

Selective alkylation and disproportionation of ethylbenzene in the presence of other aromatics

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Abstract

The alkylation and disproportionation of ethylbenzene (EB) in the presence of aromatics like *m*- and *p*-xylene isomers have been studied over a pore-size regulated HZSM-5 catalyst. The industrial feed having different compositions of ethylbenzene and xylene isomers were used for the experimentation. Hence, they were expected to hinder the movement of reactant molecules both on the external surface and within zeolite channels. It was observed that irrespective of the different feed compositions the concentration of the xylene isomers were intact in the product. There is no other byproducts formation like *p*-ethylmethyl benzene. The effect of varying the concentration of aromatic compounds in the feed on ethylbenzene conversion and product distribution over the parent and modified HZSM-5 catalyst have been discussed. The effect of catalyst *L/D* (length of the catalyst bed/inner diameter of the reactor) ratio across the reactor on the ethylbenzene conversion and selective formation of *p*-diethylbenzene (*p*-DEB) is also discussed.

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1. Introduction

Selective disproportionation of ethylbenzene produces commercially important *p*-diethylbenzene (*p*-DEB). *p*-DEB is used as a desorbent in the separation of *p*-xylene from C₈ aromatics mixture [1]. As the purity of *p*-DEB required for this application is very high (>95%), selective disproportionation can be used as a direct single-step process to produce the chemical of desired purity.

A unique feature of HZSM-5 zeolite is its shape selectivity which has been effectively made use of in various processes like xylene isomerisation, benzene alkylation, toluene disproportionation, etc [2]. The shape selectivity of the zeolite can be further enhanced by treating with suitable modifying agents and used for the synthesis of very high purity *p*-dialkylbenzenes via monoalkylbenzene alkylation [3]. A new dimension in zeolite modification has emerged with the recent efforts on fine tuning of pore opening of HZSM-5 zeolite by means of the chemical vapour deposition (CVD) tech-

nique. This approach has opened up a new domain, “precise pore-size control” which can be used to design a zeolite for a specific application [4–6]. Presently, *p*-DEB is produced either by separation from mixed isomers of DEB or by alkylation or by disproportionation of EB on selective zeolites. The latter process is the most convenient and economical one. Selectivation of zeolites is carried out through CVD of silicon containing compounds such as *ortho*-silicates onto high silica zeolites such as ZSM-5. Though this method is very good, it has certain deficiencies and practical problems. Alternatively, liquid phase deposition (LPD) of *ortho*-silicates can also be done, since this requires much lower temperature and the scale up of the liquid phase reaction is much easier than that of CVD. A lot of reports are present in literature on the use of CVD modified catalysts for reactions [7–12], but there are very few references on the use of LPD modified catalysts [13–16]. During alkylation only part of ethylbenzene was alkylated and unconverted ethylbenzene required separation from the product mixture which consist of diethylbenzenes and other aromatics in order to recycle it back into the reactor. During separation there was always a possibility of ethylbenzene being contaminated with other aromatic products of alkylation in order to convert these contaminated

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ethylbenzene to some valuable product like *p*-DEB. In view of this, the present work was aimed at studying the effect of the presence of various compositions of ethylbenzene on its alkylation and disproportionation over pore-size controlled HZSM-5 zeolite. The catalyst *L/D* (length of the catalyst bed/inner diameter of the reactor) ratio were also studied in view of the maximum reactor efficiency with respect to EB conversion and *p*-DEB selectivity.

In this paper, we report the use of LPD modified ZSM-5 zeolite for the alkylation and disproportionation of mixed feed containing EB, probably for the first time. Hence, a new liquid phase method is developed, in which the silicon deposition is carried out in the liquid phase. In this paper, (I) silica deposition and its effect on activity and selectivity of HZSM-5 catalyst, (II) the influence of various compositions of ethylbenzene feed viz. 64% EB and 36% xylene isomers (*p*-xylene: 8.24%, *m*-xylene: 20.41%, *o*-xylene: 7.35%), 70% EB and 30% xylene isomers (*p*-xylene: 6.87%, *m*-xylene: 17.01%, *o*-xylene: 6.12%), and 95% EB and 5% xylene isomers (*p*-xylene: 1.15, *m*-xylene: 3.85%) on alkylation and disproportionation reactions and (III) the catalyst *L/D* ratio on EB disproportionation over pore-size regulated HZSM-5 catalyst, are reported.

