



Ethylation of ethyl benzene by the use of acid zeolite based catalyst IM-5

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Abstract: IM-5 contributes to the isomerization of p-DEB to m-DEB. The isomerization step can generally follow two models: (i) the isomerization of p-diethyl benzene to m-diethyl benzene takes place exclusively on the outer surface, or (ii) the isomerization occurs on the acid sites located both on the outer surface and inside the zeolite channels. Therefore, their elimination of acid sites from the zeolite surface will be helpful for the reaction selectivity with respect to the desired dialkylaromatics. However, if the zeolite modification can be done, not only leading to elimination of the surface sites but also lead to narrowing of the pore opening, like, with the surface silylation or deposition of metal oxides, such zeolite modification results increase p- selectivity.

INTRODUCTION

The importance of zeolites as catalysts hardly needs to be emphasized. This, to a great extent, can be attributed to their shape selectivity. Zeolites are crystalline microporous aluminosilicates, either of natural or synthetic origin with highly ordered structures¹. Zeolites are also popularly known as '*molecular sieves*' due to their ability to differentiate between molecules of different shapes and size². Zeolites have found widespread applications as adsorbents, as ion exchange materials, detergent builders and catalysts, especially in petroleum refining, petrochemicals and as fluidized catalytic cracking catalysts (FCC)³. The catalytic sites for acid catalyzed reactions in aluminosilicate zeolites are mainly the Brönsted acid centers associated with protons. The as-synthesized form of zeolite can be converted into catalytically active protonic form (H⁺ form) by a number of techniques. All the

alkylation, disproportionation and isomerization reactions carried out on zeolites are due to acidity present in the zeolite^{4,5}

Ethylation of EB has been carried out using alkylation catalyst like AlCl_3 , FeCl_3 , BF_3 , HF and HCl . However, the conventional catalysts are not highly selective to the para-isomer (p-DEB) and can result in yields that are very close to the thermodynamic equilibrium composition of DEBs (para:meta:ortho = 30:54:16)⁶. Catalytic disproportionation of ethylbenzene over zeolite based catalyst to produce isomers of diethylbenzene amongst other products has gained tremendous attention in recent years. This is due to the wide range of application of these compounds in a variety of industrial processes. p-diethylbenzene, which is the most important of the three DEB isomers, is an important desorbent for Parex process of UOP used in separating p-xylene from a mixture of xylene. Besides, it is an important monomer for the production of copolymers, such as ion-exchange resin and viscosity modifiers of lubricant oil. Generally, the para-selectivity in these reactions is influenced by the following three factors⁷. a) Transition state shape selectivity, b) Product shape selectivity, c) Nonselective isomerization at the external surface of zeolite.

Dow Chemicals employing novel dealuminated H-mordenite (3DDM) successfully achieved the replacement of harmful and corrosive Friedel–Crafts catalysts by zeolites⁸ in 1995. This process includes both liquid phase alkylation and transalkylation units utilizing a pseudo- three-dimensional channel system of mordenite properly modified by dealumination. Ethylbenzene is produced in bulk quantities by alkylation of benzene with ethene in the presence of aluminum chloride or zeolite catalyst. Successive alkylations produce diethylbenzene (DEB) and higher ethylated benzenes, commonly referred to as poly-ethylbenzenes (PEB's). Kim et al⁹ studied the alkylation of ethylbenzene with ethanol on ZSM-5 zeolites at 673 K. They reported that the primary product in this alkylation reaction on HZSM-5 catalyst was only p-DEB because of the transition state selectivity.

A very important mechanistic investigation of Ethyl-benzene disproportionation reaction by Arsenova et al over ZSM-5 showed that the reaction scheme follows a consecutive path¹⁰. They reported that the first step in ethylbenzene disproportionation occurs in the interior of the zeolite crystal without diffusion limitations, yielding essentially p-DEB as a primary product. p-DEB is subsequently converted in a secondary isomerization mainly to m-DEB. In addition, crystal size was found to have a very important role on the product distribution, with large crystals producing higher yields of p-DEB than smaller crystals. Catalytic and sorption studies carried out by Arsonova-Hartel et al. suggest that the formation of o-DEB within the pores of ZSM-5 at low temperatures (less than 249 °C) is almost impossible¹¹.

