

# Heteropolyacid supported on acidic clay: A novel efficient catalyst for alkylation of ethylbenzene with dilute ethanol to diethylbenzene in presence of C<sub>8</sub> aromatics

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## Abstract

Vapor phase alkylation of ethylbenzene with ethanol to diethylbenzene is industrially relevant. Diethylbenzene is an important raw material for the conversion of divinyl benzene monomer. Conventionally, it is prepared from diacetophenone by reduction. It is also prepared by vapor phase alkylation of ethylbenzene with ethylene using zeolitic catalysts. The efficacy of dodecatungstophosphoric acid (DTPA) supported on acid treated clay has been evaluated in the current work in the alkylation of ethylbenzene with 80% (w/w) ethanol. 15% (w/w) DTPA/K-10 clay was found to be an efficient and robust catalyst. The use of aqueous ethanol and a mixed C<sub>8</sub> stream lowers the cost of production. A kinetic model is developed by studying the important process parameters with 15% (w/w) DTPA/K-10 as the catalyst.

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## 1. Introduction

The use of acid catalysts is very rampant in chemical and allied industries. Several reactions, such as Friedel–Crafts alkylation and acylation, isomerisation, esterification, etherification, hydration, dehydration and nitration employ liquid acids as homogeneous catalysts. The homogeneous acids are corrosive and hazardous; they require neutralization of the reaction mass and present effluent treatment problems, including loss of yield and presence of impurities in the final product. The overall process also becomes expensive and environmentally undesirable. Alkylated benzenes, which are produced by acid catalyzed processes, are very valuable precursors in a variety of industries including bulk chemicals, fine chemicals, specialties and refineries. The conventional method of preparation of these alkyl aromatics is the homogeneous catalyzed Friedel–Crafts reaction of olefins, halides and alcohols using Lewis acids (AlCl<sub>3</sub>, FeCl<sub>3</sub>, BF<sub>3</sub>, ZnCl<sub>2</sub>, TiCl<sub>4</sub>, ZrCl<sub>4</sub>) or Bronsted acids (polyphos-

phoric acid, sulfuric acid, hydrochloric acid, HF) [1]. For this purpose, the catalyst has to be employed in quantities over stoichiometric proportion of the reagent. Pressure from legislative and environmental bodies together with a growing awareness within the chemical industry has led to a search for new eco-friendly products and processes to replace polluting reactions. Solid acids that give the desired level of activity and selectivity are the best alternative to liquid acids. Solid acids can be easily removed from the reaction mixture and thus several reactor and separator configurations are possible. As a result, there is no inorganic impurity left in the final product. Several petrochemicals are manufactured by Friedel–Crafts alkylation using solid acids. Zeolites are the most widely studied solid acid catalysts in these reactions.

Diethylbenzene is an important raw material for the conversion to divinyl benzene monomer and also used in refineries for separation of close boiling isomers. Its worldwide production is a few thousand tones per annum [2]. Supported heteropolyacids (HPA) have become popular because of their redox nature, super acidic properties and the Keggin structure. They function ubiquitously in homogeneous as well as heterogeneous catalytic reactions [3–7]. We pioneered the use of supported HPA on

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### Nomenclature

A	ethylbenzene
B	ethanol
$k_2$	pseudo-rate constant (combined for all isomers), $\text{mol g-cat}^{-1} \text{atm}^{-2} \text{s}^{-1}$
$K_A$	adsorption equilibrium constant for <i>a</i>
$K_B$	adsorption equilibrium constant for <i>b</i>
$P_A$	partial pressure of <i>a</i> (atm)
$P_B$	partial pressure of <i>b</i> (atm)
$-r_A$	rate of reaction of <i>a</i> ( $\text{mol g-cat}^{-1} \text{s}^{-1}$ )
<i>w</i>	catalyst loading (g)

acidic clays as solid superacids [8]. A number of heteropolyacids supported on K10 clay were reported as novel catalysts by our laboratory for a number of reactions [9–14]. Further, we also reported the use of cesium modified heteropolyacids ( $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$ ) clay as nano-catalysts for important industrial reactions [15–18]. In the current work, the use of heteropolyacids such as dodecatungstophosphoric acid on K-10 clay was envisaged for the synthesis of diethylbenzene.

