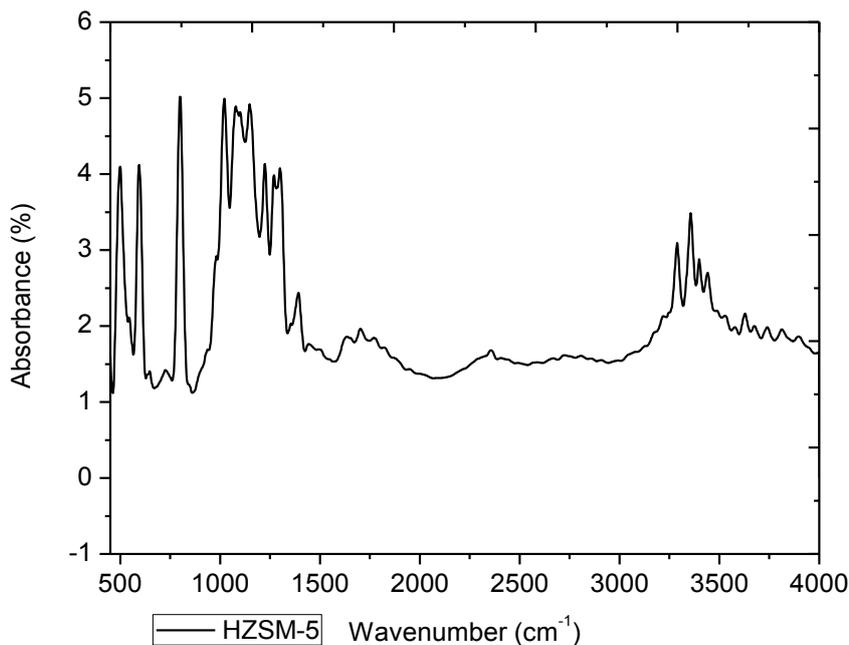


Figure 6: FTIR Spectra of HZSM-5 Zeolite

Table 1: The approximate IR band corresponding to a functional group present in the HZSM-5 are suggested as below

Si-OH	3745 cm ⁻¹	Si-O-Si	1140 cm ⁻¹
Si-OH-Al	3610 cm ⁻¹ (dependent on SAR)	Si-O-Al	1075 cm ⁻¹
Al-OH	3600 cm ⁻¹ (in structure)	Al-O	760 cm ⁻¹
H-OH	1660 cm ⁻¹		

3.4.6 Temperature Programmed Desorption of Ammonia (NH₃-TPD)

NH₃-TPD measurements in the temperature range from room temperature to 650°C were performed in Micrometrics ChemiSorb 2720. Zeolites sample was put in a quartz cell with U shape and pretreated, insitu, for 1 h at 250°C in a flow of nitrogen (>99%) of 20 ml/min. After cooling to 25°C, adsorption of ammonia was carried out in a flow of ammonia and helium mixture of 40 ml/min. After the catalyst surface became saturated some time was waited to remove the excess of ammonia. The temperature-programmed desorption was carried out with a linear heating rate of approximately 10°C/min from 25°C to 650°C in a flow of helium (>99%) of 20 ml/min. The NH₃ that desorbed was measured by a thermal conductivity detector.

IV. RESULTS AND DISCUSSION

The powder XRD patterns (Fig. 3) of HZSM-5 sample exhibited well-resolved diffraction peaks, which was characteristic of the MFI framework structure. The high intensity of peaks in the XRD patterns indicate that the zeolite sample was highly crystalline material and the highest diffraction peaks was seen at $2\theta = 23^\circ$.

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The temperature programmed desorption of a basic molecule such as ammonia (NH₃-TPD) is one of the most common methods used for measuring the surface acidity of porous materials such as zeolites, clays or mesoporous silica [14]. The acid strength was determined by measuring the heat of adsorption or desorption of a suitable probe molecule. Ammonia meets the requirements for such a probe. Firstly it is small enough to enter all the zeolite pores. Secondly it can react both with the Brønsted and Lewis acid sites [15].

