Catalysis Today 73 (2002) 65–73

www.elsevier.com/locate/cattod

Recent advances in selectivation of zeolites for *para*-disubstituted aromatics

Anand B. Halgeri*, Jagannath Das

Research Centre, Indian Petrochemicals Corporation Limited, Baroda 391 346, India

Received 9 May 2001

Abstract

The synthesis valuable *para*-dialkylbenzenes over shape selective zeolites is of immense industrial importance. The shape selectivity was achieved by regulating the pore mouth opening of ZSM-5 zeolites by employing chemical vapour deposition (CVD) of silica. Two probe molecules of different kinetic diameter were used to follow the extent of pore mouth regulation. The post synthesis modification resulted in obtaining *para*-substituted dialkylbenzenes of high purity by alkylation of monoalkylbenzenes with C_1–C_3 alcohols.

Similarly, *para*-substituted dialkylbenzene have been synthesised over pore size regulated zeolites by toluene disproportionation and paraffin aromatisation reactions. The above technique of enhancing *para*-selectivity has been successfully employed to develop an ecofriendly process for the manufacture of value added chemical *para*-diethylbenzene by ethylation of ethylbenzene. The paper highlights some of the unique advantages of pore size regulated zeolites for the synthesis of *para*-dialkylbenzenes over the conventional acid catalysed reactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: ZSM-5; Pore mouth regulation; Silica deposition; Alkylation; *para*-Dialkylbenzenes

1. Introduction

One of the unique features of ZSM-5 zeolite is its shape selectivity. In zeolites catalysed reactions, selective catalysis that occurs inside the intra-crystalline voids can be affected by non-selectivity activity taking place on the external surface sites. It has been shown that during aromatic alkylation, the *para*-isomer formed selectively inside ZSM-5 channels, while isomerisation proceeded just on the external surface, decreasing the desired product selectivity. In order to enhance the selectivity, various methods of modification of the zeolites property have been proposed [1–7]. The enhancement of shape selectivity of ZSM-5 zeolite by chemical vapour deposition (CVD) by tetraethyl *ortho*-silicate is one of the important modification technique. It has been observed that the CVD technique changes neither the channel size nor acidity. The deposited silica passivates the external surface of zeolites crystallites and at the same time narrows down the pore opening size due to coating of inert silica on the external surface. As a result, the shape selectivity property of the zeolites is enhanced to a great extent [8].

The shape-selectivity was first demonstrated based on the diffusion property by Mobil researchers [9,10] and for *para*-xylene formation. The mechanism based on the difference in diffusion rates of xylene isomers was supported by the kinetics model proposed by Wei [11]. The CVD of silica on zeolites and shape selectivity phenomenon has been extensively studied by Niwa and co-workers [12–14]. Recently, Tanabe and Holderich have comprehensively reviewed the

---

[*] Corresponding author: Fax: +91-265-272098.
E-mail address: abhalgeri@hotmail.com (A.B. Halgeri).

PII: S0920-5861(01)00519-3

application of modified solid acid catalyst like zeolites for a variety of industrial alkylation reactions and their impact on the environmental protection [15].

In the present work, the *para*-selectivity enhancement feature of pore opening size regulated, silylated pentasil zeolites during monoalkylbenzene alkylation with C_1–C_3 alcohols is reported. The pore opening size of regulation by chemical vapour of silica involves blocking of non-selective external surface and pore mouth sites without altering internal zeolites structure [16]. The development of pore size regulated zeolites catalyst and its application for various alkylation reactions of industrial importance including disproportionation of toluene and aromatisation of paraffins to produce selectively *para*-substituted aromatics has been described in the paper. An ecofriendly process based on the silylated zeolites catalyst for the manufacture of value-added chemicals, *para*-diethylbenzene has also been discussed.

2. Experimental

MFI zeolite was synthesised by the hydrothermal technique [17] under autogenous pressure using tetrapropyl ammonium bromide as a templating agent. The as-synthesized zeolites was characterised by XRD for phase purity, FT-IR for pentasil structure, SEM for morphology and crystal size, MAS NMR for Al incorporation in the framework, TPD of ammonia for acidity and a combination of wet chemical analysis and atomic absorption spectrometry for composition. The Si:Al ratio of the zeolites were in the range of 50–250, the crystals were oblong shaped and their dimension was of the order 2–6 μm. The proton form of the MFI zeolites was obtained by the calcinations of as-synthesized material at 813 K in air for 10 h followed by repeated ion exchange with an aqueous solution of NH_4NO_3 and a subsequent calcination at 773 K in air for 8 h.