This suggests that o-DEB has restricted access to ZSM-5 channels. The present study is aimed at studying the results of ethylation of ethylbenzene with ethanol using IM-5 zeolite as catalyst. The effect of reaction conditions on ethylbenzene reactivity, p-DEB selectivity, total DEB selectivity and yield will be reported. Zeolite IM-5 is a new high-silica zeolite that was recently reported by Benazzi et al. and Casci et al., respectively¹²⁻¹⁴. Although the framework structures of this synthetic zeolite still remain undetermined, recent results from various catalytic test reactions have suggested that this material may either contain the two-dimensional pore system with two intersecting 10-ring channels or the one-dimensional pore system consisting of 10-ring channels with large internal cavities. If such is the case, they should be potentially useful as shape-selective catalysts in many hydrocarbon conversions, especially in isomerization, alkylation, and/or cracking of hydrocarbons catalyzed by medium-pore zeolites. According to the initial patents for IM-5, the synthesis include the use of diquaternary alkylammonium cations with formula¹⁵



Which is formed of two 1-methylpyrrolidinium groups connected by the polymethylene bridging unit. It has been repeatedly shown that the phase selectivity of zeolite synthesis in the presence of such flexible, linear organic cations as structure-directing agents (SDAs) is sensitive not only to the length of the central alkyl chain and the nature of the groups on the ammonium ion employed but also to the oxide composition of synthesis mixtures. This has led to investigate the synthesis parameters that influence the preparation of zeolite IM-5.

EXPERIMENTAL

Synthesis of Template: The divalent 1,5-bis(N-methylpyrrolidinium)pentane (MPP) cation was prepared by reacting 5.745 g of 1,5-dibromopentane (97%, Aldrich) with 4.25 g of 1-methylpyrrolidine (97%, Aldrich) in acetone (80 ml) approx as a solvent with rapid stirring at room temperature overnight. The excess amine was removed by extraction with diethyl ether (Loba) and recrystallizations were performed in methanol–diethyl ether (Thomas Baker) mixtures. 9.62 g of MPP cation formed. Required template was dissolved in about 50 g of distilled water. To this, 9.62 g of fumed silica was added under stirring.

When the mixture is viscous, 20 g water was added to it. After complete addition of fumed silica, 4.44 g NaOH dissolved in 10 g distilled water was added dropwise. Following this, 2.03 g of $\text{Al}(\text{NO}_3)_3$ dissolved in 10 g distilled water was added to the mixture. The remaining amount of water i.e. 15.37 g was added and the mixture was stirred for 24 hours. After stirring at room temperature for 24 h, the synthesis Mixture (pH=12.07) was charged into Teflon-lined 300-mL autoclaves and heated to 160 °C under rotation (100 rpm) for 14 days. The solid products were recovered by filtration, washed repeatedly with water, and then dried overnight at room temperature. As-synthesized zeolites were calcined under flowing air at 550 °C for 8 h to remove the organic SDA occluded. The calcined samples were then refluxed using NH_4NO_3 solutions for 6 h followed by calcination at 550 °C for 8 h to get proton¹⁵ form of IM-5.

Apparatus and procedure: The reaction was carried out in a down flow fixed bed reactor of 13mm inner diameter and 35cm length in a continuous flow system. The reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature programmer cum indicator. About 2 g of sieved catalyst (20-30 mesh) was sandwiched at the center of the reactor with a thin layer of quartz wool sandwiched between glass beads. It was heated in dry air at a ramp rate of 2 K/min from room temperature to 773 K and kept for 8 h for calcination. Catalyst was cooled down to room temperature and raised to required reaction temperature in hydrogen flow.