From the NH₃-TPD experiments (Figure 7), it could be concluded that two types of acid sites were present in H-ZSM-5: Weak acid sites corresponding with desorption at low temperature and strong acid sites corresponding with desorption at high temperature.

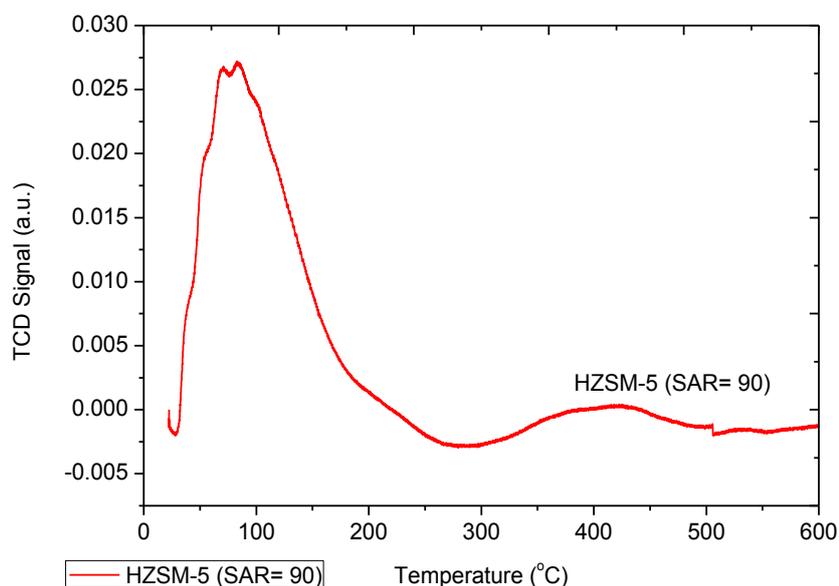


Figure 7: Ammonia Temperature Programmed Desorption (NH₃-TPD) of HZSM-5
From Ammonia Temperature Programmed Desorption (NH₃-TPD) of HZSM-5 result we observed that 0.950 mmol/g weak acid sites and 1.472mmol/g strong acid sites.

4.1 Performance of HZSM-5 (SAR = 90) catalyst

In the present study the performances of HZSM-5 catalyst with silicon to aluminium ratio 90 for the alkylation reaction of benzene with ethanol was carried out. Experiments were carried out in a fixed catalytic bed down flow reactor at a constant feed (benzene and ethanol mixture 2:1 and 4:1 by volume) rate of 0.4 ml/min and a carrier gas (N₂) flow 0.5 litres per minute (lpm). The WHSV of benzene and ethanol mixture as feed was 32.6 h⁻¹. Nitrogen was used as carrier gas to activate the catalyst. The products of the reaction were analyzed by gas chromatograph. Liquid products contained benzene, ethanol, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene and diethylbenzene. The gaseous products contained negligible amount of hydrocarbon gases (ethane, methane, ethylene, etc.).

The following equations were used to check the activity of the catalysts:

1. % benzene conversion (% X_B) = $\frac{\text{Moles of benzene converted}}{\text{Moles of benzene in the feed}} \times 100$
2. % ethylbenzene yield (% Y_{EB}) = $\frac{\text{Moles of ethyl benzene obtained}}{\text{Moles of benzene converted}} \times 100$
3. % ethylbenzene selectivity (% S_{EB}) = $\frac{\text{Moles of ethylbenzene (desired product) formed}}{\text{Moles of all products formed}} \times 100$

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The results of alkylation of benzene with ethanol using HZSM-5 (silicon to aluminium ratio 90) were presented in table (2, 3) and figure (8, 9).