The CVD of silica on proton form MFI zeolites was achieved using tetraethyl *ortho*-silicate. A 6.5% $Si(OC_2H_5)$ solution in 50:50 toluene and methanol was vaporised at 473 K and passed through the catalyst bed maintained at 503 K. The silicate solution was fed at a rate of 8 ml/h, and a flow of 50 ml/min hydrogen was maintained so that there was uniform contact of the vapour with the catalyst. After the vapour was in contact for the desired number of hours, the hydrogen flow was changed to nitrogen. The nitrogen gas was replaced by air and the reaction temperature was raised to 815 K and was kept at this temperature for 10 h to decompose $Si(OC_2H_5)$ to SiO_2. This procedure resulted in uniform silica deposition throughout the catalyst bed [19,20]. The extent of the pore size modification was monitored by a standard test reaction [21,22].

Catalytic runs were carried out in a continuous down-flow mode, fixed-bed reactor. The quantity of modified MFI zeolites used in each run was 2 g. The catalytic composite catalyst was prepared by mixing H-ZSM-5 zeolite with appropriate binder and shaping in the form of extrudates. The catalytic composite material was silylated and used for further pilot studies. High pressure catalyst testing unit was used for composite catalyst evaluation. The details of the experimental set-up and analysis procedure are reported elsewhere [23]. All the chemicals used in this study were of analytical grade.

3. Results and discussion

3.1. Alkylation of ethylbenzene with ethanol over pore size regulated zeolite

The activity and selectivity of HZSM-5 for ethylbenzene (EB) ethylation is presented in Table 1. These parameters are expressed in terms of % EB conversion

Table 1
Performance of ZSM-5 with and without silanation for ethylbenzene ethylation

Performance	ZSM-5	Silylated ZSM-5
EB conversion (%)	24.18	14.63
Selectivity (wt.%)		
Benzene	21.96	19.05
Diethylbenzene	64.45	58.26
Others	13.59	22.69
Rate of reaction (g mol/g_{cat} h)	0.0066	0.0033
Diethylbenzene isomers (%)		
para	54.41	99.78
meta	45.08	0.22
ortho	0.51	0.00

Temperature = 350 °C, WHSV = 2.5 h^{-1}, EB:ethanol = 4:1.

and % *para*-diethylbenzene (*p*-DEB) selectivities and defined as below.

$$\text{EB conversion} = \frac{\text{EB in feed} - \text{EB in product}}{\text{EB in feed}}$$

$$p\text{-DEB selectivity} = \frac{p\text{-DEB in product}}{\text{DEB in product}}$$

At the reaction conditions mentioned in the table, H-ZSM-5 zeolite showed 24% EB conversion, and 54% *p*-DEB selectivity. The % *p*-DEB selectivity is higher than the thermodynamic equilibrium composition due to bigger crystallite size of the zeolites.

3.2. para-Selectivity enhancement by silylation

The *para*-selectivity of this zeolites is further enhanced by in situ silylation with tetraethyl *ortho*-silicate. In general, the product shape selectivity in alkylation reaction is controlled by the primary product formation inside the pore, diffusional constraints in the channel and isomerisation on the external surface sites. As the molecular size of tetraethyl *ortho*-silicate is larger than the zeolites pore opening, the CVD results in fine controlling of pore opening size with the silica deposited on the external surface. The initial reaction involves –OH groups located in the zeolites external surface and of subsequent reaction between gaseous alkoxide and surface residue or between deposited molecules. This can be considered as a sort of polymerisation accompanied by hydrolysis. The internal structure remains unaffected. The activity and selectivity of pore size controlled or silylated ZSM-Zeolite is also given in Table 1. As compared to the zeolites without silylation the silica deposited zeolites showed a lower % EB conversion and higher *p*-DEB selectivity. The pore size regulated zeolites exhibited enhanced *para*-selectivity of 99% at the conversion level of 14%. This can be attributed to the higher diffusional constraints in the silylated ZSM-5 zeolite. Any desired higher *para* product selectivity can be achieved by CVD technique.