Diethylbenzene is prepared by two different approaches. Conventionally it is prepared from diacetophenone by reduction wherein diacetophenone is itself synthesized by Friedel–Crafts acylation using homogeneous acids. In the other route Friedel–Crafts alkylation is done with ethylene, ethanol or ethyl chloride using mineral acids,  $\text{AlCl}_3$  and other solid acids. This route has the disadvantage of poor selectivity. The alkylation of ethylbenzene (EB) with ethanol to produce diethylbenzene (DEB), along with polyethylated benzenes, is a well known reaction. Commercial grade (80%, w/w) ethanol is used as the alkylating agent due to its vast industrial availability. Considerable attention has been given to this chemistry because large amounts of DEB are required to satisfy ever-increasing growth in a highly competitive market. Friedel–Crafts homogeneous catalysts such as aluminum chloride [19–22], boron trifluoride [23,24], titanium tetrachloride [25], and solid acids such as silica alumina mixtures [26,27], aluminium phosphate [28] and zeolites [29,30] have been used to alkylate ethylbenzene with ethylene. A mesoporous solid super-acid based on sulfated zirconia UDCaT-1 has been used for preparation of diethylbenzene isomers by us [2].

The foregoing literature review suggests that there is still tremendous scope to develop an eco-friendly diethylbenzene process by using new catalysts including kinetic modeling. Thus, novelties of the Friedel–Crafts selective alkylation of ethylbenzene in  $\text{C}_8$  aromatic stream with dilute ethanol were investigated in this work by using HPA supported on acid-treated commercial clay (K-10) as catalysts. The use of dilute ethanol and  $\text{C}_8$  aromatic stream from refinery will reduce the cost of production. Alcohol is expected to reduce coke formation, which usually would occur in vapor phase reactions with alkenes at higher temperatures. A mathematical model is also developed to interpret the data.

## 2. Experimental

### 2.1. Chemicals and catalysts

All chemicals were procured from reputed firms: dodecatungstophosphoric acid (DTPA) was procured from M/s Loba Chemie, Mumbai. The montmorillonite clay (K-10) was procured from M/s Aldrich, Germany. The commercial grade xylene mixed ethylbenzene (65% EB and 35% xylene isomers) and ethanol (80% pure, rest is water) were procured from commercial manufacturing plant. HSZM 5 was obtained from Sud Chemie, India.

### 2.2. Catalyst synthesis

Heteropolyacid on support was prepared by incipient wetness technique. DTPA was the preferred HPA. Typically for a 10 g scale catalyst preparation the following procedure was adopted: 10 g of support and 1.5 g of HPA were weighed separately. The measured HPA was dissolved in methanol, which formed a homogeneous solution. The methanolic HPA solution was added slowly on the measured quantity of supports viz; clay with constant stirring with the help of glass rod. Initially, the clay was in powdered form but upon subsequent addition of methanolic HPA solution, it formed a paste or wet cake. The wet catalyst sample was dried on a water bath. The sample was further dried in an oven at  $120^\circ\text{C}$ , in order to remove methanol completely. The dried catalyst sample was kept in a sealed bottle. Prior to use, sample was dried in an oven, to remove the moisture.

### 2.3. Catalyst characterization

The crystallinity and the phase purity of synthesized samples were analyzed by powder X-ray diffraction (XRD) patterns using X-ray diffractometer (Rigaku Miniflex, Japan) with  $\text{Cu K}\alpha$  radiation. XRD patterns were recorded by scanning the catalyst sample within the  $2\theta$  range of  $10^\circ$ – $80^\circ$ . Specific surface area of each sample was obtained from nitrogen adsorption–desorption isotherms measured in a surface area analyzer (SA 3100, USA analyzer). Nitrogen adsorption was carried out at 77 K for 12 h under a residual presence of nitrogen. The surface area was calculated by using the BET method. Temperature programmed ammonia desorption (TPAD) was performed by using a Micromeritics AutoChem 2910 (USA). A sample weighing 0.1 g was loaded and activated at  $285^\circ\text{C}$ , in a quartz cell, under continuous helium flow (20 ml/min) for a period of 2 h. Presaturation was accomplished by passing 10% v/v ammonia in He for 1 h at ambient temperature. Then the sample was flushed with He for 1 h at  $50^\circ\text{C}$  to remove excess ammonia. The adsorbed ammonia was desorbed in He flow (30 ml/min) with a heating rate of  $10^\circ\text{C}/\text{min}$  and the temperature was raised from 50 to  $750^\circ\text{C}$ . The desorbed ammonia was detected by using a thermal conductivity detector (TCD). The TPAD profile was subjected to deconvolution by using Gaussian lineshapes for quantitative estimation. Typically HPA when heated alone goes into the so-called lacunary form but it still does not lose acidity. When HPAs

