Ethylation and disproportionation of ethylbenzene over substituted AFI type molecular sieves

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Abstract

The vapour and liquid phase ethylation of ethylbenzene was performed over $AlPO_4$-5 and its substituted counter parts. The results obtained for vapour phase reactions have shown a higher catalytic activity at 350 and 400 °C. The catalysts, however, exhibited a faster deactivation rate. The results obtained for liquid phase reaction have shown a higher selectivity for *para*-diethylbenzene (84.4%) than the vapour phase reaction (41.5%). MnAPO-5 was found to be active up to 240 h for the liquid phase reaction. *para*-Diethylbenzene, *meta*-diethylbenzene and polyalkylbenzene were the major products obtained for ethylation of ethylbenzene. When ethylbenzene passed over MnAPO-5 yielded products, such as benzaldehyde, acetophenone, styrene and 2,3-diphenylbutane. This showed a preference for oxidation rather than disproportionation followed by alkylation. Notwithstanding the better acid characteristics of ZSM-5, MnAPO-5 could be a better choice for this class of reaction essentially due to its higher *para* selectivity.

1. Introduction

Aromatics find a wide variety of applications in petrochemicals and chemical industries [1]. Benzene, toluene and xylene are the three basic materials serve as intermediates of commodity chemicals of aromatic derivatives. Dialkyl benzenes, such as xylene, diethylbenzene and dipropylbenzene are used for the production of polyesters, engineering plastics [2], as solvents [3], photodevelopers, anti-oxidants, etc. [4]. Diethylbenzenes are used as solvent and precursors for cross-linking agents in producing resins. 1,4-Diethylbenzene (PDEB) is a desorbent for parex process of UOP [5]. Following the discovery of *p*-selective zeolite catalyst [6–8], preparation of DEB (diethylbenzene) was achieved by direct alkylation of EB (ethylbenzene). High purity PDEB could also be prepared by reduction of *p*-ethyl acetophenone [9] and by the selective sorption of the *p*-isomer from an isomeric mixture. In the latter process, X or Y zeolites, containing Ba and/or K were used [9]. Kaeding [7] reported the alkylation and disproportionation of EB to

produce PDEB over modified ZSM-5 zeolites. Although ethylation of EB has been largely studied over zeolites, studies with zeotype molecular sieves are scarce. Therefore, considerable synthetic effort had been directed towards the framework substitution of Al and/or P by other elements to generate negatively charged frameworks [10] as well as the Brönsted acid sites. The present study involves the synthesis of AlPO-5 molecular sieves substituted with Mg, Mn and Zn, and a study of their activity in the vapour phase and liquid phase ethylation of EB with ethanol, and vapour phase EB disproportionation over MnAPO-5.

2. Experimental

2.1. Synthesis and characterisation

$AlPO_4$-5, MAPO-5, MnAPO-5 and ZAPO-5 were synthesised hydrothermally, in the presence of triethylamine (Merck, 99%) and dipropylamine (Merck, 99%) as templates. The aluminum and phosphorus sources were aluminum isopropoxide (Lancaster, 99%) and orthophosphoric acid (Qualigens, 85%), respectively. Metal acetate hydrates $[Mg(CH_3COO)_2\cdot 4H_2O$ (Merck, 99%), $Mn(CH_3COO)_2\cdot 4H_2O$ (Merck, 99%) and

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$Zn(CH_3COO)_2 \cdot 2H_2O$ (Merck, 99%)] were used as metal sources. The chemicals were used without further purification.

The catalysts were characterised by X-ray diffraction (XRD), MAS-NMR, ICP-MS, BET, TGA and *n*-butylamine-TPD in order to study the structure, chemical composition, surface area, thermal properties and acidity. The synthesis, calcination and characterisation procedures are reported elsewhere [11–16]. The chemical analysis of these catalysts was performed by using ICP-MS optima 4300 DV spectrometer. BET surface area measurements were carried out in Micromeritics pulse chemisorb 2700 using nitrogen as adsorbent at 97 K. Acidity measurements were determined by *n*-butylamine-TPD method [18] using Seiko SSC 5200H thermal analysis system attached to a TG/DTA 220 module.