3.3. Pore opening size regulation and selectivity enhancement

The technique chosen for the pore size regulation of ZSM-5 zeolite was vapour phase deposition of bulky molecule, tetraethyl *ortho*-silicate at 503 K followed by calcinations at 813 K to decompose the alkoxy compound. As the molecular size of tetra ethyl *ortho*-silicate is larger than the zeolite pore opening, on its decomposition, the deposition of silica takes place on the external surface and pore mouth entrance. The initial deposition reaction involves hydroxyl groups located on the zeolite external surface, and of subsequent reaction between gaseous alkoxide and surface residue or between deposited molecules. The internal structure remains unaffected, only the pore opening size is reduced.

The effect of pore opening size reduction on the diffusivity of aromatic molecule inside the zeolite was monitored by a test reaction [18]. A mixture of two reactant probe molecules of different kinetic diameter was employed. The reaction mixture consisted of 80% *meta*-xylene and 20% EB. Essentially two reactions occur on ZSM-5 zeolite with the probe molecules: (i) *meta*-xylene conversion to *para*- and *ortho*-xylenes, and (ii) EB dealkylation of benzene and ethylene. With increasing silica incorporation the *meta*-xylene conversion decreased sharply, while EB conversion decreased at a slower rate. The zeolite deposited with 16 wt.% silica showed negligible *meta*-xylene conversion, whereas EB was still appreciable. This can be ascribed to smaller kinetic diameter of EB compared to *meta*-xylene and the latter is very close to opening size. With 16 wt.% of silica deposition, the pore opening size of was getting reduced and because less than that of *meta*-xylene. With the result, *meta*-xylene could not enter inside the zeolite channel, but the size of EB being still smaller than the pore opening, it diffused inside the zeolite (Fig. 1).

The standard test with the pore molecules clearly illustrated the role of pore opening dimension on the diffusivity of reactant and product molecules inside the channel. The extent of silylation can be monitored precisely by this test.

In case of alkylation of EB, the alkyl group already present in the benzene ring activates the *ortho* and *para* positions for alkylation. Due to space constraint inside MFI zeolite, alkylation takes place only at *para* position, while *ortho*-alkylated product forms on the external surface sites. The *meta*-isomer formed from isomerisation of *ortho*- and *para*-isomers on these sites. The pore size regulation by CVD of silica covers the pore mouth and external surface sites,

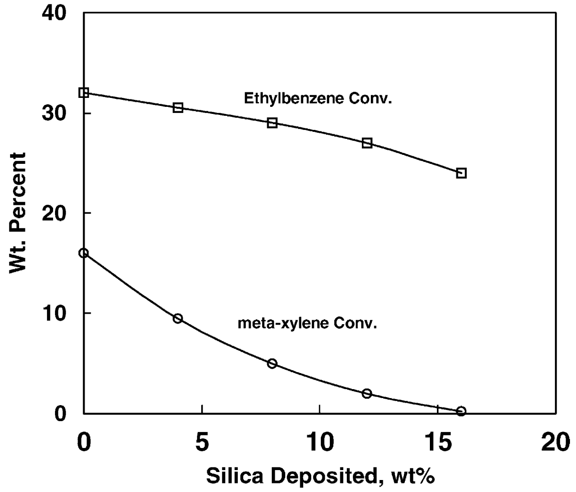

Fig. 1. Standard activity test using probe molecules ethylbenzene and *meta*-xylene. Temperature $= 400\,^{\circ}C$ WHSV $= 6\,h^{-1}$, $H_2/HC = 2$.

the extent formation of *ortho* and *meta* decreases with increase in silylation period. In other words, the *para*-diethylbenzene is formed as the primary product of alkylation and its further isomerisation is suppressed by silica deposition. A schematic mechanism to explain the above phenomena has been presented in Fig. 2. Similar reaction network holds good for other alkylation reactions as described subsequently in Table 2.

