

Ethylation of benzene with ethanol over substituted large pore aluminophosphate-based molecular sieves

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Abstract

Ethylation of benzene with ethanol in the vapour phase was studied over $\text{AlPO}_4\text{-5}$, MAPO-5 , ZAPO-5 and MnAPO-5 . The products were ethylbenzene (EB), 1,4-diethylbenzene (PDEB), 1,3-diethylbenzene (MDEB) and polyalkyl benzenes (1,2,4- and 1,3,5-triethylbenzene, and 1,2,4,5-tetraethylbenzene). MnAPO-5 was found to be more active than the other catalysts. Maximum conversion (47%) was noted at 400°C over MnAPO-5 . Although isomorphic substitution in MnAPO-5 is nearly the same as in MAPO-5 and ZAPO-5 , the increment in conversion was attributed to the presence of unpaired electrons in the d-subshell of manganese. The selectivity of the products was found to decrease with stream but the selectivity to EB showed an increase after 2 h of stream. MnAPO-5 registered nearly 14% yield of EB and 17% yield of DEB, whereas the yield of other products was found to be 16% at maximum conversion.

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1. Introduction

Ethylbenzene (EB) is an important compound in the petrochemical industry for the production of styrene [1]. EB is primarily produced by benzene alkylation with ethene, and in the commercial processes the reactions have conventionally been catalysed by mineral acids (e.g. AlCl_3) [2]. However, handling, safety, corrosion and waste disposal problems have prompted the development of new technologies in which solid acids, such as zeolite-based catalysts, are used to catalyse the direct alkylation of benzene with ethene [3]. In this way, several commercial processes have been developed in the past few years for the production of ethylbenzene based on zeolite catalysts [4–7]. In the production of EB, the AlCl_3 -based process are progressively substituted with zeolite-based processes. Since 1976, the medium pore zeolite ZSM-5 has been used in the Mobil–Badger process for the vapour-phase alkylation of benzene with ethylene [8–10]. Recently a new process was developed by UOP/Lummus/Monsanto/Unocal/Chemical Research Licensing [11]. The catalyst is based on Y-type zeolite and it operates at much lower temperatures and higher pressure, at which the feedstock is in liquid phase.

The most recently reported process makes use of MCM-22 or SSZ-25 as alkylating catalysts [12–17]. Although ethylation of benzene has been largely studied over zeolites, studies with zeotype molecular sieves are scarce. The new family of aluminophosphate molecular sieves (abbreviated as AlPOs) has drawn considerable attention since some of their members form structures with relatively wide unidimensional channels [18]. Therefore, considerable synthetic effort has been directed towards the framework substitution of Al and/or P by other elements to generate negatively charged frameworks [19] as well as the Bronsted acid sites. It has been shown that the incorporation of divalent metal ions into microporous AlPOs improves their Bronsted acidity and increases the potential of these materials as catalysts [20–25]. The present study involves the synthesis of large pore $\text{AlPO}_4\text{-5}$ molecular sieves substituted with Mg, Mn and Zn and a study of their activity in the vapour-phase ethylation of benzene with ethanol.

2. Experimental

2.1. Synthesis

$\text{AlPO}_4\text{-5}$ and $\text{MeAPO}_4\text{-5}$ (Me = Mg, Mn and Zn) were synthesised hydrothermally, in the presence of triethyl-

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Table 1

Gel composition, chemical analysis, surface area and acidity of aluminophosphate-based molecular sieves

Catalyst	Gel composition	Molar composition	BET surface area (m ² /g)	Acidity (mmol/g)
AlPO ₄ -5	Al ₂ O ₃ :P ₂ O ₅ :TEA:40H ₂ O	Al ₂ O ₃ :P ₂ O ₅	203	–
MAPO-5	0.1MgO:Al ₂ O ₃ :P ₂ O ₅ :TEA:40H ₂ O	0.083MgO:0.917Al ₂ O ₃ :P ₂ O ₅	224	0.349
ZAPO-5	0.1ZnO:Al ₂ O ₃ :P ₂ O ₅ :TEA:40H ₂ O	0.074ZnO:0.926Al ₂ O ₃ :P ₂ O ₅	252	0.301
MnAPO-5	0.1MnO:Al ₂ O ₃ :P ₂ O ₅ :TEA:40H ₂ O	0.087MnO:0.913Al ₂ O ₃ :P ₂ O ₅	260	0.361

amine (TEA) (Merck, 99%) as a template, in a stainless steel Teflon-lined autoclave under static conditions. The aluminium and phosphorus sources were aluminium isopropoxide (Lancaster, 99%) and phosphoric acid (Qualigens, 85%), respectively. Metal acetate hydrates (Mg(CH₃COO)₂·4H₂O, Merck, 99%; Mn(CH₃COO)₂·4H₂O, Merck, 99%; Zn(CH₃COO)₂·2H₂O, Merck, 99%) were used as metal sources. The chemicals were used without further purification. More details of the synthesis and calcination

procedures are described previously [20,21]. The gel compositions are given in Table 1.