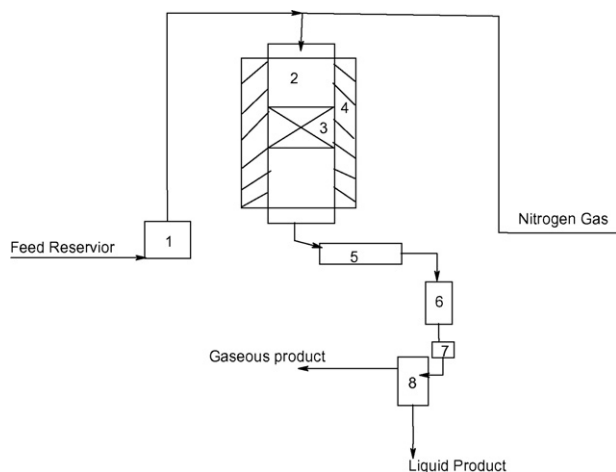


Fig. 1. Vapor phase fixed bed reaction set up 1: feed pump; 2: fixed bed reactor ( $20\text{ cm}^3$ ); 3: catalyst bed; 4: electrical furnace; 5: condenser; 6: high pressure product receiver; 7: back pressure valve; 8: atmospheric product receiver experimental conditions; catalyst loaded, 3 g, reactant (EB and ethanol); feed rate,  $2.08 \times 10^{-3}\text{ ml s}^{-1}$  at  $30^\circ\text{C}$  and nitrogen flow rate,  $0.66\text{ ml s}^{-1}$  at  $30^\circ\text{C}$ .

are supported on a suitable support, the stability is maintained up to  $500^\circ\text{C}$ . In this study, it was seen that the desorption of ammonia was negligible beyond  $500^\circ\text{C}$ , indicating all acidic sites were freed of ammonia. Further, recently the robustness of HPA on supports has been claimed up to  $750^\circ\text{C}$  on zirconia as support in some papers by Devassy and Halligudi [31].

#### 2.4. Reaction procedure and set up

All reactions were carried out in a fixed bed catalytic reactor, made of SS 316 ( $1.8\text{ cm i.d.} \times 30\text{ cm height}$ ), at atmospheric pressure containing 3.0 g of catalyst sample. The catalyst section was packed between sections of glass wool. Porcelain beads were loaded at the top of the catalyst bed to preheat the feed. Fig. 1 gives the layout of the reaction set up. The  $\text{C}_8$  stream consisting of reactants (a blend of xylenes, ethylbenzene and ethanol in a proper ratio) was fed from the top of the catalyst bed, by using a calibrated ISCO, USA syringe feed pump. Nitrogen was used as the carrier gas and the flow rate was controlled through mass flow controller at  $40\text{ ml/min}$ . The mass flow controller was calibrated carefully with a soap film as well as with wet gas meter for every run. Before the start of the reaction the catalyst was activated at  $250^\circ\text{C}$ , for 5 h in the flow of air ( $40\text{ ml/min}$ ) to drive off moisture and adsorbed hydrocarbons, if any. In the control experiments, ethylbenzene and ethanol were mixed in a 3:1 mol ratio to prepare the stock solution and the

feed was passed through the catalyst bed in a down flow reactor. The products along with unreacted ethylbenzene were passed through the cold-water condenser attached to the reactor and a gas–liquid separator.

#### 2.5. Feed and product analysis

The liquid feed and products of EB alkylation were analyzed in a HP6890 Series, using flame ionization detector (FID), in the presence of nitrogen as a carrier gas. A DBWAX capillary column was used for the analysis. The gaseous products were analyzed in a Chemito Gas Analyser 1000 Series, by using thermal conductivity detector (TCD). A spherocarb column (8 in. length  $\times$  1/8 in. diameter) was used for analysis. Identification of reaction products was done by GC and GC–MS and also by using authentic samples.