3.4. Activity and selectivity of different alkylation reactions

The studies have been extended to other types of alkylation reactions, viz. toluene ethylation, methylation, isopropylation and ethylation of EB to produce *para*-selective dialkyl aromatics in view of their industrial importance. The *p*-DEB is used as a desorbent in the selective separation of *para*-xylene from the isomeric C_8 aromatic mixtures. Perfumes are made from *para*-cymene and -ethyl toluene is the starting material for *para*-methyl styrene; the polymer of this monomer has got certain advantageous properties over the conventional polystyrene. Dimethyl tetraphthalate (DMT)/purified tetraphthalic acid (PTD) are the raw materials for polyester fibre which are obtained from oxidation of *para*-xylene.

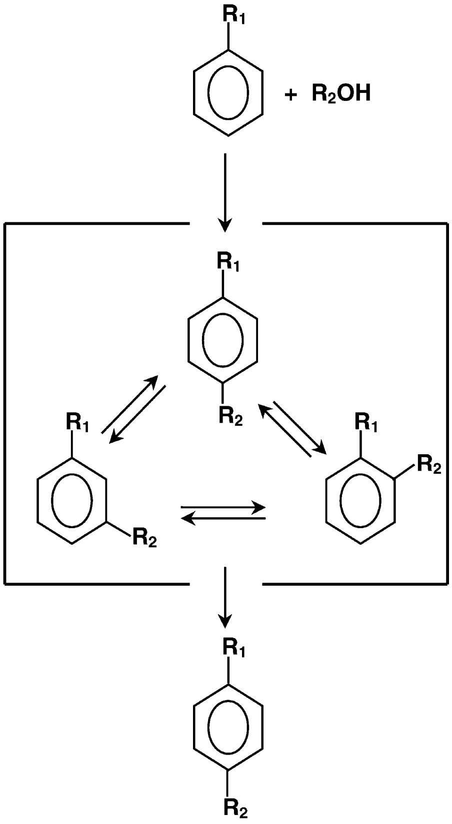

Fig. 2. Selective alkylation reactions over pore size regulated zeolite.

Table 2 compares the silylated zeolite performance for the above mentioned four alkylation reactions. Alkylbenzene conversion is higher in ethylation than methylation as the latter needs higher reaction temperature for an appreciable conversion. The *para*-dialkylbenzene selectivities were 100, 95, 93 and 88%, respectively, for *para*-cymene, -diethylbenzene, -ethyltoluene and -xylene. This is in the order of number of carbon atoms inside chains in the dialkylbenzenes, which in turn is related to diffusivity differences between *para* and other isomers of dialkylbenzenes. The dialkylbenzenes selectivity was in the order cymenes < diethylbenzene < ethyltoluene.

The lowest selectivity was for cymenes as it got transformed to *n*-propyltoluenes through transalkylation of cymenes with toluene. The silanation was not sufficient in case of xylenes to prevent trimethylbenzenes formation from secondary reactions.

Table 2
Performance comparison of silylated ZSM-5 for different alkylbenzene alkylation reactions

	Reactions			
	1	2	3	4
Monoalkylbenzene conversion (wt.%)	6.12	19.51	19.27	8.03
Selectivity to products (wt.%)				
Cymene				
meta	0.00			
para	28.98			
ortho	0.00			
Diethylbenzene				
meta		3.28		
para		70.72		
ortho		0.00		
Ethyltoluene				
meta			5.45	
para			83.55	
ortho			0.00	
Xylene				
meta				5.16
para				63.88
ortho				0.00
Others	71.02	26.00	10.04	27.42
Dialkylbenzenes				
Isomer				
meta	0.00	4.43	6.12	7.11
para	100	95.57	93.88	88.02
ortho	0.00	0.00	0.00	4.87

Conditions: temperature = 350 °C, H_2/HC = 3, alkylbenzene/alcohol = 5 and WHSV = $5.2\,h^{-1}$, silanation period = 180 min (16% silica), 1: toluene isopropylation, 2: ethylbenzene ethylation, 3: toluene ethylation, 4: toluene methylation.

Diethylbenzene and ethyltoluene are of higher kinetic diameter than xylenes. The selectivity was lower for the former as the extent of dealkylation is more due to the ethyl groups present in the benzene ring.

3.5. *Selective disproportionation of toluene*

The selective disproportionation of toluene to produce *para*-xylene is one of the important petrochemical processes [8]. Xylenes produced through disproportionation of toluene over ZSM-5 zeolite contained composition near to thermodynamic equilibrium. Commercially, *para*-xylene is the most important and desired among the xylene isomers and efforts are continuously made to enhance its composition beyond thermodynamic value. The performance of ZSM-5 zeolite with and without pore size reduction for toluene disproportionation has been presented in Table 3. The activity of catalysts are compared under similar conversion levels.