2.2. Catalytic studies

A fixed-bed, vertical, flow type reactor was used for vapour phase reactions. The comprehensive information on the reactor has been discussed elsewhere [13]. Chemito fixed-bed catalytic reactor with a volume of 50 ml was employed for the liquid phase reaction. The catalyst, MnAPO-5 was milled to 200–300 mesh and about 30 g of catalyst was employed for each catalytic run. The reactants EB and ethanol were mixed using a pre-mixer and then pumped into the reactor at a rate of 1 ml/min using micro volume double plunger pump about 10 μl/stroke. The pump could be operated at a wide range of flow rate, 0.001–10 ml/min. and a pressure maximum of 220 kg/cm². The reactor outlet was cooled in a chilling unit in which ethylene glycol–water mixture was employed as coolant. The products were identified using Shimadzu GCMS-QP5000 and analysed using Shimadzu gas chromatograph. The conversion of EB (C), yield (Y_i) and selectivity (S_i) of the *i*th product are defined on the basis of aromatic products.

$$\text{Conversion } (C) = \frac{\text{wt\% of aromatics reacted}}{\text{wt\% of aromatics fed}} \times 100\%$$

$$\text{Selectivity } (S_i) = \frac{\text{wt\% of } i\text{th product}}{\text{wt\% of all the products}} \times 100\%$$

$$\text{Yield } (Y_i) = \frac{\text{wt\% of } i\text{th product}}{\text{wt\% of aromatics fed}} \times 100\%$$

3. Results and discussion

3.1. Structure

The chemical composition, acidity and BET surface area measurements were carried out for the calcined samples. The results are presented in Table 1. The catalysts have surface areas between 203 and 260 m²/g, similar to those of unsubstituted aluminophosphate molecular sieves. Fig. 1 shows TPD curves of *n*-butylamine on AlPO-5, MAPO-5, ZAPO-5 and MnAPO-5. There are three peaks observed in each run; The peak exists in the temperature range 50–90 °C is due to desorption of physisorbed *n*-BA. The second peak in the range of 110–200 °C is due to des-

Table 1
Chemical composition, surface area and acidity of aluminophosphate based molecular sieves

Catalyst	Chemical composition	BET surface area (m²/g)	Acidity (mmol/g)
AlPO-5	$Al_2O_3{:}P_2O_5$	203	0.05
MAPO-5	$0.083MgO{:}0.917Al_2O_3{:}P_2O_5$	224	0.14
ZAPO-5	$0.074ZnO{:}0.926Al_2O_3{:}P_2O_5$	252	0.28
MnAPO-5	$0.087MnO{:}0.913Al_2O_3{:}P_2O_5$	260	0.34

orption of *n*-BA from acid sites. The third peak in the range of 360–450 °C is due to the decomposition of *n*-BA into butane, etc. AlPO-5 shows low acidity values, due to lattice imperfections. MnAPO-5 is more acidic than ZAPO-5 and MAPO-5, indicating a higher level of substitution of Mn than Zn and Mg. The acidity values obtained by this method are in good agreement with the calculated values obtained from the chemical composition for all the catalysts except MAPO-5. The chemical composition indicates [MnAPO-5 > MAPO-5 > ZAPO-5] higher substitution of Mg than Zn and the acidity order shows [MnAPO-5 > ZAPO-5 > MAPO-5] lower substitution of Mg, suggests the presence of extra framework Mg in the sample. The chemical composition, acidity and BET surface area results show the substitution of the elements in the framework.

3.2. Effect of temperature

The vapour phase ethylation of EB with ethanol over $AlPO_4$-5, MAPO-5, ZAPO-5 and MnAPO-5 was studied at 250, 300, 350 and 400 °C, at EB to ethanol ratio 1:3, and WHSV 2 h⁻¹. The change in conversion and yield with temperature is shown in Table 2.