The alkylation reaction was carried out at different temperatures i.e. 250, 275, 300, 325 and 350°C with molar ratios of ethylbenzene: ethanol of 1:1, 2:1 and 3:1. Pressure was maintained at 10 bar while the feed was pumped at $\text{WHSV}=3.0 \text{ h}^{-1}$. The products were passed through a water-cooled condenser attached at the end of the reactor. The liquid products of the first hour were discarded and only products collected 2nd hour onwards was analyzed using GC. This is done to ensure the attainment of steady state for the reaction over the catalyst and also to eliminate initial temperature fluctuations. The products were collected at intervals of 1 h. The reaction was carried out for 7-8 hrs at each experimental condition. After each run, the catalyst was heated at 500 °C for regeneration in order to remove the deposited coke.

RESULT AND DISCUSSION

Analysis of products using Gas chromatography : Gas chromatography - specifically gas-liquid chromatography - involves a sample being vaporized and injected onto the head of the

chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase, which is adsorbed onto the surface of an inert solid. The major instrumental components are the carrier gas, columns and the detector. The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium and argon. The choice of carrier gas is often dependant upon the type of detector being used. The carrier gas system also contains a molecular sieve to remove water and other impurities.

Product Analysis: The products were analyzed using Agilent 7890A series GC system employing Flame Ionization Detector (FID) and Zebron capillary column (50 m x 320 μ m x 1.05 μ m). The response of an FID is different for different compounds, hence the response factor (RF) is determined from the response of a mixture of known composition – the standard. This standard is first injected into the GC-FID and analyzed. After GC separation of known mixture, the area of each component is related to it's actual concentration and the Rf is calculated.

$$Rf = \text{Area\%} / \text{wt\%}$$

Conversion and selectivity are calculated as follows:

$$\% \text{ Conversion of EB} = \frac{(\Sigma \text{wt\% of alkylated aromatic products})}{(\Sigma \text{wt\% of alkylated aromatics} + \text{wt\% of ethylbenzene})} * 100$$

$$\text{DEB selectivity} = \frac{(\Sigma \text{wt\% of DEB isomers})}{(\Sigma \text{wt\% of alkylated aromatics})} * 100$$

$$\text{p-DEB selectivity} = \frac{(\text{wt\% of 1,4-DEB})}{(\Sigma \text{wt\% of total DEB isomers})} * 100$$

$$\% \text{ DEB Yield} = \frac{\text{DEB selectivity} * \text{Conversion of Ethylbenzene}}{100}$$

Ethylation of ethylbenzene (EB) was investigated on IM-5 zeolite using ethyl alcohol (EA) as the alkylating agent. The reactions were conducted in a continuous flow fixed bed reactor at 10 bar H_2 . Effect of various parameters viz. temperature, ethylbenzene: ethanol mole ratio and WHSV (weight hourly space velocity) etc. were investigated to understand their influence on the conversion of EB, DEB selectivity, p-DEB selectivity and yield.

Effect of reaction temperature on IM-5 catalyst: Ethylation of EB was investigated at various temperatures on IM-5 catalyst. It may be seen from Fig.1 that as the reaction temperature increases, the conversion of ethylbenzene has also increased. Ethylbenzene conversion has increased with time on stream (TOS) for the reaction at 250 and 275 $^{\circ}\text{C}$, whereas at higher temperatures (300, 325 and 350 $^{\circ}\text{C}$) it has decreased with TOS. It may be due to the formation of higher aromatics as the dealkylation and other side reactions are dominant at higher temperatures, leading to coke formation, which in turn led to deactivation of the catalyst.

On the other hand, at lower temperatures, the alkylating agent is utilized for side reactions, particularly at acid sites with strong acidity. Once, these strong acid sites are neutralized, the alkylating agent is utilized for ethylation reaction. As the temperature increases, DEB selectivity for the ethylation reaction decreases rapidly reaching about 27% at 350 $^{\circ}\text{C}$ temperature. This is as a result of dealkylation and cracking of DEB to produce EB and benzene. When the temperature increases, the