The pore size regulated zeolite exhibited enhanced *para*-selectivity of 90% at the conversion level of 23%. Benzene formation was slightly higher than that on the unmodified zeolite. A similar trend was observed by Hibino et al. [5] at very low conversion levels. These results can be explained on the basis that deposition of silica narrows the pore opening size and simultaneously deactivates the external surface, because the inert silica coats external surface. The *para*-selectivity is enhanced by one of these two effects. These modifications create additional diffusional constraints for the reactant molecule. Due to this, dealkylation of toluene is increased which results in an increase in the benzene to xylene ratio [23].

Table 3
Performance comparison of MFI aluminosilicate with and without pore size reduction for toluene disproportionation

Product composition	Catalysts	
	MFI zeolite	Pore size regulated MFI zeolite
Benzene	9.86	11.02
Toluene	77.15	76.86
p-Xylene	2.91	9.83
m-Xylene	6.25	0.88
o-Xylene	2.93	0.17
Others	0.90	0.26
Performance		
Toluene conversion (%)	22.85	23.14
Benzene/xylene	1.10	1.58
Xylene distribution		
p-Xylene (wt.%)	24.10	90.29
m-Xylene (%)	51.66	8.65
o-Xylene (%)	24.24	2.56

Temperature = 773 K, H_2/HC = 2, WHSV = 1.52 h^{-1}.

Table 4
The effect of silica deposition on catalytic activity of Ga_2O_3-ZSM-5 zeolite

	Ga_2O_3-ZSM-5 zeolite	Silanated Ga_2O_3-ZSM-5 zeolite
Paraffin conversion	98.6	76.5
Yield of aromatics	43.2	33.7
Aromatic distribution (%)		
Benzene	17.92	16.59
Toluene	40.48	49.34
Ethylbenzene	3.64	4.19
p-Xylene	7.28	24.19
m-Xylene	14.86	0.27
o-Xylene	7.19	0.03
C_9+ aromatics	8.63	5.60
Xylene isomer distribution		
p-Xylene	24.82	98.78
m-Xylene	50.66	1.10
o-Xylene	24.52	0.12

Temperature = 773 K, WHSV = 0.85 h^{-1}, C_9+: *p*-ethyltoluene + *p*-diethylbenzene + *n*-propylbenzene.

3.6. Aromatisation of paraffins to aromatics

Aromatisation of paraffins to aromatic is one of the important conversion processes for the production of the aromatics which is of great interest in both petroleum and petrochemical industry. The conversions of lower alkanes to higher value products like benzene, toluene and xylenes over zeolite catalysts have been well established [24–27]. A process for the transformation of propane and butane to aromatics has been developed and commercialised jointly by UOP and BP [28]. The technical feasibility of C_3–C_4 stream aromatisation has been demonstrated by 1000 bbl per day Cyclar process at Grangemouth, UK and 100 bbl per day *Z*-forming pilot plant at Kawasaki Refinery of Mitsubishi Oil, Japan. Both these processes employ high silica, medium pore ZSM-5 zeolite based catalysts for aromatisation.

In aromatisation of pentane to BTX, the xylene fractions, which constitute about 20–30% of total aromatics, contain nearly thermodynamic equilibrium comparison. The aromatisation of *n*-pentane was carried over pore size regulated Ga_2O_3-ZSM-5 zeolite to enhance the *para*-isomer content in xylene fraction [29,30]. The results are presented in Table 4.

It can be seen from the Table 4 that distributions of xylene isomers are very close to thermodynamic equilibrium compositions over unmodified Ga_2O_3-HZSM-5 zeolite. The distribution of xylene isomers got altered over pore size regulated Ga_2O_3 incorporated H-ZSM-5. With the increase in silica deposition from 0 to 22%, the *para*-xylene selectivity as the percentage of *para*-xylene among the isomeric xylenes went up from 24 to 99%. The increase in concentration of *para*-isomer in xylenes can be ascribed to the fact that the molecular size of tetraethyl *ortho*-silicate is longer than the zeolite pore opening, the chemical vapour phase deposition of this molecule results in fine control of pore opening size with the silica deposited on the external surface. The narrowing of pore size affects the diffusion of the bulky xylene isomers *ortho* and *meta*, but not *para* out of the channels.