2. Materials and methods

NaZSM-5 catalyst with SiO₂/Al₂O₃ ratio of 250 was synthesized as per the established procedures [17] and analyzed by XRF. The hydrogen form of the sample was obtained by ammonium exchange with 1 M ammonium nitrate solution followed by drying and calcination at 823 K. The calcined samples were refluxed in a mixture of 20% TEOS + 35% MeOH + 45% toluene at 353 K for 12 h. Methanol, used since on acid sites, generates dimethyl ether and water which helps in the hydrolysis of TEOS at 353 K. After 12 h, the sample was washed to remove any loosely adsorbed TEOS on the surface and dried in an oven for 2 h at 393 K and calcined at 823 K to obtain 4% silica deposited on the sample. The same procedure was repeated twice and three times to obtain samples with 8% and 12% silica loading.

The weight of silica deposited was obtained by the formula: [(weight of the sample after silylation – weight of the sample before silylation)/weight of the sample before silylation] × 100.

The catalysts were characterized by XRD for crystallinity and TPD of ammonia for acidity.

3. Experimental procedure

The ethylbenzene alkylation and disproportionation reactions were carried out in a 1.8 cm i.d. × 30 cm length, having a volume of 30 cc, glass continuous down flow fixed bed reactor, at atmospheric pressure. Each experiment was carried out with a 2 g of fresh catalyst sample. Before the start of the

reaction the catalyst was activated at 773 K for 10 h in air to drive off moisture and adsorbed hydrocarbon, if any. The reactant of different compositional xylene mixed EB feed for disproportionation and blend of these xylene mixed EB feed with ethanol for alkylation, were fed through ISCO, USA syringe pump into the reactor at the desired reaction temperature.

4. Product analysis

The liquid products of EB alkylation and disproportionation were analyzed in a HP6890 Series, using flame ionization detector (FID), in the presence of nitrogen as a carrier gas. The DBWAX capillary column was used for the analysis. The gaseous products were analyzed in a Chemito Gas Analyzer 1000 Series, using temperature control detector (TCD). The Spherocarb column of 8 in. length × 1/8 in. diameter was used for the analysis.

5. Result and discussion

5.1. Catalyst characterization

The XRD patterns (Fig. 1) of the parent and modified silylated HZSM-5 zeolites indicate that the structure of the zeolite remained intact after the silylation. Thus, silylation affects only the external surface of the zeolite, without destroying the parent HZSM-5 structure.

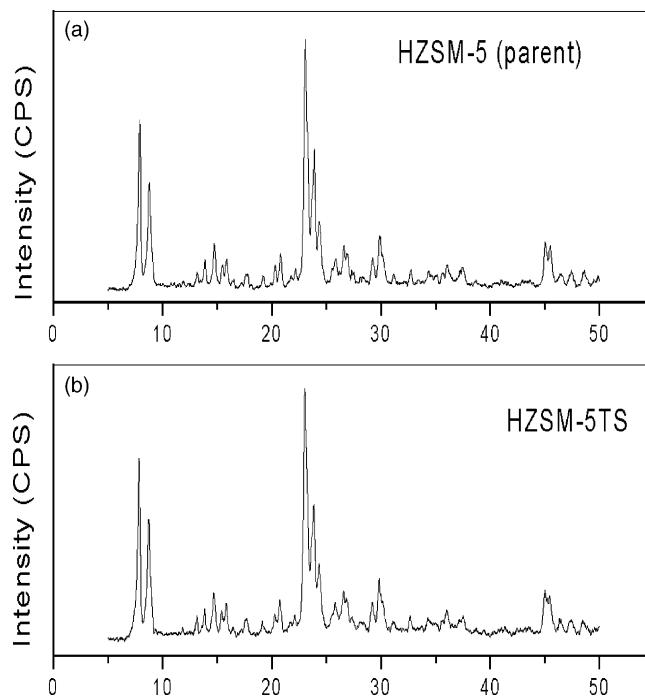


Fig. 1. XRD pattern of parent and modified HZSM-5 catalysts.