ethylation products undergo cracking or dealkylation leading to the formation of benzene. As a result, benzene selectivity is enhanced at the expense of DEB. The DEB selectivity is almost constant at 300°C with TOS. The selectivity towards 1,4-diethylbenzene (p-DEB) decreases with increase in temperature, whereas, selectivity to 1,2- and 1,3-diethylbenzene increases. IM-5 is a high silica zeolite, it appears to have medium size pores. Hence, when the reaction temperature increases, the diffusion of 1,2-DEB and 1,3-DEB is better facilitated, which in turn led to higher formation of these two DEB isomers as against p-DEB. The yield of DEB is maximum at 300°C initially which goes on decreasing with TOS, same is the case for 325°C with slightly less yield, this may be because of high DEB selectivity and considerable conversion at this temperature. So 300°C can be considered as the optimum temperature for carrying out this reaction.

Reaction conditions: EB:EtOH = 2:1, WHSV=3h⁻¹, Pressure=10 bar.

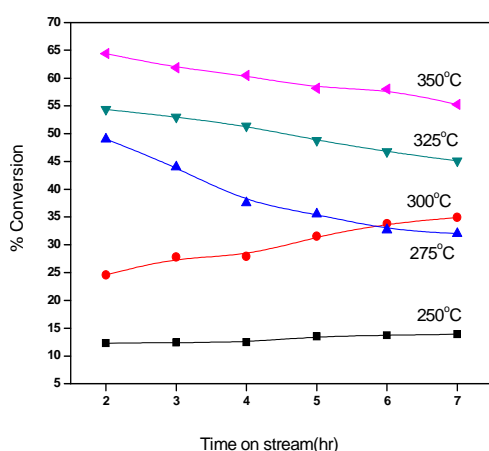


Fig. 1. EB conversion at various temperatures

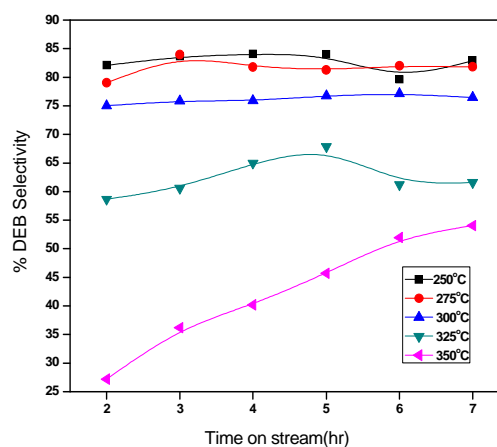


Fig. 2. DEB Selectivity at various temperatures

Reaction conditions: EB:EtOH = 2:1, WHSV=3h⁻¹, Pressure=10 bar

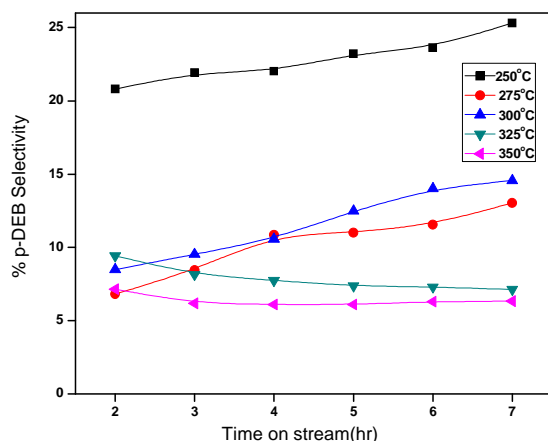


Fig. 3. p-DEB Selectivity at various temperatures

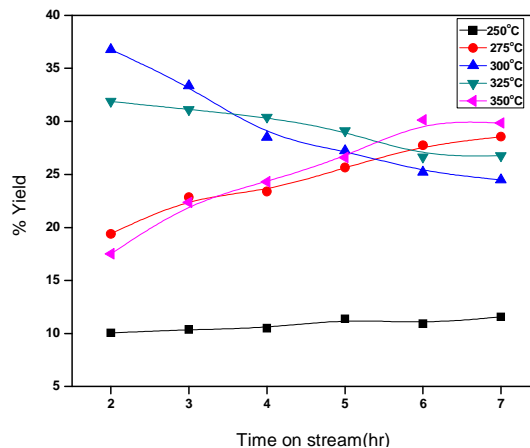


Fig. 4. DEB Yield at various temperatures

Effect of Mole Ratio: Ethylation of EB using various mole ratios of EB:EtOH was investigated on IM-5 catalyst. It was decided to study the influence of feed ratio at EB:EtOH = 1:1, 2:1 and 3:1 on conversion, selectivity and Yield at 300 °C temperature. The results are illustrated in Fig.5 and 6.