It can be seen from the schematic model of the chemistry of aromatisation (Fig. 3) that the carefully controlled diffusivity of the zeolite by CVD allows *n*-paraffins free access to the interior of the channels. The usual aromatisation reaction sequence takes place inside the pores of the zeolite. Benzene, toluene and an equilibrium mixture of xylene isomers are formed in accordance with the thermodynamics. It is the shape selectivity constraint imposed on diffusion of the products from within the pores to the outside brings about enhanced *para*-selectivity.

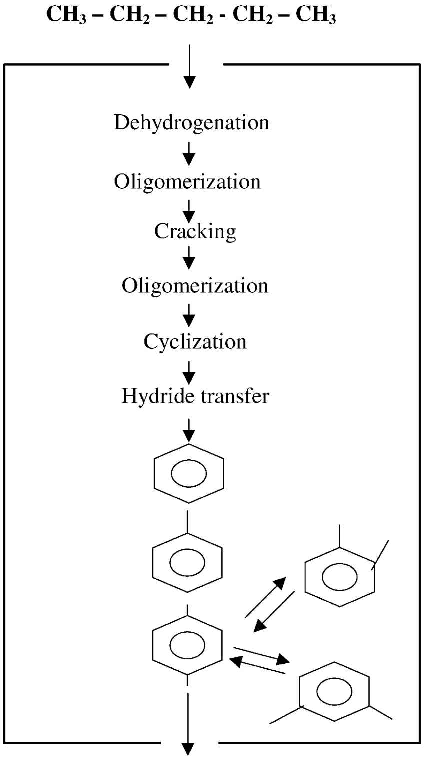

Fig. 3. Schematic model of aromatisation within the pores of chemical vapour deposited Ga_2O_3-HZSM-5 zeolite.

The smaller *para*-xylene, benzene, toluene, C_1–C_5 hydrocarbons exit from the pores many times faster than *ortho*- and *meta*-xylenes. Decrease in the *para*-isomer concentration inside the channel causes the xylene mixture within the pore system to re-equilibrate forming more *para*-xylene. The overall effect of this is a very high *para*-selectivity in the product stream [31].

3.7. Selective synthesis of para-ethylphenol

The *para*-ethylphenol has important commercial use as intermediates for the production of synthetic resins and antioxidants. The tedious, multistep conventional process for making *para*-ethylphenol comprises sulfonation of EB, separation of *para*-EB sulfonic acid mixture thus formed, and alkali fusion of *para*-EB sulfonic acid. Although the process is being practised in industry, however, it is associated with disadvantages like handling of dangerous sulfuric acid and sodium hydroxide at high temperature, corrosion of equipment, disposal of wastewater, etc. On the other hand, direct alkylation of phenol with an alkylating agent, over zeolite catalyst ca. ZSM-5, for the preparation of a mixture of alkylphenol isomers is beneficial and ecofriendly as compared to the conventional process. However, in such cases, the product mixture contains thermodynamic equilibrium composition of *para*-, *meta*- and *ortho*-alkylphenol. Moreover, the boiling points of *para*- and *meta*-isomers are so close, it is virtually impractical to separate *para*-alkylphenol from the mixture by distillation.

One way to circumvent the above problems is to design a zeolite catalyst which will produce selectively *para*-ethylphenol during ethylation of phenol over pore size regulated zeolite catalyst. The results of ethylation of phenol over parent as well as pore size tailored ZSM-5 are shown in Table 5, at a comparable yields of phenol.

It can be seen from the above table that the selectivity for *para*-ethylphenol (*p*-EtPhOH) is only 37% with parent (unmodified) ZSM-5, while with pore size controlled ZSM-5 the selectivity for the said isomer reached to 88%. The plausible scheme for the selective formation of *para*-ethylphenol through ethylation of phenol over pore size controlled ZSM-5 zeolite as due to shape selectivity constraints imposed on diffusion of the products from within the pores to the outside bring about enhanced *para*-selectivity [32].