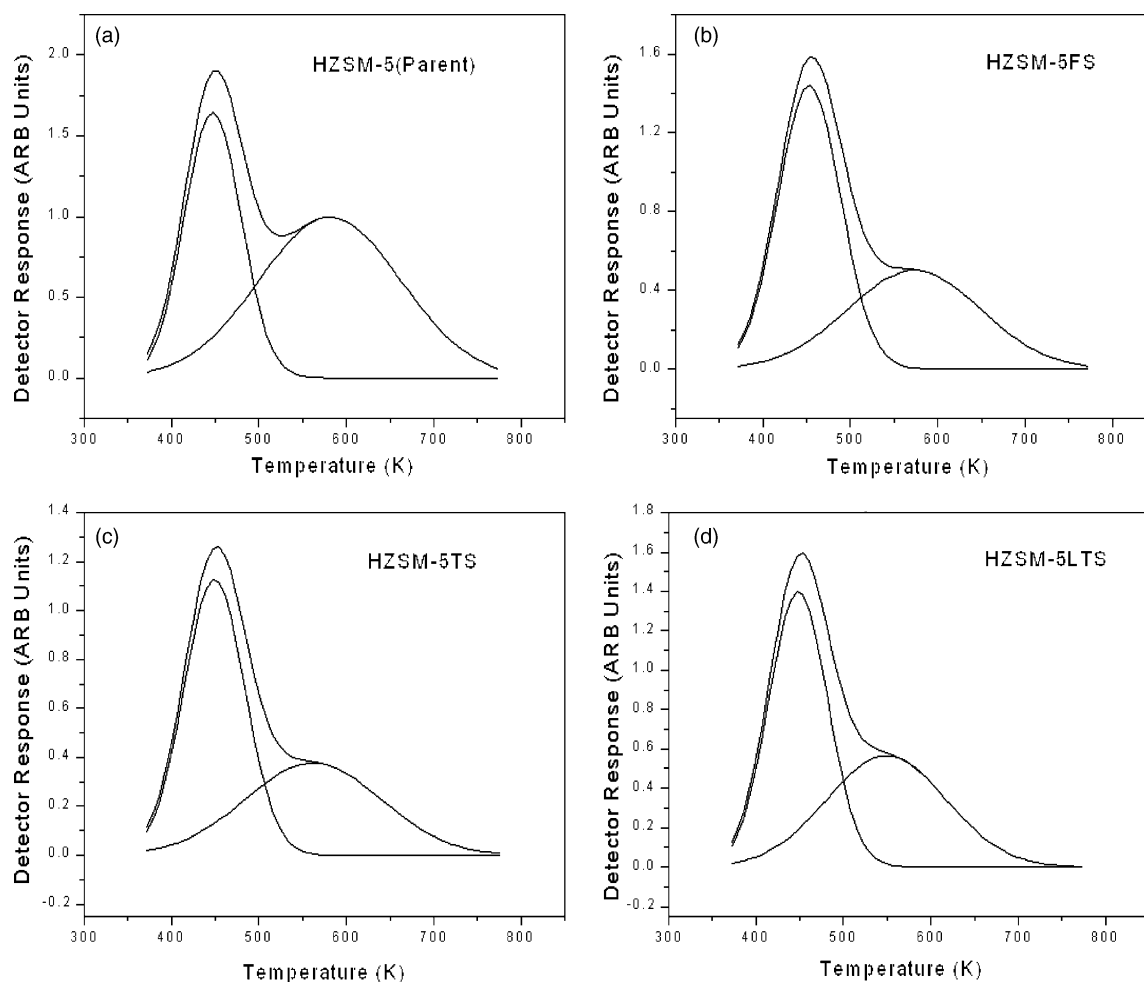


Fig. 2. TPD of parent and different silylated HZSM-5 catalysts.