Reaction conditions: EB:EtOH = 2:1, WHSV=3h⁻¹, Pressure=10 bar

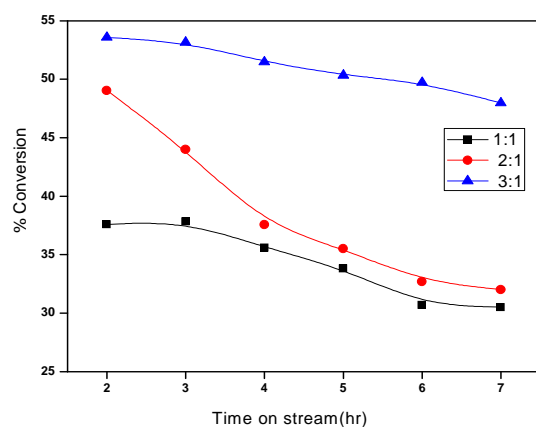


Fig. 5. EB conversion at various EB:EtOH ratios.

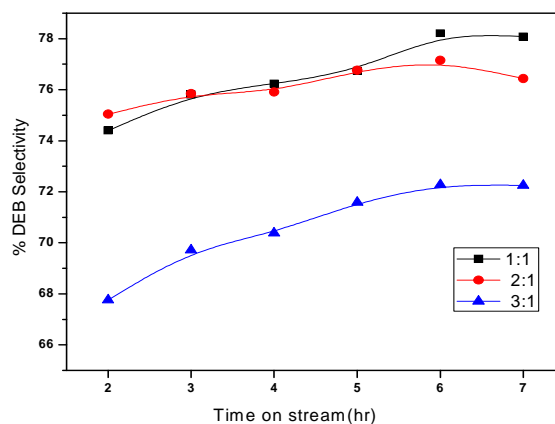


Fig. 6. DEB selectivity at various EB:EtOH ratios

Conversion of ethylbenzene decreases with increasing ethanol content in the feed. Increase in ethanol content in the feed could dilute ethylbenzene in the vapour phase, thus, reducing its reaction with ethyl cation adsorbed on the Brönsted acid sites of the catalysts¹⁶ [16]. The Conversion increases with increase in mole ratio because of the excess amount of ethylbenzene, the disproportionation reaction also takes place to considerable extent along with ethylation reaction. DEB Selectivity is near about same for mole ratios 1:1 and 2:1, at TOS of 3 hours. However, there are some minor changes in DEB selectivity with time on stream, as 1:1 offers slight advantage. p-DEB selectivity is maximum at mole ratio 1:1 and it increased with time on stream, whereas p-DEB selectivity decreased with increasing mole ratio. However, with both 1:1 and 2:1 ratios, the p-DEB yield fell with TOS, whereas it was almost constant at mole ratio 3:1. As a result, Yield is lower for 1:1 and 2:1 ratios after few hours on stream. It appears that when feed contains higher fraction of ethanol, it preferably occupies the active sites, which leads to side reactions, particularly olefin formation followed by its oligomerization leading to coke. As a result the catalyst is deactivated resulting in the lower yields of DEB as well as p-DEB after few hours on stream, but DEB and p-DEB selectivity is very less at 3:1 mole ratio. Hence, it is better to use EB:EtOH ratio of 2:1 to get optimum yields of DEB and p-DEB.