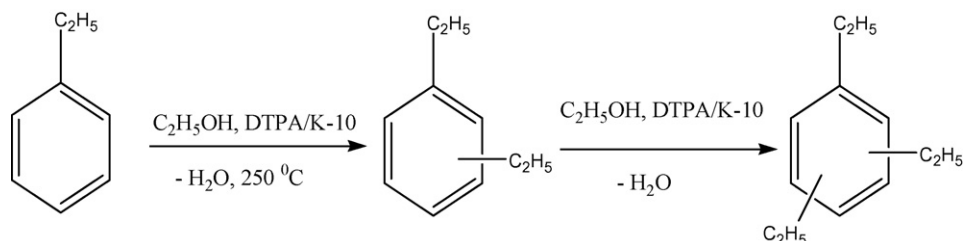
The reaction is shown in Scheme 1. Ethylene generated in situ due to acid catalyzed cracking of ethanol reacts with ethylbenzene and produces mono-alkylated and dialkylated products. Depending on conditions tetra-ethylbenzenes can also be produced if the residence time is increased. The products of reaction were DEB, triethylbenzenes (TEB) and tetra-ethylbenzenes (TE).

### 3. Results and discussion

#### 3.1. Catalyst characterization

Preliminary experiments indicated the DTPA/K-10 is a good catalyst and hence characterization studies were undertaken on successful and most promising catalysts. The XRD patterns of DTPA show that it is crystalline in nature. When DTPA is supported on K-10 clay, additional intensity was observed in the XRD peaks. This confirms that DTPA is properly deposited on the clay and improved the crystallinity of the supported catalyst. This helps in enhancement of catalytic activity of the supported catalyst (Fig. 2).

The micropore surface areas obtained from low-temperature nitrogen adsorption data were found to decrease in a nonlinear fashion with increasing DTPA loading K-10 clay (Table 1). As the DTPA loading is increased, some of the finer pore junctions in the clay support are likely to be clogged by DTPA particles, which would have cut-off accessibility to nitrogen used for the BET measurements. Thus, some surface area is not measured and a nonlinear behavior is observed. TPA shows that there is an increase in acid strength on catalyst surface due to DTPA loading (Table 1). The role of the support is to increase dispersion



Scheme 1. Alkylation of ethylbenzene with aqueous ethanol over 15% (w/w) DTPA/K-10 clay.

Table 1  
BET surface area and acidity measurement

No.	Catalyst	BET surface area (m <sup>2</sup> /g)	Total acidity (mmol g <sup>-1</sup> )	Increase in acidity after DTPA loading on clay (%)
1	K-10 clay	223	0.139	–
2	15% (w/w) DTPA/K-10	156	0.348	150.3
3	20% (w/w) DTPA/K-10	135	0.378	172.0

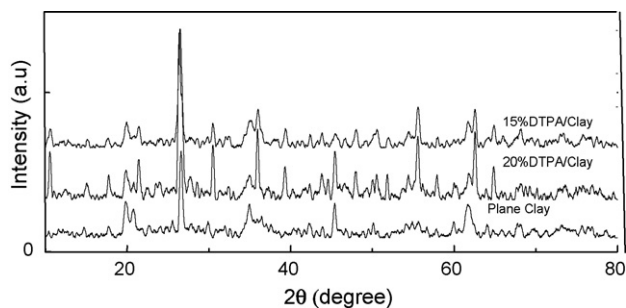


Fig. 2. Powder X-ray diffraction for different loadings of DTPA/K-10.

of the catalyst on pore walls and also the acidity of the support participates in the reaction along with the Bronsted acidity of the HPA. The increase in total acidity increased to 150.2% and 172% for 15% and 20% (w/w) DTPA/K-10. All acidity is not available to the reactants as it would be for the probe molecule ammonia.