Table 2 shows a linear response in conversion with temperature over $AlPO_4$-5 and its substituted counterparts. As the temperature of the system increases, the number of molecules that carry enough energy to react when they collide also increases. As the ethylation of EB with ethanol requires prior formation of
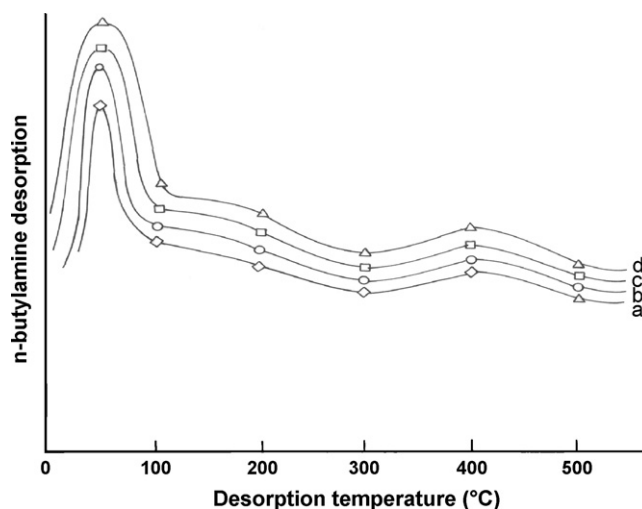

Fig. 1. Temperature programmed desorption curves of *n*-butylamine on: (a) AlPO-5, (b) MAPO-5, (c) ZAPO-5 and (d) MnAPO-5.

Table 2
Effect of temperature on the conversion and product yield

Catalysts	Temperature (°C)	Conversion (wt%)	Product yield (wt%)			
			PDEB	MDEB	ODEB	PAB
AlPO$_4$-5	250	0.9	0.4	0.1	0.1	0.3
	300	1.8	0.8	0.3	0.2	0.5
	350	3.4	1.3	0.7	0.4	1.0
	400	3.9	1.5	0.7	0.4	1.3
MAPO-5	250	2.5	1.0	0.4	0.2	0.9
	300	5.1	1.9	1.1	0.4	1.6
	350	10.2	4.3	2.1	0.7	3.1
	400	11.3	4.4	2.2	0.7	4.0
ZAPO-5	250	4.0	1.6	0.7	0.2	1.5
	300	8.3	3.3	1.4	0.4	3.2
	350	13.5	5.2	2.4	0.8	5.1
	400	15.1	5.1	2.8	1.3	5.9
MnAPO-5	250	6.3	2.4	1.1	0.6	2.2
	300	13.2	5.2	2.3	0.9	4.8
	350	20.0	8.3	3.6	1.1	6.9
	400	22.2	8.3	4.3	1.5	8.1

WHSV = 2 h^{-1}; feed ratio = 1:3 (EB:ethanol); time on stream = 1 h.

ethyl cation on the catalyst surface, the presence of Brönsted acid sites on the catalyst surface is essential. Since AlPO$_4$-5 possesses a neutral framework, the acid sites required to adsorb and yield ethyl cations are to be derived from the defective –OH groups of the catalyst on its surface. A significant conversion observed suggests the presence of sizeable defective sites. The study of reaction over MAPO-5, ZAPO-5 and MnAPO-5 showed higher conversion than AlPO$_4$-5. The order of EB conversion is found to be MnAPO-5 > ZAPO-5 > MAPO-5 > AlPO$_4$-5, following the order of acidity and surface area. EB conversion over AlPO$_4$-5 is nearly zero at 250 °C indicating the absence of ethyl cation formation due to suppression of ionisation of ethanol. The conversion over substituted aluminophosphate molecular sieves is significant at 300 °C, viz. 5.1%, suggesting sufficient concentration of alcohols in the pores.