Effect of WHSV: Ethylation of ethylbenzene at various WHSV's was investigated on IM-5 catalyst. We have studied the influence of WHSV at 1h⁻¹, 3h⁻¹, 5h⁻¹ and 7h⁻¹ on EB conversion, DEB and p-DEB selectivity at 300 °C temperature. The results are illustrated in Fig. 9 and 10 EB conversion decreased with increase in WHSV because of the lower contact time. It decreases with increase in TOS for WHSV 3h⁻¹, 5h⁻¹ and 7h⁻¹. But at WHSV 1h⁻¹, conversion increased initially and then decreases gradually. DEB Selectivity increased with increase in WHSV, which may be due to suppression of dealkylation and other side reactions. At WHSV =1h⁻¹, DEB selectivity increased rapidly with increase in TOS, whereas in other cases it increases very slightly. p-DEB selectivity increased with increase in WHSV and also with TOS. It has increases rapidly for WHSV 3h⁻¹ and reached maximum at TOS 7. But p-DEB Selectivity is low when WHSV is 1h⁻¹. This may be due to isomerization of p-DEB into m-isomers because of increase in contact time. Yield of DEB is maximum at WHSV 1h⁻¹, at WHSV 3h⁻¹ it has decreasing with TOS. It is more or less same for WHSV 5 h⁻¹ and WHSV

Reaction conditions: Temp 300 °C, WHSV=3h⁻¹, Pressure=10 bar

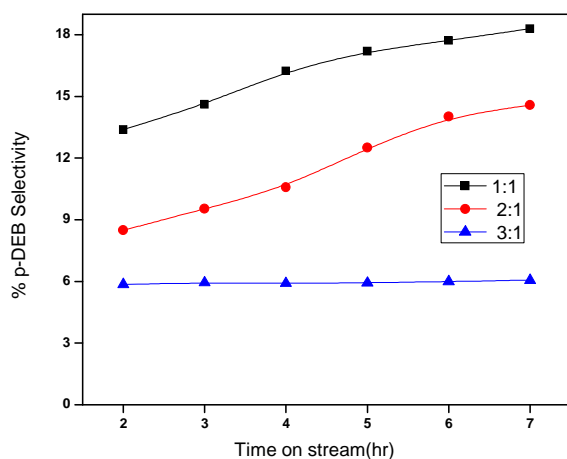


Fig. 7. p-DEB selectivity at various
EB:EtOH ratios

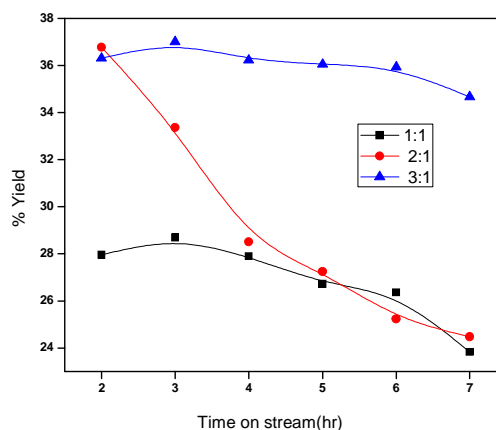


Fig. 8. DEB yield at various
EB:EtOH ratios.

Reaction conditions: Temperature=300°C, EB:EtOH =2:1 Pressure=10 bar.