### 3.2. Catalyst screening

Eight catalysts were used to find their activity and selectivity in the conversion of ethylbenzene to diethylbenzene. The reference catalysts were HZSM-5 and K-10 clay (Table 2). Theoretically maximum possible conversion of ethylbenzene is 33.3% for mono-alkylation. K-10 gives the least conversion and selectivity to diethylbenzenes per pass. It was observed that K-10 clays were least active and selective in comparison with all others. HZSM-5 catalyst gives per pass conversion of 21.9% with a selectivity of DEB of 70.3%. When the DTPA loading on the clay support was increased from 5% to 15% (w/w), there was an increase in conversion and selectivity. A per pass EB conversion of 21.1 was obtained with 90.5% selectivity to DEB.

Table 2  
Effect of various catalysts on conversion of ethylbenzene (for one pass)<sup>a</sup>

No.	Catalyst used	Ethylbenzene conversion (%)	% Selectivity		
			DEB	TEB	Tetra EB
1	HZSM-5	21.9	70.3	20.8	8.9
2	K-10 clay	10.2	67.4	16.5	16.1
3	20% (w/w) DTPA	18.5	82.4	9.5	8.4
4	5% (w/w) DTPA/K-10	13.5	77.3	14.3	8.4
5	10% (w/w) DTPA/K-10	16.8	84.6	8.6	6.8
6	15% (w/w) DTPA/K-10	21.1	90.5	5.2	4.3
7	20% (w/w) DTPA/K-10	21.8	91.3	5.0	3.7
8	30% (w/w) DTPA/K-10	21.9	91.8	4.5	3.7

<sup>a</sup> Ethylbenzene:ethanol, 3:1 mole ratio; catalyst loading, 3 g; temperature, 250 °C; reactant feed rate,  $2.08 \times 10^{-3}$  ml s<sup>-1</sup> at 30 °C and nitrogen flow rate, 0.66 ml s<sup>-1</sup> at 30 °C.

However, further increase from 15% to 30% (w/w) DTPA/K-10, there was no significant effect on conversion per pass and selectivity profile. The pore size distribution measurements of the catalysts showed that the surface area of 15% (w/w) DTPA/K-10 is higher than that of 20% (w/w) DTPA/K-10. The DTPA crystals are trapped in a few junctions in the porous network of the clay and thus part of the network is cut off resulting into lowering of surface area. Also, the XRD patterns had shown that fidelity of DTPA was in tact. The molecules of ethylbenzene and diethylbenzene can access these acidic centre easily in comparison with the tri and tetra-ethylbenzenes. A sort of shape selectivity is thus obtained with 15% (w/w) DTPA/K-10. When higher loading of DTPA is used, it reduces the surface area for the probe molecule in BET measurements (Table 1). In the alkylation reaction, many channels would not be available in these catalysts and thus there is a reduction in activity and selectivity. This would suggest that there was an onset of intra-particle diffusion beyond 15% (w/w) loading. A theoretical calculation was done by using the Wiesz–Prater criterion ( $C_{WP}$ ) as given by Fogler to find it was indeed the case [32]. It is the ratio of observed rate to the rate of intra-particle diffusion. Any value of  $C_{WP}$  above 0.1 shows onset of intra-particle diffusion. This was the case here. It appears that the improvement in activity and selectivity to DEB (in which *p*-DEB is maximum) is due to more acidity and narrow channels of the supported catalyst. Thus 15% (w/w) DTPA/K-10 was used for further investigation. Interestingly, none of the catalysts were active for xylene alkylation. Thus, if a C<sub>8</sub> mixed stream is used, the conversion and selectivity to EB are not affected.

In the current case, the reactions were all in vapor phase at 190–280 °C where the residence time of vapors is low. HPAs at operating temperatures do not vaporize or degrade to be carried with the products and the catalysts were robust and stable. No HPA was found in the condensed products. A few comments on stability of HPAs is in order. HPAs were found to retain their Keggin type structure when impregnated on silica provided its

Table 3  
Effect of ethylbenzene (EB)/ethanol (E) molar ratio on conversion of ethylbenzene (for one pass)<sup>a</sup>

No.	Mole ratio (EB:E)	Ethylbenzene conversion (%)	% Selectivity		
			DEB	TEB	Tetra EB
1	1:1	30.4	75.4	15.4	9.2
2	2:1	25.6	77.6	13.5	8.9
3	3:1	21.1	90.5	5.2	4.3
4	4:1	18.2	93.1	4.8	2.1

<sup>a</sup> Catalyst, 15% (w/w) DTPA/K-10 Clay; catalyst loading, 3 g; temperature, 250 °C; reactant feed rate,  $2.08 \times 10^{-3}$  ml s<sup>-1</sup> at 30 °C and nitrogen flow rate, 0.66 ml s<sup>-1</sup> at 30 °C.