The products of the reaction were found to be PDEB (*para*-diethylbenzene), MDEB (*meta*-diethylbenzene), ODEB (*ortho*-diethylbenzene) and PAB (polyalkylbenzene). The yield of all the products was found to increase with temperature. The selectivity to PDEB over MnAPO-5 increases with temperature and a maximum is observed at 350 °C. PDEB is produced at higher selectivity than the other products due to free diffusion through the pores. The higher *para* selectivity points out that the alkylation proceeds on the acid sites located inside the cat-
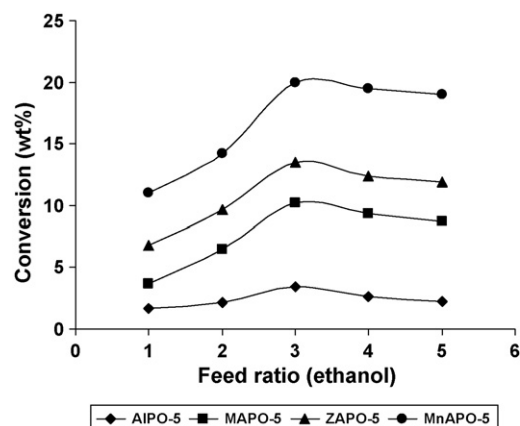

Fig. 2. Effect of feed ratio on ethylbenzene conversion (WHSV = 2 h^{-1}; temperature = 350 °C; TOS = 1 h).

alyst channels. The yield of MDEB is about 50% of PDEB at all temperatures and this could be due to: (i) steric hindrance arising from *meta* substitution, (ii) greater diffusion coefficient of PDEB than MDEB and to the (iii) *para*-directing influence of the ethyl group in EB. The selectivity to ODEB is also found to be less at all temperatures and this might be due to steric hindrance for *ortho* substitution. PAB, shows a high selectivity up to 300 °C, which is due to the poor diffusion of the primary products resulting in polyalkylation.

The vapour phase ethylation of EB was also performed over ZSM-5 under similar conditions and the results are presented in Table 3. EB conversion of 24.5% and ethanol conversion of 100% was obtained over the catalyst. The EB conversion obtained over ZSM-5 is by 2.2–3.9% higher than MnAPO-5, which exhibits the highest activity among the AlPO-5 series studied. It appears that in case of ZSM-5 the PAB formation is somewhat higher than PDEB, and it increases with temperature. It shows the presence of strong acid sites over ZSM-5 resulting in aggressive reaction and formation of PAB.

3.3. Effect of feed ratio

The influence of feed ratio on conversion over AlPO$_4$-5, MAPO-5, ZAPO-5 and MnAPO-5 was studied at 350 °C at EB to ethanol feed ratios 1:1, 1:2, 1:3, 1:4 and 1:5 and WHSV 2 h^{-1}. Fig. 2 shows an increase in conversion with feed ratios up to 1:3 and a small decrease is observed thereafter over all the catalysts. The decreased conversion results in lowered selectivity to PDEB. The increase in conversion over the catalysts up to a feed

Table 3
Effect of temperature on the conversion and product yield over ZSM-5

Temperature (°C)	Conversion (wt%)	Product yield (wt %)				Selectivity (wt%)			
		PDEB	MDEB	ODEB	PAB	PDEB	MDEB	ODEB	PAB
300	15.4	6.2	1.9	0.9	6.4	40.3	12.3	5.8	41.6
350	23.2	9.8	2.5	0.6	10.3	42.2	10.8	2.6	44.4
400	26.1	9.9	2.4	0.6	13.2	37.9	9.2	2.3	50.6

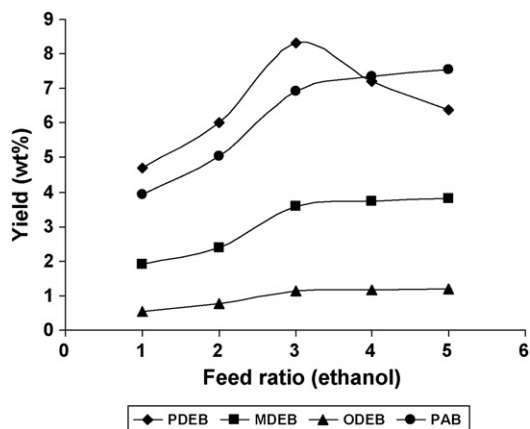WHSV = 2 h^{-1}; feed ratio = 1:3 (EB:ethanol); time on stream = 1 h.