Table (2) shows the effect of reaction temperature on catalytic performance of HZSM-5 (SAR=90) catalyst for the alkylation of benzene with ethanol (benzene/ethanol = 2:1 by volume). According to our investigation we observed that Ethylbenzene, 1, 2-diethylbenzene and 1, 4-diethylbenzene were obtained as a major products while xylenes, toluene and gaseous hydrocarbons were also present in small amounts.

Table 2: Effect of reaction temperature on catalytic performance of HZSM-5 (SAR = 90) catalyst for alkylation of benzene with ethanol (Benzene/ethanol = 2:1)

Products (mol %)	Temperature (°C)				
	300	350	400	450	500
Ethanol	0.96	1.07	1.32	0.22	1.78
Benzene	21.19	14.87	28.15	17.91	22.55
Toluene	0.34	0.37	0.26	0.33	0.66
Ethylbenzene	35.79	34.42	45.03	41.63	37.63
p-Xylene	0.45	0.30	0.31	0.16	0.19
m-Xylene	0.03	0.02	0.01	0.01	1.07
o-Xylene	0.15	0.39	0.52	1.76	0.73
1, 2-Diethylbenzene	9.14	11.77	4.97	7.82	0.60
1, 4-Diethylbenzene	16.26	20.73	12.57	21.43	30.21
Others	15.69	16.06	6.86	8.73	4.58

Similarly table (3) shows the effect of reaction temperature on catalytic performance of HZSM-5 (SAR=90) catalyst for the alkylation of benzene with ethanol (benzene/ethanol = 4:1 by volume). According to our investigation we observed that Ethylbenzene, 1, 2-diethylbenzene and 1, 4-diethylbenzene were obtained as a major products while xylenes, toluene and gaseous hydrocarbons were also present in small amounts. However, the amount of ethylbenzene obtained for benzene to ethanol (benzene/ethanol = 4:1 by volume) ratio was better than that of 2:1. This happened due to decrease of further reactions such as ethylation of ethylbenzene to diethylbenzene and disproportionation of ethylbenzene to benzene and diethylbenzene.

Table 3: Effect of reaction temperature on catalytic performance of HZSM-5 (SAR = 90) catalyst for alkylation of benzene with ethanol (Benzene/ethanol = 4:1)

Products (mass %)	Temperature (°C)				
	300	350	400	450	500
Ethanol	1.00	0.65	0.85	0.95	0.75
Benzene	23.45	16.77	26.84	22.94	15.03
Toluene	0.93	1.86	2.85	3.29	3.93
Ethylbenzene	39.65	37.87	45.00	43.95	37.82
p-Xylene	0.41	0.63	0.34	0.40	0.21
m-Xylene	0.00	0.00	0.00	0.00	0.00
o-Xylene	1.05	0.87	1.13	1.33	1.87
1, 2-Diethylbenzene	6.71	10.69	5.57	6.61	10.20
1, 4-Diethylbenzene	14.11	16.19	9.91	11.71	16.80
Others	12.69	14.47	7.51	8.82	13.39

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Fig. 8 demonstrates the effect of reaction temperature on catalytic performance of HZSM-5 (SAR=90) catalyst such as selectivity and yield of ethylbenzene and conversion of benzene for the alkylation of benzene with ethanol (benzene/ethanol = 2:1 by volume). The highest yield (45.03%) and selectivity (63.84%) of ethylbenzene resulted at 400°C. However, the highest conversion (77.65%) of benzene was obtained at 350°C.