The NH_3 TPD spectra of the parent and modified silylated HZSM-5 catalysts are shown in Fig. 2, and the amount of desorbed ammonia (total acidity) and decrease in acid sites concentration after modification are summarized in Table 1. The TPD profile consists of two peaks—one at low temperature and the other at high temperature—corresponding to weak and strong acid sites. There is a decrease in the amount of both weak and strong acid sites on silylation. The single, twice and thrice cycle silylation for HZSM-5 catalyst led to a decrease in the concentration of acid sites by 23.64, 42.78

Table 1
Total acidity of the samples investigated

S. no.	Catalyst	Total acidity (mmol g^{-1})	Decrease of acid sites concentration after modification (%)
1	HZSM-5 (Parent)	0.423	–
2	HZSM-5-FS	0.323	23.64
3	HZSM-5-TS	0.242	42.78
4	HZSM-5-LTS	0.330	21.98

HZSM-5-FS: first silylated; HZSM-5-TS: twice silylated; HZSM-5-LTS: twice silylated and lanthanum exchanged.

and 21.98%, respectively. The apparent increase in acidity of the lanthanum exchanged catalyst may be due to the interaction of the ammonia with lanthanum itself.

6. Performance comparison with and without pore-size regulation

A comparison of the performance of HZSM-5 zeolite with and without pore-size regulation for the ethylbenzene disproportionation as a test reaction is presented in Table 2. Each reaction was carried out for a period of 5 h on stream. The stable fourth hour data are included in all the tables for comparison. The catalyst was observed to be stable for a period of 5 h, without any coke formation.

The change in reduction of pore opening size after silylation was monitored by a xylene mixed EB disproportionation reaction. The reactant mixture containing maximum xylene isomers (64% EB and 36% xylene isomers) was used for the reaction. The pore-size regulated zeolite exhibited enhanced para selectivity of 86.43% at the conversion level of 16.84%. Benzene formation was also lower than that on

Table 2
Performance comparison with and without pore-size regulation

Product composition (%)	HZSM-5 catalyst	Pore-size regulated HZSM-5 catalyst (8%)
Benzene	6.77	3.26
Toluene	1.07	1.10
Ethylbenzene	49.98	53.22
∑ Xylenes	36.44	36.00
<i>p</i> -DEB	1.89	5.54
<i>m</i> -DEB	3.76	0.43
<i>o</i> -DEB	–	–
∑ DEB	5.65	6.41
Performance		
EB conversion	21.90	16.84
<i>p</i> -DEB selectivity	33.45	86.43

Reactions conditions: temperature 583K; LHSV 1 h⁻¹; feed xylenes mixed EB feed (64% EB and 36% xylene isomers). The stable fourth hour data are included in the Table. EB conversion (%): [(EB in feed – EB in product)/(EB in feed)] × 100; *p*-DEB Selectivity (%): [(*p*-DEB in product/∑ DEB isomers in product)] × 100.

the unmodified zeolite. The literature [18] reported that, the deposition of silica narrows the pore opening size and simultaneously, deactivates the external surface, because the inert silica coats the external surface. The para selectivity is enhanced either by narrowing the pore opening size or by inactivation of the external surface. This modification by silica deposition creates additional diffusional constraints for the reactant molecule.

7. Para selectivity and silica deposition

The effect of progressive silylation (extent of pore-size regulation) on EB conversion and selectivities to *p*-DEB, by ethylbenzene alkylation and disproportionation, are reported in Figs. 3 and 4, respectively.

As the % silylation increases from 0 to 8%, the EB conversion was observed to decrease from 21.53 to 18.22% and from 23.09 to 16.75%, for EB alkylation and disproportionation reactions, respectively. The *p*-DEB selectivity was observed to be increased with increase in % silylation. The *p*-DEB selectivity increased from 41.03 to 87.36% and from 42.44 to 86.44%, for EB alkylation and disproportionation,

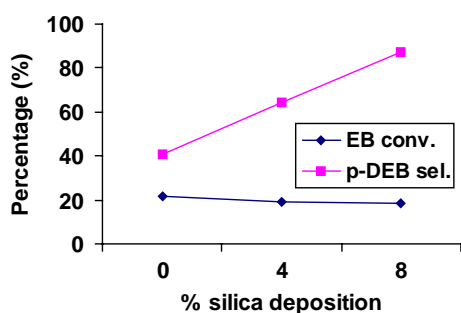


Fig. 3. Effect of silica deposition on ethylbenzene alkylation.