Fig. 3. Effect of feed ratio on product yield over MnAPO-5 (WHSV = 2 h^{-1}; temperature = 350 °C; TOS = 1 h).

ratio of 1:3 should be due to an increase in the formation of ethyl cation on the catalyst surface and attains plateau after 1:3 ratio possibly due to dilution of EB by ethanol. Fig. 3 shows the influence of feed ratio on the yield of products over the catalysts. The yield of PDEB increases with feed ratios and attains a maximum at 1:3, and thereafter a decrease is observed. PAB yield increases with feed ratios and attains a maximum at 1:5. At higher feed ratios, concentration of ethyl cations is more and alkylation is expected to proceed with ease. However, polyalkylation appears to compete with monoalkylation suggesting complete coverage of catalyst surface with ethyl cation keeping EB entirely in the vapour phase. At any given feed ratio, MnAPO-5 shows higher conversion than the other catalysts. Though the activity is attributed to the higher acidity and surface area, a role for the unpaired electrons in the d subshell of Mn is an interesting possibility.

3.4. Effect of WHSV

Table 4 shows the effect of WHSV on EB conversion over the catalysts of the present study. A feed ratio of 1:3 was chosen as the selectivity to PDEB being greater at this feed ratio. As expected, increase in WHSV results in a decrease in conversion. The decrease in conversion when WHSV is changed from 1 to 2 may not be regarded as significant. A steep drop in conversion is observed when the WHSV is changed from 2 to 3. This observation manifests itself in the selectivity to PDEB. The selectivity to PDEB and PAB is nearly same at WHSV 1 h^{-1} and the selectivity to PDEB is higher than PAB at WHSV 2 h^{-1}. Due to a reasonable PDEB selectivity and not so marked drop in conversion in comparison with WHSV h^{-1}, WHSV 2 h^{-1} is chosen for the entire study of this reaction to investigate the effect of temperature, feed ratio on conversion and selectivity.

3.5. Effect of time-on-stream

Fig. 4 shows the effect of TOS on the yield [17] of products. A decrease in yield is observed for all the products with TOS due to blocking of active sites by coke. Fig. 5 shows the effect of TOS on product selectivity [17] over MnAPO-5. A

Table 4
Effect of WHSV on the conversion and product yield

Catalysts	WHSV	Conversion (wt%)	Product yield (wt%)			
			PDEB	MDEB	ODEB	PAB
AlPO$_4$-5	1	3.1	1.2	0.4	0.2	1.3
	2	3.4	1.3	0.7	0.4	1.0
	3	1.9	0.9	0.3	0.1	0.6
	4	1.2	0.5	0.2	0.1	0.4
MAPO-5	1	10.4	4.5	1.8	0.5	3.6
	2	10.2	4.3	2.1	0.7	3.1
	3	7.3	3.2	1.3	0.5	2.3
	4	5.6	2.4	1.0	0.4	1.8
ZAPO-5	1	14.2	5.3	2.5	0.9	5.5
	2	13.5	5.2	2.4	0.8	5.1
	3	7.8	3.1	1.3	0.5	2.9
	4	5.9	2.6	0.8	0.2	2.3
MnAPO-5	1	22.2	8.8	3.7	1.2	8.5
	2	20.0	8.3	3.6	1.1	6.9
	3	11.3	4.6	2.2	0.6	3.8
	4	8.2	3.4	1.7	0.5	2.6

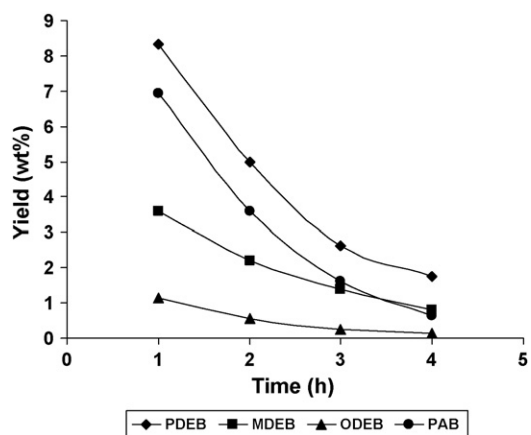Temperature = 350 °C; time on stream = 1 h; feed ratio = 1:3 (EB:ethanol).