Table 4  
Effect of mole ratio and residence time on the rate of reaction<sup>a</sup>

No.	Mole ratio (EB:E)	EB flow rate <sup>a</sup> (cm <sup>3</sup> /s)	Ethanol flow rate <sup>a</sup> (cm <sup>3</sup> /s)	N <sub>2</sub> flow rate <sup>a</sup> (cm <sup>3</sup> /s)	Q <sub>[EB+E+N<sub>2</sub>]</sub> <sup>a</sup> (cm <sup>3</sup> /s)	Rate (mol/s g cat)	τ (s)
1	1:1	0.2787	0.2787	0.2727	0.8301	5.06 × 10 <sup>-7</sup>	11.0
2	2:1	0.3344	0.1672	0.2727	0.7743	3.43 × 10 <sup>-7</sup>	11.8
3	3:1	0.3513	0.1171	0.2727	0.7411	2.38 × 10 <sup>-7</sup>	12.3
4	4:1	0.3632	0.0908	0.2727	0.7267	9.10 × 10 <sup>-8</sup>	12.6

<sup>a</sup> Catalyst loading, 3 g; temperature, 250 °C; V, 9.15 cm<sup>3</sup> and τ, residence time flow rate of gases at 250 °C and 1 atm.

Table 5  
Effect of temperature on conversion of ethylbenzene (for one pass)<sup>a</sup>

No.	Temperature (°C)	Ethylbenzene Conversion (%)	% Selectivity		
			DEB	TEB	Tetra EB
1	190	38.0	80.7	10.7	8.6
2	220	32.4	86.4	7.4	6.2
3	250	21.1	90.5	5.2	4.3
4	280	20.0	91.8	4.6	3.6

<sup>a</sup> Catalyst, 15% (w/w) DTPA/K-10 Clay; catalyst loading, 3 g; mole ratio (EB:ethanol), 3:1; reactant feed rate, 2.08 × 10<sup>-3</sup> ml s<sup>-1</sup> at 30 °C and nitrogen flow rate, 0.66 ml s<sup>-1</sup> at 30 °C.

contents are greater than 2% (w/w) [8]. Our work has shown that DTPA/K-10 clay and also on HMS are stable catalysts in liquid phase reactions involving alcohols, anhydrides and acids. An independent study was undertaken to evaluate the stability of the catalyst under experimental conditions. If DTPA was physically adsorbed on the clay surface, it would have been slowly leached out and no steady state would have been achieved. It was observed that the DTPA/K-10 showed a consistent activity up which suggested that DTPA was chemically bonded to the support [8–10]. For further confirmation, the stability was evaluated by the characteristic heteropoly blue color test [33]. HPA solutions develop blue color when reacted with a mild reducing agent like ascorbic acid. This property was used for quantitative determination of leaching, if any. 5 g of the catalyst was refluxed in 25 ml of methanol with vigorous stirring for 1 h. 5 ml aliquot of the refluxing solution was drawn to which 2 ml of 10% ascorbic acid solution was added. The solution remained clear and colorless and there was no development of the blue color which otherwise is an instantaneous phenomenon in authentic HPA solutions.

### 3.3. Effect of EB to ethanol mole ratio

The effect of EB to ethanol molar ratio on EB conversion and DEB selectivity was investigated at 250 °C by taking several EB to ethanol molar ratios over the 15% (w/w) DTPA/K-10 Clay

Table 6  
Effect of temperature and residence time on the rate of reaction<sup>a</sup>

No.	Temperature (°C)	EB flow rate <sup>a</sup> (cm <sup>3</sup> /s)	Ethanol flow rate <sup>a</sup> (cm <sup>3</sup> /s)	N <sub>2</sub> flow rate <sup>a</sup> (cm <sup>3</sup> /s)	Q <sub>[EB+E+N<sub>2</sub>]</sub> <sup>a</sup> (cm <sup>3</sup> /s)	Rate (mol/s g cat)	τ (s)
1	190	0.2670	0.0890	0.2062	0.5622	1.88 × 10 <sup>-7</sup>	16.27
2	220	0.3090	0.1030	0.2387	0.6507	1.85 × 10 <sup>-7</sup>	14.06
3	250	0.3501	0.1167	0.2712	0.7380	1.37 × 10 <sup>-7</sup>	12.39
4	280	0.3921	0.1307	0.3038	0.8266	1.46 × 10 <sup>-7</sup>	11.07