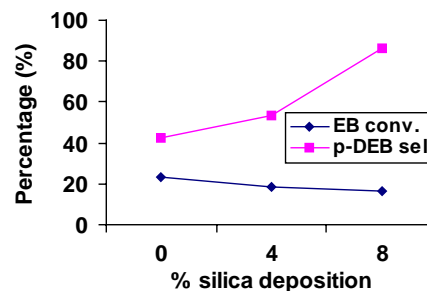


Fig. 4. Effect of silica deposition on ethylbenzene disproportionation.

respectively, with increased silylation from 0 to 8%. In the case of EB alkylation with ethanol, the negligible amount of ethylene by dehydration of ethanol was observed in the gas product. It is reported that, the water formed during the EB alkylation, prolong the life of the catalyst, without affecting the catalyst activity [11]. These results can be explained on the basis that, in the beginning, silica covered only the catalytic sites located on the external surface, thereby reducing the conversion slightly. With increase in silica deposition, the pore openings narrowed and the silica layers covered all the external surfaces. Due to this, the diffusional constraints on the reactant and product increased. EB conversion decreases while the para product increases as the isomerization on the external surface decreases. The para isomer formed selectively inside ZSM-5 channels, while isomerization proceeded just on the external surfaces and the improvement in para selectivity by the modification was due to the inactivation of the acid sites on the external surfaces [19]. In contrast, the improvement in para selectivity by the modification of HZSM-5 with oxides was due to the suppression of the isomerization of the primarily produced para isomer [20]. It has also been reported that selective poisoning of the external surface of zeolite crystallites will improve the shape selectivity of the para isomer [21]. In the present case, the EB alkylation and disproportionation were observed to be the well comparable reaction routes, in order to get maximum *p*-DEB selectivity. The presence of xylene isomers was intact in the product. These observations also concluded that, the present catalyst could withstand its activity, without forming any byproduct like *p*-ethylmethyl benzene from xylene isomers. The optimum silica deposition on HZSM-5 catalyst was 8%, as 12% silica deposition further lower down the ethylbenzene conversion by marginally increasing *p*-DEB selectivity (not shown). The further experiments were carried out on 8% silica deposited HZSM-5.

8. Effect of different compositions of xylene mixed ethylbenzene feed on catalytic activity

The experiments were carried out for the different feed compositions of EB and xylene isomers viz., 64% EB and

Table 3
Effect of feed composition for EB alkylation

GC product distribution (wt.%)	Catalyst I			Catalyst II			Catalyst III		
	Feed I	Feed II	Feed III	Feed I	Feed II	Feed III	Feed I	Feed II	Feed III
Benzene	3.57	5.03	4.88	4.96	2.86	4.54	3.43	1.77	2.82
Toluene	0.95	0.86	0.59	1.17	0.78	0.12	1.15	1.02	0.19
Ethylbenzene	50.22	56.64	82.32	51.77	57.85	84.78	52.34	59.62	84.55
∑ Xylenes	33.40	28.54	4.25	32.89	29.67	2.69	33.53	27.91	3.65
∑ C9Aromatics	0.70	0.37	–	0.81	–	–	0.74	0.97	0.17
<i>m</i> -DEB	5.82	4.22	3.82	2.68	2.34	1.99	1.06	0.92	0.45
<i>p</i> -DEB	4.05	3.56	3.80	4.82	5.98	5.25	7.33	7.22	7.72
HBF	1.06	0.69	0.34	0.53	0.52	0.53	0.42	0.57	0.37
Performance									
EB conv.	21.53	19.08	13.34	19.10	17.36	10.75	18.22	14.82	11.00
<i>p</i> -DEB Sel.	41.03	45.76	49.86	64.26	71.87	72.51	87.36	88.69	94.49

Reactions conditions: temperature 598 K; LHSV 2.5 h⁻¹, mole ratio (aromatics/EtOH = 4/1); catalyst I: 0% silylated HZSM-5 (plane); catalyst II: 4% silylated HZSM-5; catalyst III: 8% silylated HZSM-5; feed I: 64% ethylbenzene + 36% xylene isomers; feed II: 70% ethylbenzene + 30% xylene isomers; feed III: 95% ethylbenzene + 5% xylene isomers; HBF: higher boiling fractions.