2.2. Characterisation

AlPO₄-5, MAPO-5, ZAPO-5 and MnAPO-5 were characterised by X-ray diffraction (XRD), MAS-NMR, ICP-MS, FT-IR, BET and SEM measurements, in order to study the structure, chemical composition, surface area and phase

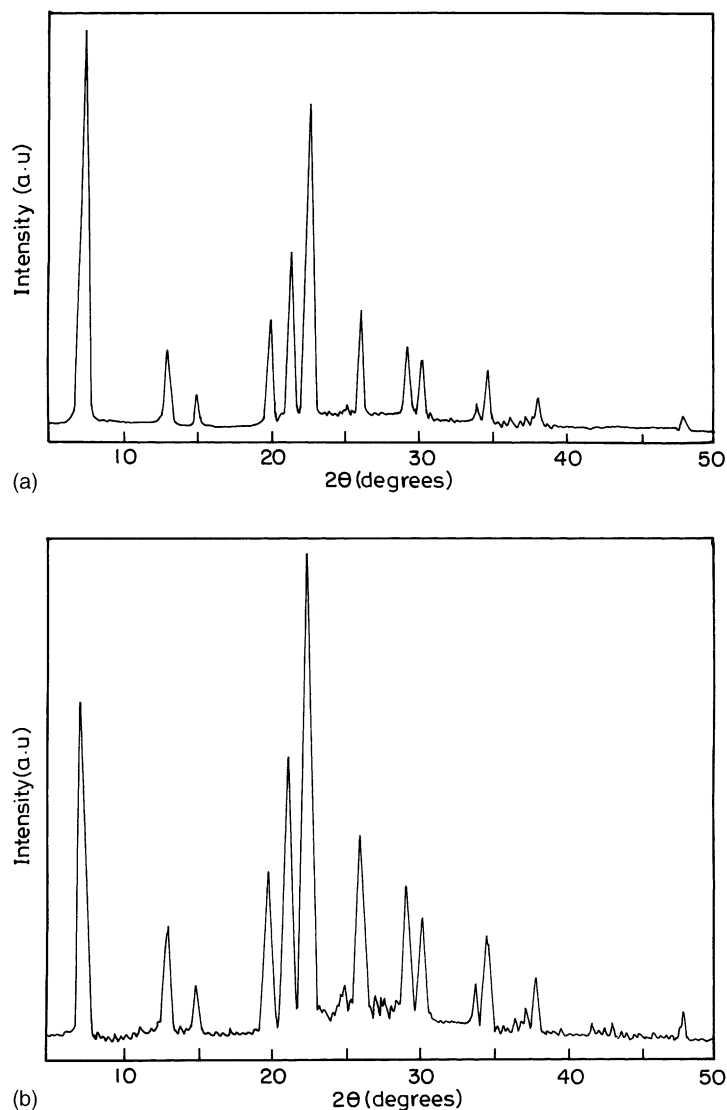


Fig. 1. X-ray diffraction patterns of the calcined samples: (a) AlPO₄-5; (b) MAPO-5; (c) ZAPO-5; (d) MnAPO-5.

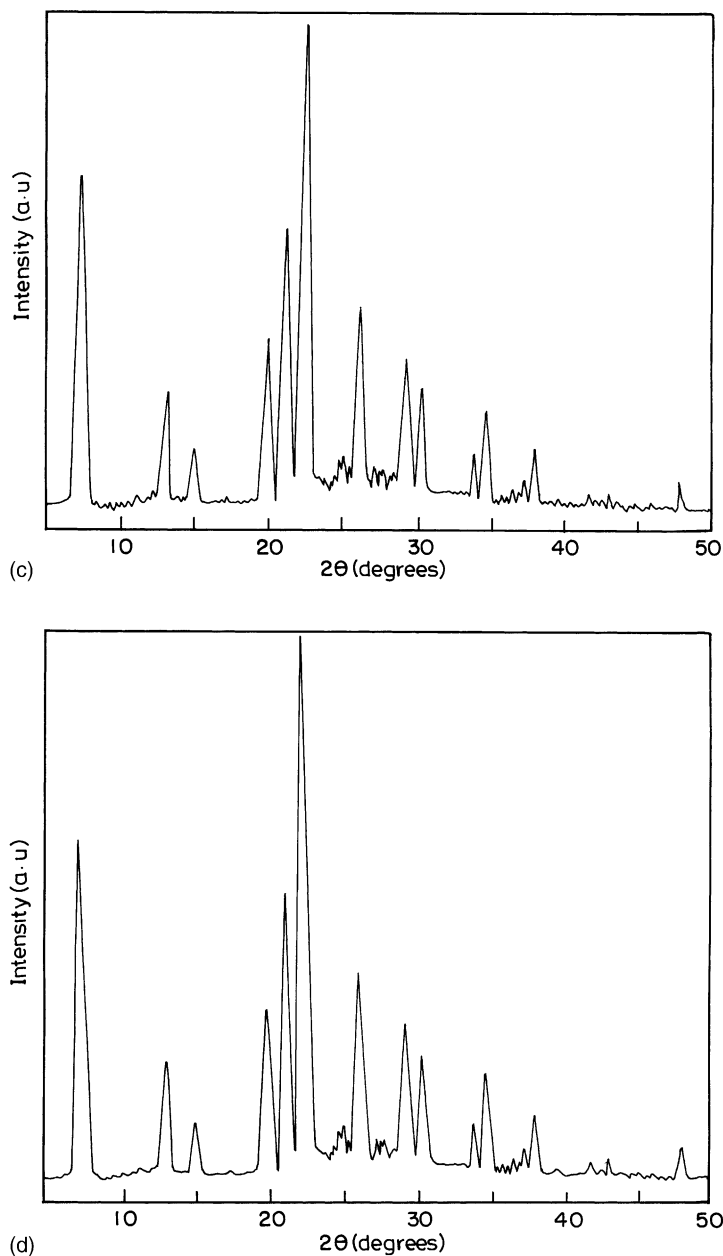


Fig. 1. (Continued).