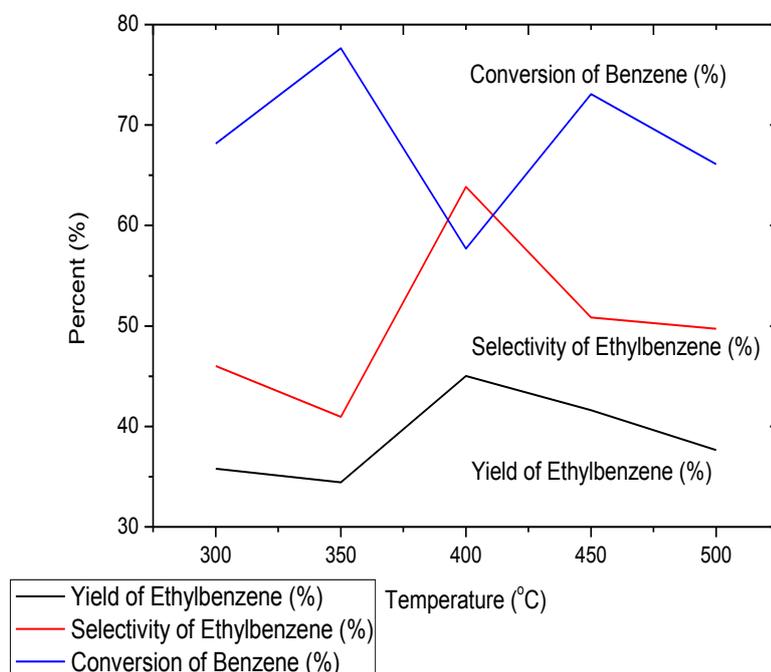


Figure 8: Effect of reaction temperature on the performance of HZSM-5 SAR = 90 for benzene to ethanol ratio 2:1

Fig. 9 demonstrates the effect of reaction temperature on catalytic performance of HZSM-5 (SAR=90) catalyst such as selectivity and yield of ethylbenzene and conversion of benzene for the alkylation of benzene with ethanol (benzene/ethanol = 4:1 by volume). In the case of 4:1 benzene to ethanol ratio similarly the highest yield (45.00%) and selectivity (62.23%) of ethylbenzene were obtained at 400°C. The highest conversion of benzene was 81.23% at 500°C but the selectivity of ethylbenzene was poor at this temperature. From our investigation we observed that HZSM-5 zeolite with silicon to aluminium ratio 90 was promising.

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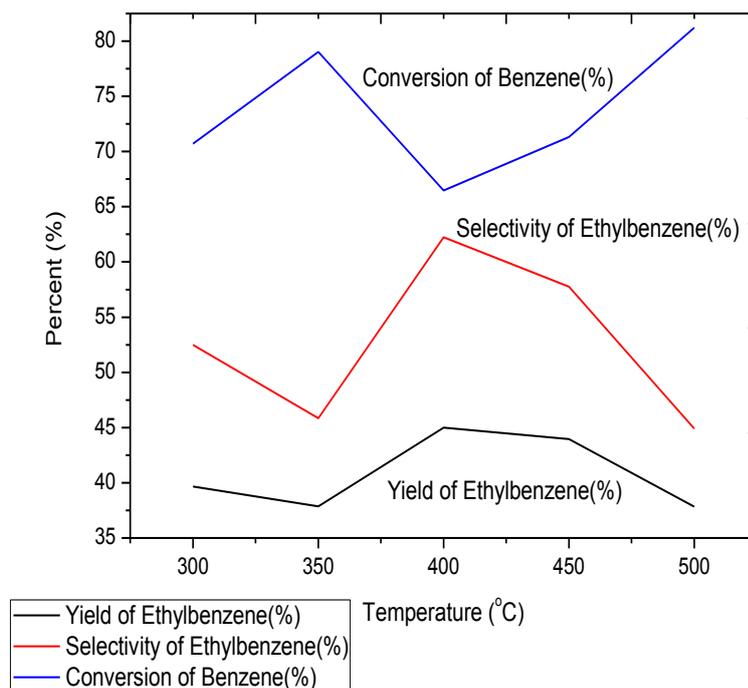


Figure 9: Effect of reaction temperature on the performance of HZSM-5 SAR = 90 for benzene to ethanol ratio 4:1

V. CONCLUSION

The results conclude that the performance of HZSM-5 SAR = 90 in terms of yield and selectivity of ethylbenzene was promising.

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