36% xylene isomers, 70% EB and 30% xylene isomers, and 95% EB and 5% xylene isomers feed. All these feed compositions were tested for the different % of silylated HZSM-5 catalysts. The results are tabulated as Tables 3 and 4, for EB alkylation and disproportionation reactions, respectively.

In the case of EB alkylation, as the % silylation of the catalyst samples increases, the decreasing trend of EB conversion were observed for all the studied feed compositions. The EB feed containing maximum xylene isomers (64% EB and 36% xylene) has shown more EB conversion. It is reported that, as the ethylbenzene to alcohol ratio increased, the ethylbenzene conversion decreased. Ethylbenzene conversion and the yield of *p*-DEB increase with the enhancement in *m*-xylene concentration. The alcohol available for alkylation is found more inside the channel as

m-xylene can diffuse inside the pore only to a negligible extent [22]. The presence of *p*-xylene in the feed may hinder the movement of ethylbenzene inside the channel, which decreases the yield of *p*-DEB. This was observed in the present case.

In the case of EB disproportionation, as the % silylation on HZSM-5 catalyst increases, the decreasing trend of EB conversion and increasing trend of *p*-DEB selectivity were observed with all the studied feed. The 95% EB feed, has shown a maximum *p*-DEB selectivity of 94.88% (over 8% silylated HZSM-5 catalyst) as against 88.74%, with maximum xylene containing EB feed over the same catalyst, at a lower conversion level of 4.66% as compared to 12.75% for maximum xylene mixed feed. The activity trends of EB alkylation and disproportionation were observed to be similar. The presence of *m*-xylene, which cannot diffuse inside

Table 4
Effect of feed composition for EB disproportionation

GC product distribution (wt.%)	Catalyst I			Catalyst II			Catalyst III		
	Feed I	Feed II	Feed III	Feed I	Feed II	Feed III	Feed I	Feed II	Feed III
Benzene	3.47	4.69	3.75	3.28	3.68	3.24	3.80	3.6	2.36
Toluene	0.49	0.81	0.13	0.32	0.89	0.14	0.55	0.66	0.12
Ethylbenzene	53.90	59.89	87.28	55.41	60.80	89.00	55.84	61.53	90.57
∑ Xylenes	36.00	27.68	5.21	34.82	30.45	5.23	34.89	28.39	5.14
∑ C9Aromatics	0.25	0.22	–	0.51	–	–	0.17	0.42	–
<i>m</i> -DEB	3.13	3.50	1.79	2.44	1.35	0.39	0.52	0.54	0.09
<i>p</i> -DEB	2.36	2.65	1.49	3.01	2.47	1.62	4.10	4.64	1.67
HBF	0.37	0.53	0.32	0.21	0.36	0.37	0.13	0.22	0.05
Performance									
EB conv.	15.78	14.44	8.13	13.40	13.14	6.31	12.75	12.11	4.66
<i>p</i> -DEB Sel.	42.98	43.09	45.42	55.20	64.66	80.50	88.74	89.57	94.88

Reactions conditions: temperature 598K; LHSV 2.5 h⁻¹; catalyst I: 0% silylated HZSM-5 (plane); catalyst II: 4% silylated HZSM-5; catalyst III: 8% silylated HZSM-5; feed I: 64% ethylbenzene + 36% xylene isomers; feed II: 70% ethylbenzene + 30% xylene isomers; feed III: 95% ethylbenzene + 5% xylene isomers.

the pore of modified HZSM-5, mainly acts as a diluent. The *p*-xylene inside the pore may create more hindrance to *p*-DEB, which decreases the *p*-DEB selectivity.