Fig. 4. Effect of TOS on product yield over MnAPO-5 (WHSV = 2 h^{-1}; temperature = 350 °C; ethylbenzene:ethanol = 1:3).
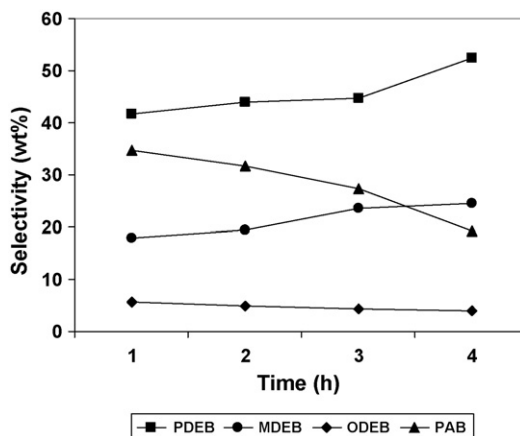

Fig. 5. Effect of TOS on product selectivity over MnAPO-5 (WHSV = 2 h^{-1}; temperature = 350 °C; ethylbenzene:ethanol = 1:3).

Table 5
Effect of temperature and pressure on liquid phase ethylation of EB over MnAPO-5

Temperature (°C)	Pressure (kg/cm^2)	Conversion (wt%)	Product yield (wt%)				Selectivity (wt%)			
			PDEB	MDEB	ODEB	PAB	PDEB	MDEB	ODEB	PAB
175	5	24	16.1	3.5	1.2	3.2	67.1	14.6	5.0	13.3
	10	29	22.6	2.9	1.1	2.4	77.9	10.0	3.8	8.3
	15	32	26.4	2.5	0.9	1.9	82.5	7.8	2.8	5.9
200	5	33	23.7	4.4	1.9	2.9	71.8	13.3	5.8	8.8
	10	39	32.9	3.0	1.3	1.8	84.4	7.7	3.3	4.6
	15	40	35.1	2.6	0.8	1.5	87.8	6.5	2.0	3.8

WHSV = 2 h^{-1}; feed ratio = 1:3 (EB:ethanol).

decrease in PAB and increase in PDEB and MDEB selectivity was observed beyond 3 hours of TOS. The selectivity for ODEB remained unchanged with TOS. At 350 °C, EB undergoes oxidation to give styrene and styrene molecules may combine to form high molecular weight products, such as 2,3-diphenyl butane, etc. (*vide infra*). Similarly, ethanol undergoes dehydration to give ethylene, which may combine with other ethylene and/or styrene molecules to form high molecular weight products, such as 2-phenyl butane, etc. The product distribution obtained for the reaction did not show the products, such as 2,3-diphenyl butane, 2-phenyl butane, etc. due to faster diffusion of smaller products. It appears, the bulky product remains in the catalyst pore for a longer time and preferably undergoes a secondary transformation to form smaller products or deactivate the catalyst by blocking the pores. This possibly results in coverage of certain active sites and a partial decrease in the pore size of the catalyst with TOS. This accounts for the decrease in yield and increase in selectivity to PDEB and MDEB with TOS. In contrast to the vapour phase reactions, the liquid phase reactions show a steady conversion up to 240 h and thereafter a gradual decrease in conversion was observed. The rapid decrease in activity of the catalyst during vapour phase reactions is essentially due to the temperatures at which the reactions were performed.