<sup>a</sup> Catalyst loading, 3 g; mole ratio (EB: ethanol), 3:1; V, 9.15 cm<sup>3</sup> and τ, residence time flow rate of gases at the respective temperature and 1 atm.

catalyst (Table 3). The major product formed was DEB along with small quantities of TEB and tetraethylbenzene (Tetra EB). There was no conversion of xylene isomers (35%, w/w) in any experiments. To confirm the regio-selectivity of DEB, GC-MS analysis was carried out and it was found to be a mixture of *m* and *p*-diethylbenzene. At 250 °C, the product distribution among the diethylbenzenes was 45% *p*-diethylbenzene and rest was meta isomer. Similarly the byproducts tri and tetraethylbenzene had many isomers. An attempt was made to optimize the conversion per pass and also to improve yield of *p*-diethylbenzene. The results are presented in Table 3. A molar ratio of 3:1 was selected for further study due to its better selectivity.

### 3.4. Effect of mole ratio and residence time

The effect of residence time on rate of reaction for different mole ratios is shown in Table 4. As the mole ratio of EB to ethanol was increased, the concentration of ethanol (and hence partial pressure) was decreased and hence the rate of reaction measured at steady state was observed to decrease. At the same time the volumetric flow rate of the vapor feed was correspondingly decreased to increase the residence time.

### 3.5. Effect of temperature

The EB conversion and selectivity to DEB as a function of temperature is summarized in Table 5. Per pass conversion of EB decreased from 38% to 20% with increasing temperature

Table 7  
Inlet partial pressure (PP) of ethanol and ethylbenzene<sup>a</sup>

No.	Mole Ratio (EB:E)	Inlet (mol/h)			Inlet Total moles	PP (EB)	PP (E)
		EB	E	N <sub>2</sub>			
1	1:1	0.049	0.049	0.048	0.146	0.336	0.336
2	2:1	0.058	0.029	0.048	0.135	0.429	0.215
3	3:1	0.060	0.020	0.048	0.128	0.469	0.156
4	4:1	0.064	0.016	0.048	0.128	0.500	0.125

<sup>a</sup> PP of ethanol, mol ethanol/total mols and PP of EB, mol EB/total mols.

Table 8  
Outlet partial pressure (PP) of ethanol and ethylbenzene<sup>a</sup>

Outlet (mol/h)						Outlet			Average PP (E)
EB	E	N <sub>2</sub>	DEB × 10 <sup>-2</sup>	TEB × 10 <sup>-3</sup>	Tetra EB × 10 <sup>-3</sup>	Total mol	PP (EB)	PP (E)	
0.034	0.034	0.048	2.25	4.59	2.74	0.146	0.23	0.233	0.284
0.043	0.021	0.048	1.73	3.01	1.98	0.135	0.32	0.155	0.185
0.047	0.016	0.048	1.52	0.877	0.726	0.128	0.37	0.125	0.140
0.052	0.013	0.048	1.35	0.699	0.306	0.128	0.41	0.101	0.113

<sup>a</sup> PP of ethanol, mol ethanol/total mols and PP of EB, mol EB/total mols.

from 190 to 280 °C, which is due to the decrease in residence time of the reactant due to increased flow rate; correspondingly the DEB selectivity increased to attain a maximum of 91.8% at 280 °C. The conversion and selectivity at 250 °C were 21.1% and 90.5%, respectively, which are marginally lower than those at 280 °C. It appears that intra-particle diffusion limitation sets in at 280 °C. All further studies were carried out at 250 °C.

### 3.6. Effect of temperature and residence time

The effect of temperature and residence time on rate of reaction is shown in Table 6. It was observed that with increase in temperature from 190 to 280 °C, the rate of reaction and hence the conversion of EB decreased, which is due to the corresponding decrease in residence time of reactants. The use of high temperature also suggests that *o*-DEB is transformed to *m*-DEB, which is further transformed to *p*-DEB. Therefore *p*-DEB is the most predominant species in the products at higher temperatures.