9. Effect of catalyst *L/D* ratio

The effect of catalyst *L/D* (length of the catalyst bed/inner diameter of the reactor) ratio was studied by using the same reactor as mentioned above. The EB disproportionation route was used to study this effect, as this route has shown similar activity as compared with EB alkylation route and this route is more difficult than the alkylation route. The maximum xylene (36%) containing EB feed was used, in order to see the effect of xylene presence with the increase in catalyst *L/D* ratio. The catalyst bed was varied in the reactor from 2 to 10 g, which corresponds to the catalyst *L/D* ratio of 1.29–3.89. The fresh catalyst was loaded for each experiment. Then each reaction was carried out at identical reaction conditions of 583 K and LHSV of 1 h^{-1} , in order to establish similar reaction environment and activity comparison inside the reactor. The reactions were carried out at lower operating conditions to get better experimental results in the kinetic control regime. The results are tabulated as Table 5. The fourth hour stable data were used for the comparison.

The increasing trend of EB conversion from 15.45 to 21.09% was observed with increase in catalyst *L/D* ratio from 1.29 to 3.11 and decrease in EB conversion was observed at catalyst *L/D* ratio of 3.89. In the present case, the catalyst *L/D* ratio of 3.11 was observed to be optimum. The *p*-DEB selectivity was observed to be identical at around 90%, for all the catalyst *L/D* ratio. This catalyst *L/D* ratio study helps for further reactor design, process scale up, catalyst diffusion study, etc.

Table 5
Effect of catalyst *L/D* ratio on reactor efficiency

GC product distribution (wt.%)	<i>L/D</i>				
	1.29	1.56	2.33	3.11	3.89
Benzene	2.96	2.35	4.07	4.70	3.13
Toluene	1.02	0.98	1.14	1.19	1.01
Ethylbenzene	54.11	52.96	51.48	50.50	52.09
∑ Xylenes	36.63	36.92	36.20	35.93	36.46
∑ C9Aromatics	0.39	0.24	0.46	0.27	0.66
<i>m</i> -DEB	0.37	0.62	0.62	0.68	0.51
<i>p</i> -DEB	4.49	5.93	5.72	6.01	5.77
HBF	–	–	0.11	0.26	0.22
Performance					
EB conv.	15.45	17.23	19.56	21.09	18.6
<i>p</i> -DEB Sel.	92.29	90.53	90.16	89.81	91.92

Reaction conditions: temperature 583K; LHSV = 1 h^{-1} ; feed 64% EB; 36% xylene isomers; catalyst 8% silylated HZSM-5; *L* is the length of the catalyst bed; *D* is the inner diameter of the reactor.

10. Conclusion

The effect of % silylation on HZSM-5 catalysts for the alkylation and disproportionation reactions by using various compositional xylene mixed ethylbenzene feed, are presented. The *p*-DEB selectivity was observed to be maximum with 95% EB feed by EB disproportionation (94.88%) and by EB alkylation (94.49%). The EB conversion was observed to be 11.00 and 4.66%, for EB alkylation and disproportionation, respectively. The presence of xylene isomers in the feed, does not lead to any byproduct formation like *p*-triethylmethyl benzene. The presence of *m*-xylene in the feed enhances the EB conversion, both by alkylation and disproportionation route, as only negligible amount of *m*-xylene can diffuse inside the pore. This increases the EB and alcohol concentrations inside the catalyst pore. The presence of *p*-xylene was observed to have adverse effect on the *p*-DEB selectivity. This may be due to the hindrance for *p*-DEB to come out of the pore.

The effect of catalyst *L/D* ratio was also studied, in order to study the reactor efficiency with respect to catalyst volume. The maximum xylene (36%) containing EB feed by EB disproportionation route was used, in order to see the effect of xylene presence with increase in the catalyst *L/D* ratio. The present study observed that the reactor of 30 cc volume require catalyst *L/D* ratio of 3.11, in order to get maximum catalyst as well as reactor efficiency. This study will also help to design the reactor, process scale up, etc.

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