Table 5
Comparison of parent and pore size tailored ZSM-5 zeolite for phenyl ethylation

	Parent ZSM-5 zeolite	Pore size regulated ZSM-5 zeolite
Lighters and other aromatics	2.74	0.64
Phenol	92.44	94.60
o-Ethylphenol	1.76	0.15
p-Ethylphenol	1.43	3.90
m-Ethylphenol	0.66	0.37
Heaviers	0.97	0.34
Performance		
Phenol conversion (wt.%)	7.56	5.3
p-Ethylphenol selectivity (%)	37.1	88.2

Temperature $= 400\,^{\circ}\mathrm{C}$, WHSV $= 12\,\mathrm{h}^{-1}$, PhOH:EtOH (mol) $= 2.1$, WHSV $= 4$.

3.8. Design and development of zeolite catalyst through pore size engineering for para-diethylbenzene manufacture

The above technique of enhancing *para*-selectivity has been successfully employed to develop an ecofriendly process for the manufacturing of *p*-DEB by selective alkylation of EB with ethanol over pore size regulated zeolite catalyst. *p*-DEB is a high value chemical used as a desorbent in the separation of *para*-xylene from a mixture of C_8 aromatics in the UOP's "PAREX" process. The development and commercialisation of zeolite-based catalytic process for *p*-DEB has been achieved through different stages. Preparation of catalyst has been scaled up to commercial level while on the other hand; process for *p*-DEB manufacture was optimised in pilot plant. The activity, selectivity and life of catalyst was established in the pilot plant and reproduced in semi-commercial unit [32,33]. A grass root plant of 1200 TPA capacity plant for the manufacture was erected based on the data generated from the pilot plant and semi-commercial unit. The commercial plant has been successfully commissioned and regular production of *p*-DEB has commenced. The commercial performance of the catalyst and process has been excellent in terms of EB conversion and *p*-DEB selectivity. The zeolite catalyst exhibited a steady state activity of 9–10% EB conversion with 97–99% *p*-DEB selectivity across single catalyst bed. A good cycle life of catalyst and also regenerability have also been established.

The pore size regulated zeolite catalyst has shown unique advantages for the manufacture of *p*-DEB over conventional catalyst. The catalyst and process are environmentally friendly and do not involve corrosive or pollutive chemicals. The new process due to space restrictions inside the zeolite channel, products higher than dialkylated benzenes are not formed. The process selectively produces *p*-DEB and a simple distillation is sufficient to separate the desired product with purity suitable for commercial application. The zeolite catalyst used in the process is regenerable and can be regenerated several times. The present process saves lot of capital investment as well as operating costs compared to multistep conventional alkylation process. It also reduces raw material requirements, energy consumption and maintenance.

With this development, India becomes third country in the world to develop and commercialise the ecofriendly technology for *p*-DEB manufacture [34,35]. The other two countries who have earlier successfully commercialised this process by using different catalysts and process are UOP, USA and TSMS, Taiwan [36–40]. This entire development marks one significant step towards progress of catalysis science in India and self-reliance in catalyst technology development.

4. Conclusions

It has been demonstrated that very high *para*-selectivity can be achieved by the CVD of silica on ZSM-5 zeolites. The pore size regulated zeolite catalyst can be employed to synthesis *para*-dialkylbenzenes of very high purity through alkylation reactions, value added *para*-xylene through selective disproportionation of toluene and aromatisation of paraffins. An ecofriendly process for the manufacture of *p*-DEB has been developed and commercialised using pore size controlled zeolite. Some of the unique features of silylated zeolite catalyst for synthesis of *para*-dialkylbenzenes over conventional acid catalyst have also been highlighted.

Acknowledgements

Authors are grateful to the management of Indian Petrochemicals Corporation Limited, Baroda for the encouragement during the course of this work and also permission to publish the paper.

References

[1] W.W. Kaeding, C. Chu, L.B. Young, B. Weinstein, S.A. Butter, J. Catal. 67 (1981) 159.
[2] T. Yashima, Y. Sakaguchi, S. Namba, Stud. Surf. Sci. Catal. 7 (1981) 739.
[3] I. Wan, B.J. Lee, M.H. Chen, Appl. Catal. 54 (1989) 257.
[4] M.B. Sayed, A. Auroux, J.C. Vedrine, J. Catal. 116 (1989) 1.
[5] T. Hibino, M. Niwa, Y. Murakami, J. Catal. 128 (1991) 551.
[6] J.H. Kim, S. Namba, T. Yashima, Zeolites 11 (1991) 59.
[7] J.H. Kim, S. Namba, Y. Yahima, Appl. Catal. 100 (1993) 27.
[8] N.Y. Chen, W.E. Garwood, F.G. Dwyer, Shape Selective Catalysis in Industrial Applications, Marcel Dekker, New York, 1989.