### 3.7. Effect of partial pressure

The partial pressures of ethanol and EB were calculated at the inlet and outlet of the bed (Tables 7 and 8). The effect of average partial pressure of ethanol on the rate of reaction was studied. It was observed that rate varied linearly with the ethanol partial pressure (Fig. 3).

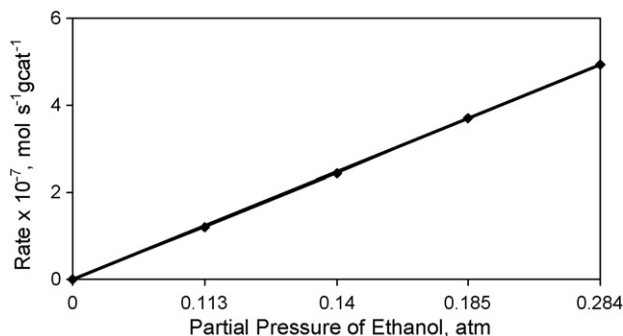


Fig. 3. Effect of partial pressure of ethanol on rate of reaction experimental conditions: catalyst, 15% (w/w) DTPA/K-10; catalyst loading, 3 g; temperature, 250 °C; reactant feed rate,  $2.08 \times 10^{-3}$  ml s<sup>-1</sup> at 30 °C and nitrogen flow rate,  $0.66$  ml s<sup>-1</sup> at 30 °C.

### 3.8. Reaction kinetics

By assuming a Langmuir–Hinshelwood model, the rate of reaction of ethylbenzene is given by

$$-r_A = \frac{k_2 K_A K_B P_B P_A}{(1 + K_A P_A)(1 + K_B P_B)} \quad (1)$$

Where  $k_2$  = a pseudo rate constant for all isomers; A = ethylbenzene; B = ethanol; and  $k_2 = k_{2(\text{ortho})} + k_{2(\text{para})} + k_{2(\text{meta})}$ . There was an insignificant presence of ortho derivative.

If adsorption of ethanol is weak in comparison with EB, then Eq. (1) reduces to the following:

$$-r_A = \frac{k_2 K_A K_B P_B P_A}{(1 + K_A P_A)} \quad (2)$$

Thus, for large partial pressure of EB, the  $1 + K_A P_A \gg 1$  and then Eq. (2) will become:

$$-r_A = k_2 K_B P_B \quad (3)$$

The rate would be linear in partial pressure of ethanol. The kinetics of reaction clearly demonstrates that there is a weak adsorption of ethanol and the dehydration reaction is very fast to generate ethylene. Fig. 3 suggests that the adsorption of EB is much stronger than that of ethanol and thus a linear relationship is obtained in ethanol partial pressure for different values of partial pressure of EB. Thus, at lower temperatures the catalyst will be poisoned by EB. Therefore this reaction should be carried out in vapor phase at high temperatures.

## 4. Conclusions

Vapor phase alkylation of ethylbenzene was studied with aqueous ethanol over DTPA supported on K-10 clay. The support increases dispersion of the catalyst on pore walls. The acidity of the support clay also participates in the reaction along with the Bronsted acidity of the HPA. The effect of DTPA loading on K-10 was studied to find that the activity and selectivity increased up to 15% (w/w) DTPA/K-10 beyond which it did not offer any advantages. 15% (w/w) DTPA/K-10 was an efficient and robust catalyst. This catalyst was not poisoned by the presence of xylene isomers (up to 35%, w/w) in C<sub>8</sub> aromatic stream and there was no alkylation of xylenes. Instead of using pure ethanol or azeotropic ethanol (96%), dilute ethanol can be used as an alkylating agent without any adverse effect on activity. There was no leaching of DTPA from the support. The optimum temperature was found to

be 250 °C at molar feed ratio of 3:1 of ethylbenzene to ethanol. Majority of the product was *p*-diethylbenzene. It gives a per pass conversion of 21.1% of ethylbenzene and a selectivity of 90.5% to diethylbenzenes. A kinetic model is developed to show a pseudo-first order reaction. There is no poisoning of the catalyst by ethylbenzene at the operating temperature, which would be the case if operated at lower temperatures.

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