purity. The XRD patterns were recorded on Siemens D 500 diffractometer using Cu $K\alpha$ radiation in the scan range of $2\theta = 5\text{--}50^\circ$ with a scan rate of $1^\circ/\text{min}$. FT-IR spectra were obtained from KBr pellets using a Bruker Vector 22 FT-IR spectrometer. The morphology of these molecular sieves was taken on a JEOL JSM 5600 LV SEM. The chemical analysis of these catalysts was performed by using ICP-MS optima 4300 DV spectrometer. ^{27}Al and ^{31}P MAS-NMR were recorded with a DSX 300 NMR spectrometer at 78.20 and 121.48 MHz, respectively. Magic angle spinning speeds of 5 kHz were used for ^{27}Al and ^{31}P . BET surface area measurements were carried out in Micromeritics Pulse Chemisorb 2700 using nitrogen as adsorbent at

97 K. The chemical compositions, surface area and acidity values of these catalysts are presented in Table 1.

2.3. Catalytic studies

The reactor system was a fixed-bed, vertical, flow-type reactor made of glass tube of 40 cm length and 2 cm i.d. The glass reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. About 1 g of the catalyst was placed in the middle of the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The reactants were fed into the reactor by a syringe infusion

pump that could be operated at different flow rates. The reaction was carried out at atmospheric pressure. The products were passed through a water-cooled condenser attached to the end of the reactor. The liquid products collected for the first 15 min were discarded and analysis was made only with the products collected after this time. This has been done to ensure the attainment of steady state for the reaction over the catalyst and also to eliminate temperature fluctuations. After each run, the catalyst was regenerated by passing zero air through the reactor at 500 °C for 6 h in order to remove the deposited coke. The products were identified using Shimadzu GCMS-QP5000. The products were analysed using Shimadzu gas chromatograph using CP-Sil 19 column.

3. Results and discussion

3.1. Structure

Fig. 1 shows the XRD patterns of $\text{AlPO}_4\text{-5}$, MAPO-5 , ZAPO-5 and MnAPO-5 . The materials are crystalline and do not contain detectable impure phases. It was also found from XRD that the structure is stable even after calcination at 550 °C for 8 h in a stream of dry air. MAS-NMR indicated the isomorphous substitution of Mg, Zn and Mn in the framework of aluminophosphate molecular sieves. Figs. 2 and 3 show ^{27}Al and ^{31}P NMR of $\text{AlPO}_4\text{-5}$, MAPO-5 , ZAPO-5 and MnAPO-5 , respectively. Strong signals are observed

at 35.85 ppm ($\text{AlPO}_4\text{-5}$), 37.51 ppm (MAPO-5), 38.83 ppm (ZAPO-5) and 34.46 ppm (MnAPO-5) for aluminium and at -26.68 ppm ($\text{AlPO}_4\text{-5}$), -28.39 ppm (MAPO-5), -29.67 ppm (ZAPO-5) and -25.92 ppm (MnAPO-5) for phosphorus in the lattices [21,26]. The spinning side bands in the ^{31}P resonance indicate Mg, Zn and Mn incorporated in the framework. The ^{31}P MAS-NMR spectra of MnAPO-5 show characteristic side bands, arising from strong dipolar interactions [27] with paramagnetic manganese. This spectrum is the result of contributions from both dipolar interactions and chemical shift anisotropy. If manganese is substituting for framework aluminium, one would expect more than a single resonance in the ^{31}P spectrum. The chemical composition of the catalysts is given in Table 1. The results show the substitution of the elements in the framework. Fig. 4 shows the FT-IR spectra of the catalysts. The observed patterns are similar to those shown in previous reports and are characteristic of $\text{AlPO}_4\text{-5}$ molecular sieves [20,21]. Table 1 also presents the BET surface area of all these catalysts. The catalysts have surface areas between 203 and 260 m^2/g . The surface areas of the substituted aluminophosphate molecular sieves are similar to those of unsubstituted aluminophosphate molecular sieves. This suggests that the substitution of metals in the framework does not block the pores of the structure [28]. The scanning electron micrographs of $\text{AlPO}_4\text{-5}$, MAPO-5 , ZAPO-5 and MnAPO-5 are shown in Fig. 5. The catalysts appear as polycrystalline aggregates of spherical morphology. Each tiny crystal is of