[9] W.O. Haag, R.M. Lago, P.B. Weisz, Disc Faraday Soc. 72 (1981) 371.
[10] D.H. Olson, W.O. Haag, Catal. Mater. ACS Symp. Ser. 248 (1984) 257.
[11] J. Wei, J. Catal. 76 (1982) 433.
[12] N. Katada, H. Igi, J.H. Kim, M. Niwa, J. Phys. Chem. 101 (1997) 5965.
[13] J.H. Kim, J.H. Ishida, M. Okajima, M. Niwa, J. Catal. 161 (1996) 387.
[14] J.H. Kim, T. Kunieda, M. Niwa, J. Catal. 173 (1998) 443.
[15] K. Tanabe, W.F. Holderich, Appl. Catal. 181 (1999) 399.
[16] M. Niwa, M. Katu, T. Hattori, Y. Murakam, J. Phys. Chem. 90 (1986) 6233.
[17] R.J. Argaur, G.R. Landolt, US Patent 3702886 (1972) to Mobil Oil.
[18] J. Das, Y.S. Bhat, A.B. Halgeri, Appl. Catal. Gen. 115 (1994) 257.
[19] A.B. Halgeri, Y.S. Bhat, S. Unnikrishnan, T.S.R. Prasada Rao, ACS Symp., N.Y. 36 (4) (1991) 792.
[20] P.A. Parikh, N. Subrahmanyam, Y.S. Bhat, A.B. Halgeri, Catal. Lett. 14 (1992) 107.
[21] Y.S. Bhat, J. Das, A.B. Halgeri, Appl. Catal. 122 (1995) 161.
[22] J. Das, Y.S. Bhat, A.B. Halgeri, Catal. Lett. 20 (1993) 349.
[23] J. Das, Y.S. Bhat, A.B. Halgeri, Ind. Eng. Chem. Res. 32 (1993) 2525.
[24] Y. Ono, Catal. Rev. Sci. Eng. 34 (1992) 179.
[25] T. Inui, Y. Makino, F. Okazumi, S. Nagano, A. Miyamoto, Ind. Eng. Chem. Res. 26 (1987) 647.
[26] R.L.V. Mao, L. Defresne, Appl. Catal. 52 (1989) 1.
[27] G. Giannetto, R. Mongue, R. Galiasso, Catal. Rev. Sci. Eng. 36 (1994) 271.
[28] SRI Report No. 203, 1992.
[29] Y.S. Bhat, J. Das, A.B. Halgeri, Appl. Catal. A 130 (1995) L1.
[30] Y.S. Bhat, J. Das, A.B. Halgeri, Stud. Surf. Sci. Catal. 105 (1997) 1309.
[31] J. Das, Y.S. Bhat, A.B. Halgeri, Stud. Surf. Sci. Catal. 113 (1998) 447.
[32] J. Das, A.B. Halgeri, Appl. Catal. A 194 (2000) 359.
[33] A.B. Halgeri, Appl. Catal. 115 (1994) 1–4.
[34] Y.S. Bhat, J. Das, A.B. Halgeri, Bull. Catal. Soc. India 4 (1994) 19.
[35] Y.S. Bhat, J. Das, A.B. Halgeri, US Patent No. 5811613 (1998) to IPCL.
[36] I. Wang, C.L. Ay, B.J. Lee, M.H. Chen, Appl. Catal. 54 (1989) 257.
[37] I. Wang, T.C. Tsai, S.T. Huang, Ind. Eng. Chem. Res. 29 (1990) 2005.
[38] I. Wang, B.J. Lee, M.H. Chen, US Patent 4950385 (1990).
[39] T.C. Tsai, C.L. Ay, I. Wang, Appl. Catal. 77 (1991) 199.
[40] T.C. Tsai, S.B. Liu, I. Wang, Appl. Catal. 181 (1999) 355.