3.6. Ethylbenzene disproportionation

The vapour phase disproportionation of EB is aimed at whether disproportionation of EB takes place in the ethylation of EB with ethanol, leading to the formation of isomers of DEB. EB was passed over MnAPO-5 at 350 and 400 °C, at WHSV 1 h^{-1}. A conversion of 4.8% was obtained over the catalyst. The products were found to be benzene, styrene, benzaldehyde, acetophenone and 2,3-diphenylbutane. Among the various products styrene (0.7%) and 2,3-diphenylbutane (3%) were found to be formed predominantly. The other byproducts were found to be less than 1%. The non-observance of DEB indicates that (i) oxidation followed by alkylation predominates over disproportionation of EB and (ii) the presence of medium and weak acid sites in aluminophosphates. The oxidation of EB leads to the formation of styrene molecules, which may dimerise to form 2,3-diphenylbutane. The product distribution obtained for ethylation of EB and EB disproportionation show that transformation of EB into DEB during ethanol-EB reaction is not due to EB disproportionation.

3.7. Liquid phase ethylation of EB over MnAPO-5

In the vapour phase ethylation, the catalyst activity was found to deteriorate rapidly. One of the means of improving the catalyst stability would be to increase the WHSV. In the present study, the conversion was lower at higher WHSV. In order to improve the conversion, selectivity and stability, liquid phase ethylation in which milder reaction conditions are employed was attempted.

Ethylation of EB was performed in liquid phase over MnAPO-5 at 175 and 200 °C and 5–15 kg/cm^2 pressure. Data in Table 5 show an increase in conversion with pressure at both 175 and 200 °C, and the effect of pressure on conversion is higher at 200 °C. There is no significant change in conversion when the pressure increased from 10 to 15 kg/cm^2. It illustrates a pressure of 10 kg/cm^2 is more favourable for the reaction. PDEB selectivity found to increase with pressure and the other products selectivity, such as MDEB, ODEB and PAB found to decrease with increase in pressure. It indicates an increase in pressure influences faster diffusion of the primary products, which is resulting in higher selectivity for PDEB. A higher selectivity for PAB is observed at 5 kg/cm^2 pressure and at 175 °C, which is due to poor diffusion of primary products, leading to poly alkylation. When comparing the data for liquid phase (Table 5) and vapour phase (Table 2) reactions, the conversion is found to be higher in liquid phase than vapour phase, which may be due to decrease in intermolecular distances, resulting higher concentration of ethanol in the pores of the catalyst. The liquid phase reaction has shown a *para* selectivity of 84.4% where as the vapour phase reaction has shown only 41.5% *para* selectivity. A temperature of 200 °C and a pressure of 10 kg/cm^2 and a WHSV of 2 h^{-1} and a feed ratio of 1:3 for EB and ethanol were found to be optimum for the reaction. The catalyst was found to be active up to 240 h.

4. Conclusion

In the vapour phase ethylation of EB with ethanol over AlPO-5 and its substituted counterparts, the products of the reaction are the three isomers of DEB and PAB. The conversion was generally observed to increase with increase in temperature over all the catalysts. The selectivity to the desired product PDEB increased with TOS. This study suggests that a temperature of 350 °C, a WHSV of 2 h^{-1} and EB: ethanol feed ratio of 1:3 are the optimum parameters for ethylation of EB. At higher temperatures (e.g. 350 and 400 °C), catalysts were found to show higher

activity, at the same time deactivation was also faster. MAPO-5, ZAPO-5 and MnAPO-5 gave higher conversion than AlPO-5 due to isomorphous substitution of metal ion in the framework of the catalyst. EB disproportionation over MnAPO-5 at 350 and 400 °C has shown preference for oxidation followed by alkylation rather than disproportionation. The liquid phase ethylation of EB has shown a selectivity of 84.4% for PDEB. In addition, the catalyst was found to be active up to 240 h. The results obtained for liquid and vapour phase reactions over MnAPO-5 indicates, at particular reaction conditions aluminophosphate molecular sieves with lower acidity could be a better preference for this class of reaction essentially due to higher selectivity of PDEB.

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