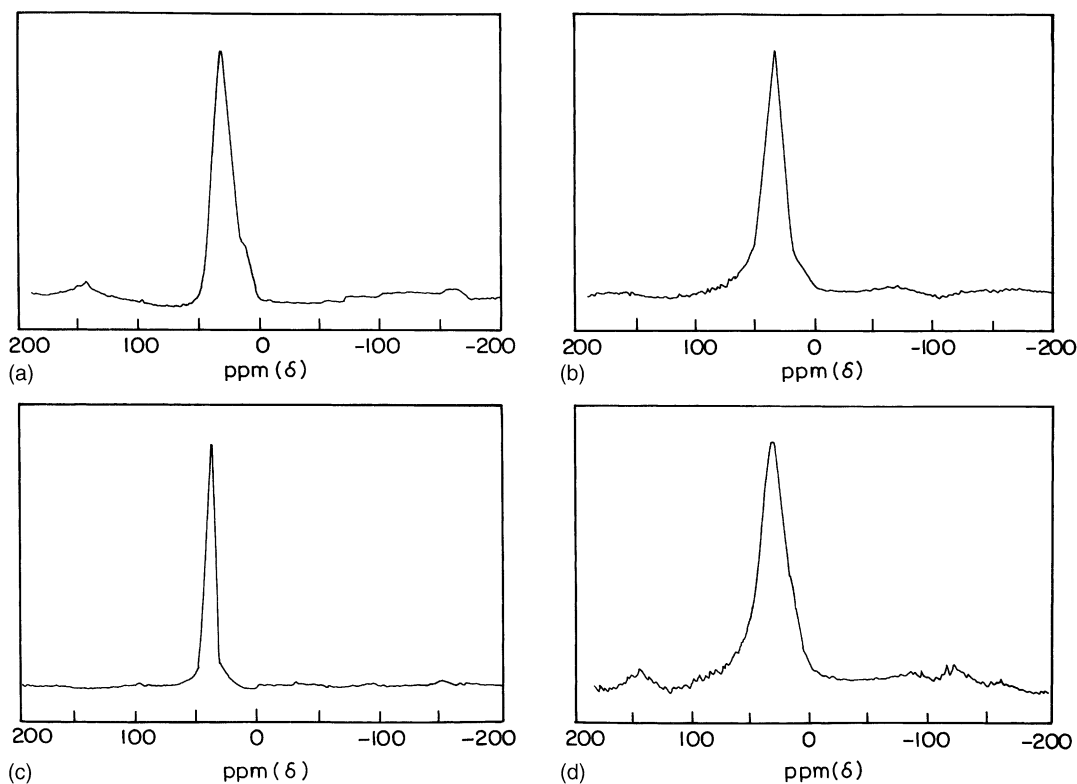


Fig. 2. Solid-state ^{27}Al NMR spectra of the calcined samples: (a) $\text{AlPO}_4\text{-5}$; (b) MAPO-5 ; (c) ZAPO-5 ; (d) MnAPO-5 .

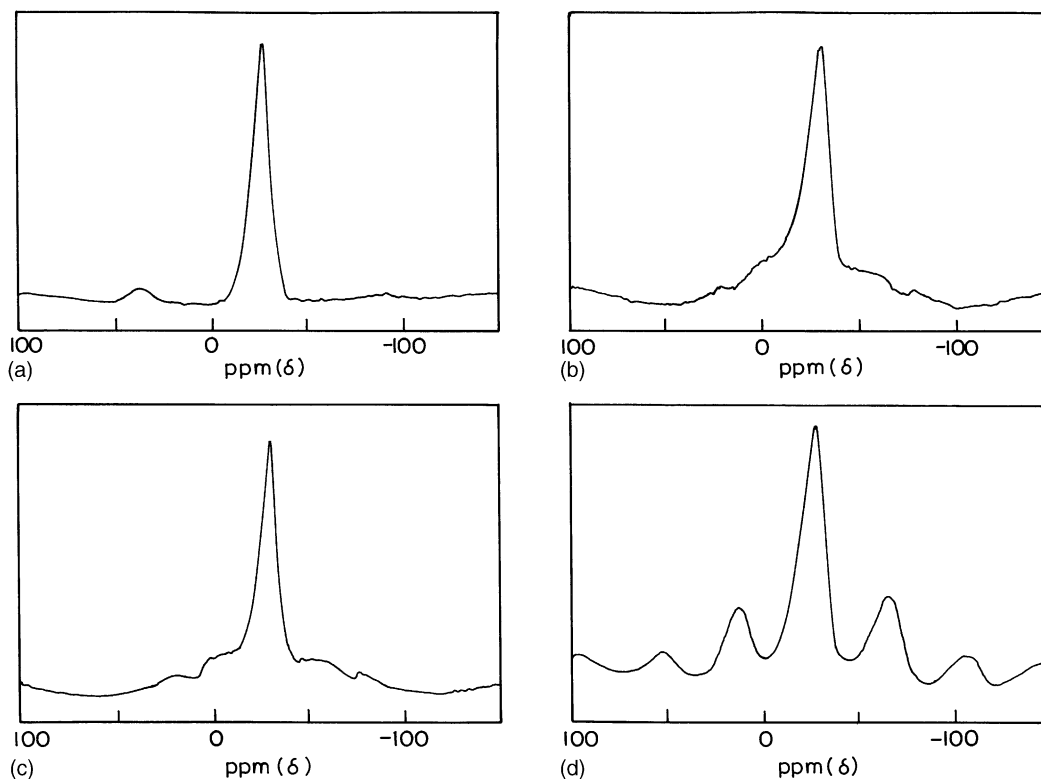


Fig. 3. Solid-state ^{31}P NMR spectra of the calcined samples: (a) $\text{AlPO}_4\text{-5}$; (b) MAPO-5 ; (c) ZAPO-5 ; (d) MnAPO-5 .

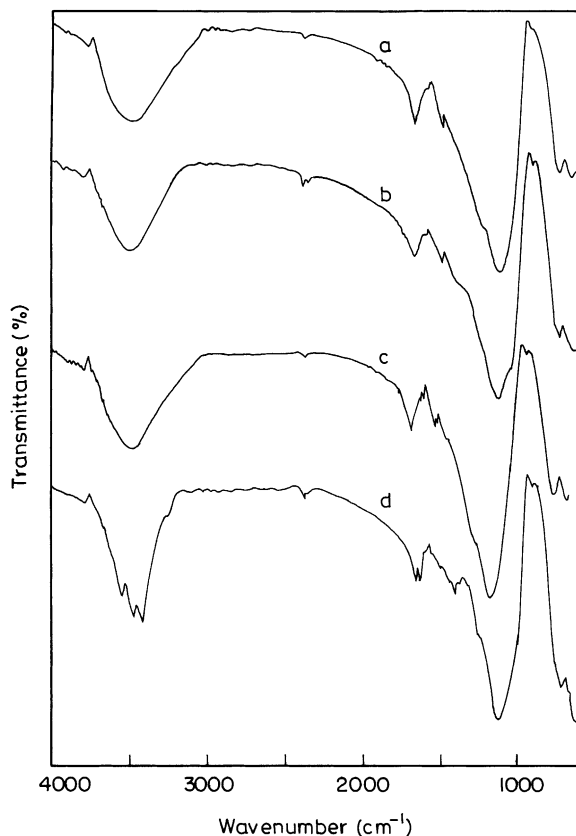


Fig. 4. FT-IR spectra of the as-synthesized samples: (a) $\text{AlPO}_4\text{-5}$; (b) MAPO-5 ; (c) ZAPO-5 ; (d) MnAPO-5 .