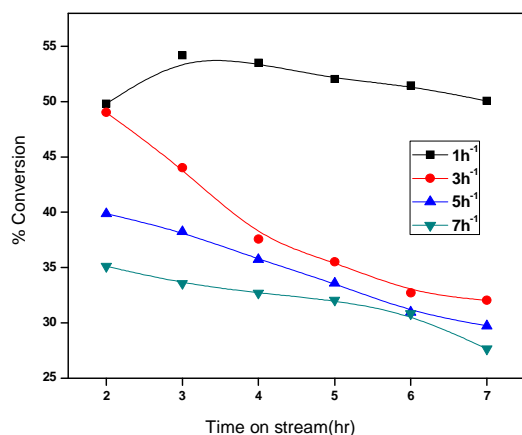


Fig. 9. EB conversion at various WHSV

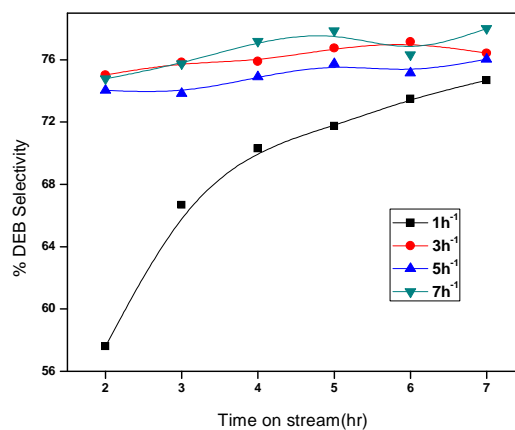


Fig. 10. DEB selectivity at various WHSV

Reaction conditions: Temperature=300°C, EB:EtOH =2:1 Pressure=10 bar.

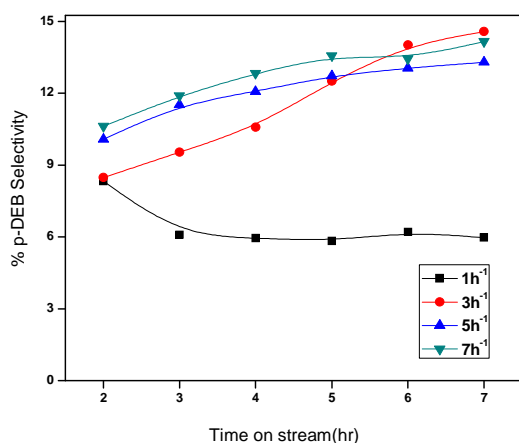


Fig. 11. p-DEB selectivity at various WHSV

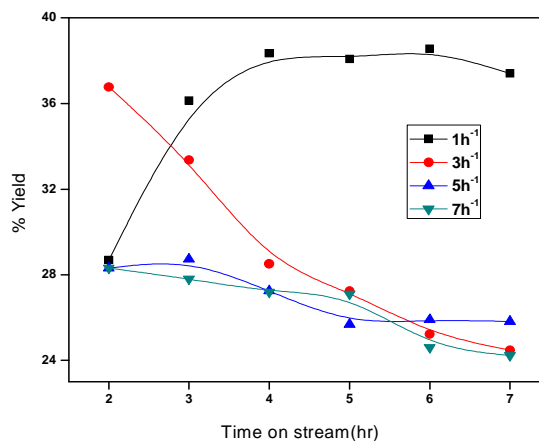


Fig. 12. DEB yield at various WHSV

CONCLUSIONS

IM-5 was suggested as a new multidimensional large-pore zeolite that probably consists of intersecting 12- and 10-ring windows [15]. From the literature survey, it was clear that zeolite based catalyst could be used for this purpose. Catalysts like MCM-22, ZSM-5, beta have shown good activity's. Here IM-5 catalyst was used for this purpose whose exact structure is not revealed till date. From the results it can be concluded that the use of higher temperature, higher mole ratio and low WHSV gives good conversion but DEB selectivity decreases so it was found out that at moderate conditions i.e. temperature of 300 °C, mole ratio 2:1 and WHSV=3h⁻¹, the conversion of EB and DEB, p-DEB selectivity's and yield are much better. The percent of m-DEB isomers in DEB is more than that of p-DEB, may be because of the acid active sites present on the outer surface zeolite crystals which are not diffusionally constrained. Therefore, they contribute to the isomerization of p-DEB to m-DEB. The isomerization step can generally follow two models: (i) the isomerization of p-diethyl benzene to m-diethyl benzene takes place exclusively on the outer surface, or (ii) the isomerization occurs on the acid sites located both on the outer surface and inside the zeolite channels. Therefore, their elimination of acid sites from the zeolite surface will be helpful for the reaction selectivity with respect to the desired di-alkylaromatics. However, if the zeolite modification can be done, not only leading to elimination of the surface sites but also lead to narrowing of the pore opening, like, e.g., with the surface silylation or deposition of metal oxides, such zeolite modification results increase p- selectivity.

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