platy type with definite edges and sharp corners. The morphology of the catalysts $\text{AlPO}_4\text{-5}$, MAPO-5 , ZAPO-5 and MnAPO-5 appears to be same, indicating phase purity. Similar morphology was also reported in earlier literature [29]. Each crystal with which the aggregates are produced is of different dimensions for different catalysts; for example, it is more elongated for ZAPO-5 . As nearly all of the crystals in each aggregate are tiny during formation and growth, they are to be collected separately and pasted subsequently. It reflects a high surface area for each crystal due to which it can diffuse and get pasted over the growing aggregate.

3.2. Benzene alkylation

Ethylation of benzene with ethanol over $\text{AlPO}_4\text{-5}$, MAPO-5 , ZAPO-5 and MnAPO-5 was studied at 250, 300, 350 and 400 °C, with the feed ratio 1:1 for benzene:ethanol, and $\text{WHSV} = 2 \text{ h}^{-1}$. The plots of conversion versus temperature for all the catalysts are shown in Fig. 6. The products of the reaction were found to be EB, 1,4-diethylbenzene (PDEB), 1,3-diethylbenzene (MDEB) and polyalkyl benzene. The plot of product yield versus temperature for MnAPO-5 is shown in Fig. 7.

3.3. Effect of temperature

Fig. 6 shows a linear response of conversion with increase in temperature over $\text{AlPO}_4\text{-5}$. As the ethylation of benzene

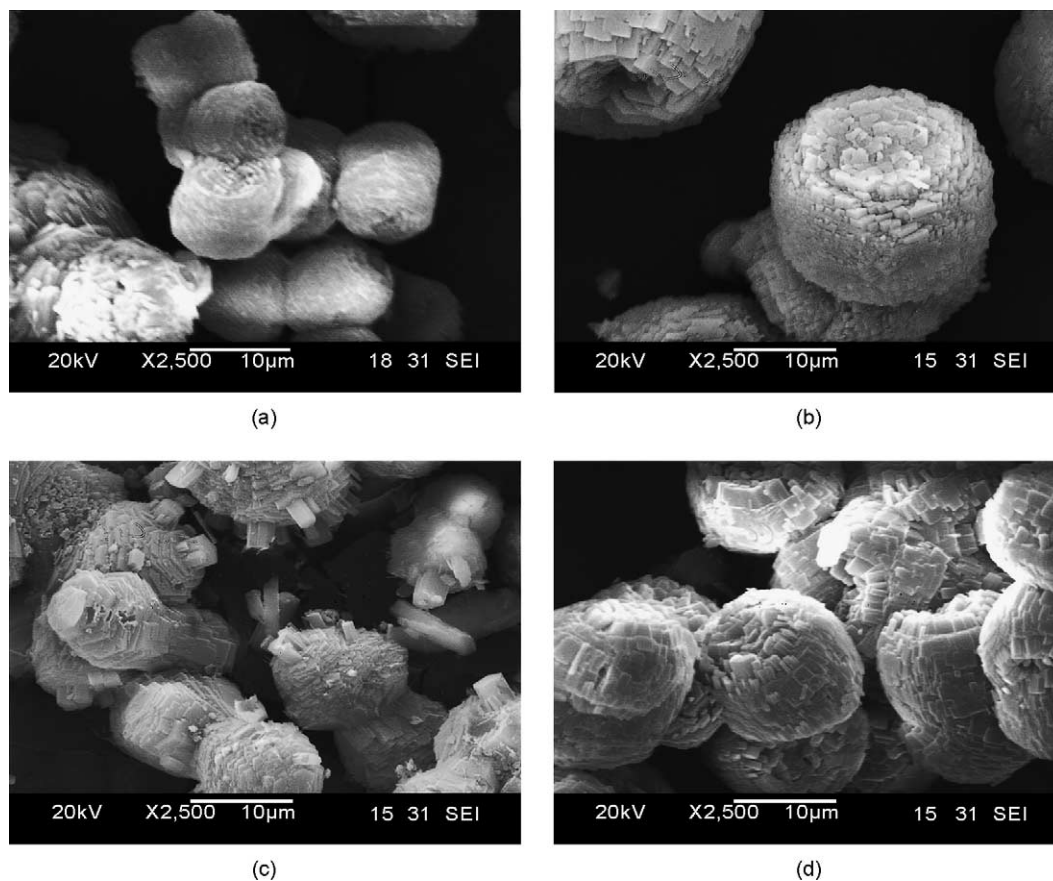


Fig. 5. SEM photographs of the calcined samples: (a) AlPO₄-5; (b) MAPO-5; (c) ZAPO-5; (d) MnAPO-5.

with ethanol requires prior formation of ethyl cation, the reaction requires the presence of Bronsted acid sites on the catalyst surface. Since AlPO₄-5 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. As the conversion is sufficiently significant (0.2–6%), the catalyst is expected to have a significant number of defective sites. As the isomorphous substitution of M²⁺ ion in the framework would produce a higher density of acid

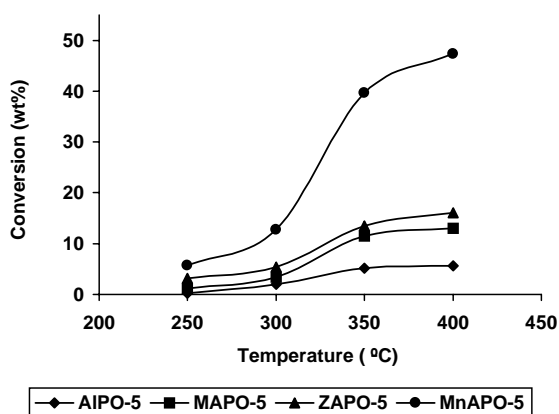


Fig. 6. Effect of temperature on benzene conversion (WHSV = 2 h⁻¹; feed ratio = 1:1).

sites, the reaction was also studied over MAPO-5, ZAPO-5 and MnAPO-5. These catalysts show higher conversion than AlPO₄-5. The order of benzene conversion is found to be AlPO₄-5 < MAPO-5 < ZAPO-5 < MnAPO-5. This order of conversion does not reproduce the order of acidity, as isomorphous substitution of Mg is more than that of Zn. The decrease in conversion over MAPO-5 compared to ZAPO-5

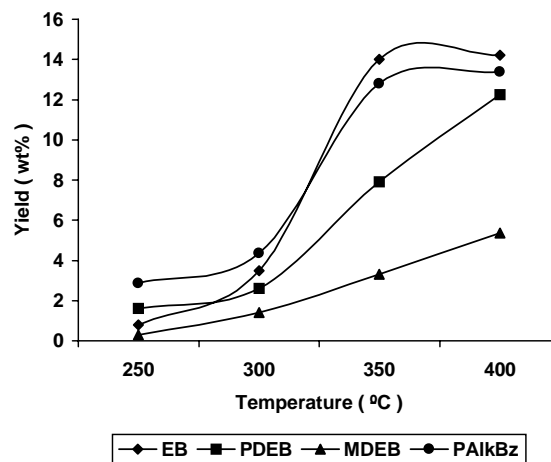


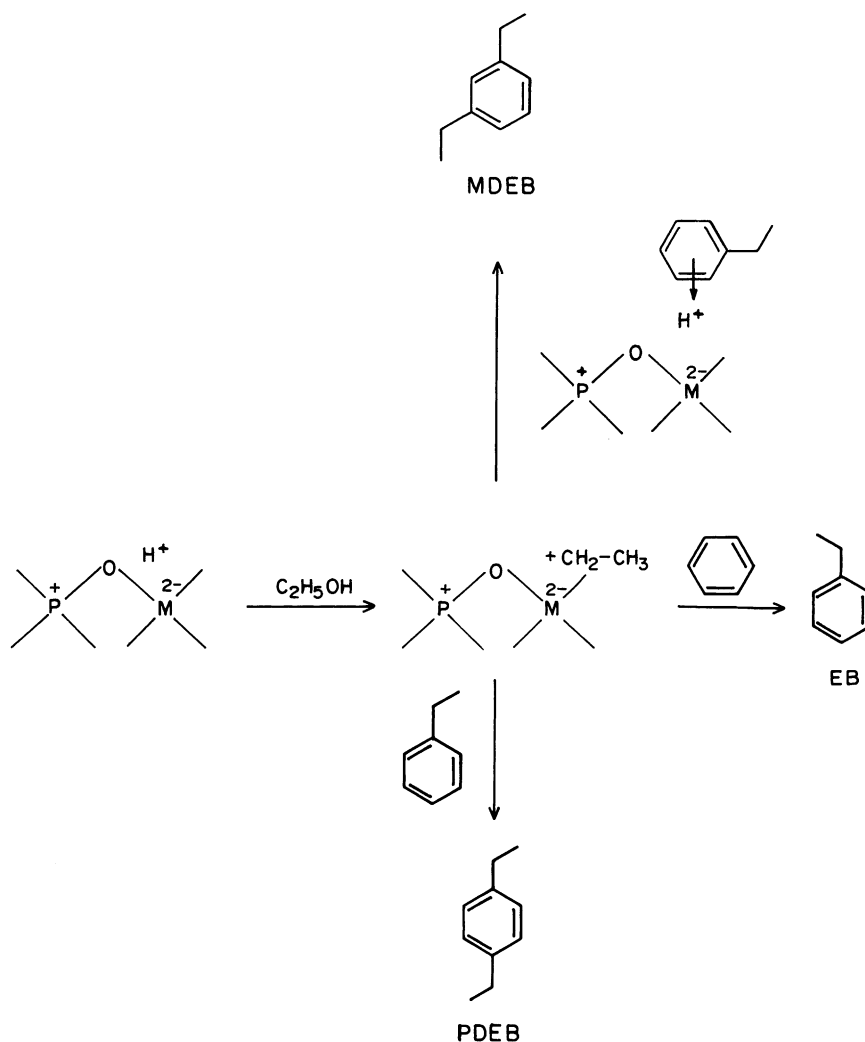
Fig. 7. Effect of temperature on product yield over MnAPO-5 (WHSV = 2 h⁻¹; feed ratio = 1:1).

might be due to the formation of non-framework metal clusters. This is also supported by the lower surface area and the lower density of MAPO-5 compared to ZAPO-5. The benzene conversion over $\text{AlPO}_4\text{-5}$ is nearly zero at 250°C indicating the absence of ethyl cation formation. Formation of hydrogen bonded alcohol clusters may cause the suppression of ionisation of ethanol over Bronsted acid sites of the catalyst. Such clusters could also exist in $\text{AlPO}_4\text{-5}$ at 250°C , indicating low conversion at this temperature. The conversion over MAPO-5 is significant even at 300°C , viz. 4%, suggesting sufficient dispersal of alcohols in the pores. A similar trend of increasing conversion at 300°C is also observed with ZAPO-5 and MnAPO-5. Among the catalysts MnAPO-5 gives higher conversion than $\text{AlPO}_4\text{-5}$, MAPO-5 and ZAPO-5.

The effect of temperature on product yield was examined over MnAPO-5 and the results are shown in Fig. 7. The selectivity to EB over MnAPO-5 increases with temperature up to 350°C , and remains the same at 400°C . The yield of PDEB, MDEB and polyalkyl benzene (PAlkBz) increases with temperature but the yield of MDEB is nearly 50% less

than PDEB at all temperatures. Polyalkyl benzene, although giving a high yield up to 300°C , is found to show lower yield at higher temperatures. Formation of EB with high selectivity might be due to its free diffusion without steric hindrance through the pores. The lower selectivity towards PDEB and MDEB might be due to steric hindrance to diffusion facilitating their subsequent conversion to polyalkyl benzene. Formation of nearly 14% EB, 12% PDEB and 5% MDEB yield at 400°C is an important observation to note in this study. On Bronsted acid catalysts the mechanism of the ethylation may be described as shown in Scheme 1. EB could be obtained on the reaction between benzene in the vapour phase and ethyl cation on the catalyst surface, whereas PDEB would require reaction between ethylbenzene in the vapour phase and ethyl cation on the catalyst surface and formation of MDEB would require reaction between co-adsorbed ethylbenzene and ethyl cation on the catalyst surface, as shown in Scheme 1.

Although ZAPO-5 gives higher conversion next to MnAPO-5 the yield patterns obtained with ZAPO-5 indicate a similar selectivity to polyalkyl benzene and hence the



Scheme 1.

results obtained with MnAPO-5 alone are discussed. There is an increase of selectivity to PDEB at temperatures up to 350 °C and remains the same at 400 °C. Polyalkyl benzene, although showing a high selectivity at 250 and 300 °C, shows lower selectivity at 350 and 400 °C. The high selectivity towards polyalkyl benzene at lower temperatures may be due to the poor diffusion of the primary products facilitating polyalkylation. The lower selectivity for polyalkyl benzene compared to EB at higher temperatures may be due to rapid diffusion of the products. The selectivity to MDEB is not as high as PDEB, and this might be due to steric hindrance for *meta*-substitution. Formation of PDEB with higher selectivity than MDEB at 400 °C might be due to free diffusion without steric hindrance, preventing isomerisation to MDEB, and to the activating influence of ethyl group which would stabilise the arhenium ion. Since AlPO₄-5 is of a large pore type, formation of MDEB with lower selectivity might be due to the lower stability of arhenium ion when ethyl cation attaches on EB at the *meta* position.

3.4. Effect of feed ratio

The influence of feed ratio on conversion over AlPO₄-5, MAPO-5, ZAPO-5 and MnAPO-5 was studied at 400 °C with feed ratios of benzene:ethanol at 1:1, 1:2, 1:3, 1:4 and 1:5 for each catalyst with WHSV = 2 h⁻¹. The results are presented in Fig. 8. The plot indicates steady trend of conversion with higher feed ratios over ZAPO-5, attainment of steady state at feed ratios ≥ 1:1 over AlPO₄-5, decrease of conversion over MAPO-5 up to 1:3; and beyond this a steady trend is observed. A non-linear response is observed over MnAPO-5. The decrease in conversion over MnAPO-5 up to 1:3 should be due to large increase in diffusional constraint for the products facilitating polyalkylation, but however a steady trend in conversion is observed beyond 1:3. Similar observation might also be made for ZAPO-5. But the conversion remained unchanged for different feed ratios. The difference between ZAPO-5 and MnAPO-5 is only the small difference in the molar composition, viz. [Zn²⁺] < [Mn²⁺]

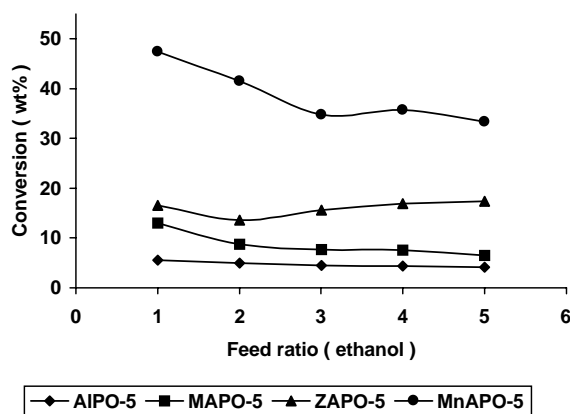


Fig. 8. Effect of feed ratio on benzene conversion (temperature = 400 °C; WHSV = 2 h⁻¹).

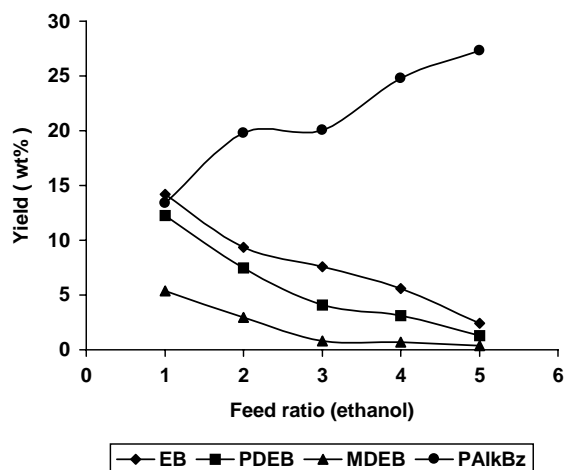


Fig. 9. Effect of feed ratio on product yield over MnAPO-5. Feed ratio of ethanol varied from one to five parts keeping benzene as one part (temperature = 400 °C; WHSV = 2 h⁻¹).

and difference in the electron subshell filling: Mn possesses 5 unpaired d-electrons and Zn, 10 d-electrons. Since the conversion obtained at each feed ratio over MnAPO-5 is more than ZAPO-5, besides showing non-linearity. The influence of the unpaired d-electron in Mn would have some influence on the properties of the feed. Fig. 9 illustrates the influence of feed ratio on yield of products over MnAPO-5. The temperature was set at 400 °C. A non-linear variation of selectivity to polyalkyl benzene with feed ratio is observed. There is increase in its selectivity at the feed ratio 1:2 and remains the same at the ratio 1:3. The selectivity to polyalkyl benzene increases, suggesting complete coverage of catalyst surface with ethyl cation, keeping benzene entirely in the vapour-phase facilitating polyalkylation. EB selectivity is more at the feed ratio 1:1 as there would be a lower probability for polyalkyl benzene. The trend for PDEB is more similar to EB, here also the selectivity to MDEB is less, due to steric hindrance.

3.5. Effect of WHSV

Fig. 10 illustrates the influence of WHSV on the yield of products. It was studied at 1–4 h⁻¹ at 400 °C over MnAPO-5. The feed ratio was set at 1:1, the selectivity to EB being greater at this feed ratio. The selectivity to polyalkyl benzene is maximum at WHSV = 1 h⁻¹ and less than to EB at WHSV = 2 h⁻¹.

3.6. Effect of time-on-stream

Fig. 11 illustrates the effect of time-on-stream on the yield of products. There is a decrease in conversion with increase in stream due to blocking of active sites by coke. The rapid decrease in activity of the catalysts with stream might be due to the microporous nature which offers much diffusional constraint for the primary products facilitating formation

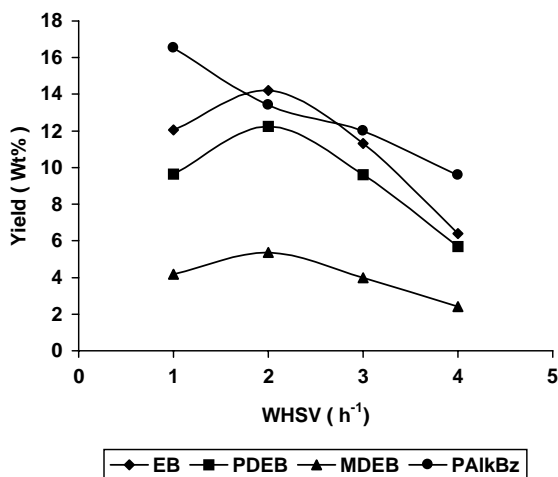


Fig. 10. Effect of WHSV on product yield over MnAPO-5 (temperature = 400 °C; feed ratio = 1:1).

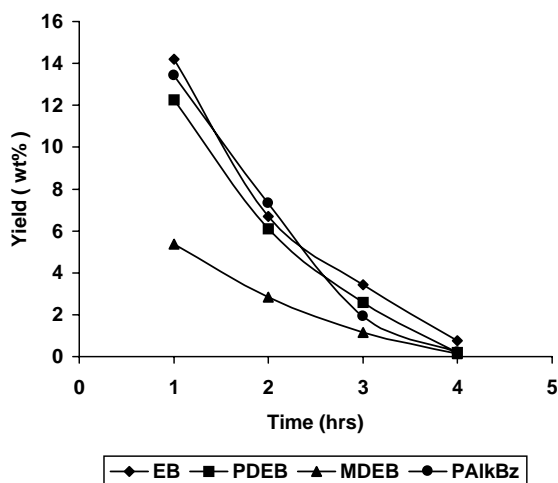


Fig. 11. Effect of time-on-stream on product yield over MnAPO-5 (temperature = 400 °C; feed ratio = 1:1; WHSV = 2 h⁻¹).

of multialkylated products with the precursors of coke. A decrease in yield is observed for all the products up to 3 h but then there is a slight increase in selectivity for EB and PDEB. The selectivity to polyalkyl benzene increases up to 2 h of stream with a decrease at the end of the third hour, as there is coke formation with stream at the end of third hour leading to a partial decrease in the pore size.

4. Conclusion

The vapour-phase reaction of ethylation of benzene with ethanol over AlPO₄-5 shows a conversion of about 6% at 400 °C. The activity of this catalyst is attributed to defect sites containing OH group. MAPO-5, ZAPO-5 and MnAPO-5 give higher conversion than AlPO₄-5 due to isomorphous substitution of metal in the framework of the catalyst. Of the catalysts, MnAPO-5 is observed to be more

active than others. Although the isomorphous substitution is nearly the same, this observation appears to reflect a role for the unpaired electrons in the d-subshell of Mn. An interesting observation in this study is the increase in the selectivity to EB with increase in stream. It may be due to a gradual reduction in the pore size of the catalyst by coke deposition.

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