Shape-selective reactions with AEL and AFI type molecular sieves alkylation of benzene, toluene and ethylbenzene with ethanol, 2-propanol, methanol and *t*-butanol

K. Joseph Antony Raj, E.J. Padma Malar [1], V.R. Vijayaraghavan *

Department of Physical Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, TN, Chennai 600025, India

Abstract

The vapour and liquid phase alkylation of various reactions are studied over MnAPO-5 and MnAPO-11. The product distribution and selectivity are discussed in terms of dimensions of the molecules. The coke content, regeneration time required by the catalyst and TOS are studied. The studies suggest that a strong deactivation of the catalyst occurs with increase in bulkiness of the reactants. The vapour phase reactions carried out at high temperatures (350 and 400 °C) result in faster deactivation of the catalyst, whereas the liquid phase reactions showed good conversion and extended catalyst life.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Aluminophosphates; Molecular sieves; Alkylation; Alkyl aromatics

1. Introduction

High selectivity for *para* formation over cation-exchanged Y zeolites has been observed by Yashima et al. [1,2] and was associated with the Bronsted acidity of the catalysts. Chen et al. [3] and Kaeding et al. [4] have observed high *para* selectivity over modified ZSM-5 and ZSM-11 zeolite catalysts. This was explained on the basis of an isomerisation–diffusion process which promoted the selective removal of *p*-xylene from the reaction zone. However, alkylation within a restricted pore size was also suggested as promoting *para* selectivity. Near-equilibrium mixtures of the xylenes were usually obtained with the unmodified zeolites [5,6]. When the ZSM-5 catalysts were modified to incorporate oxides of phosphorus and a variety of metals, dramatic increases in the concentration of the *para* isomer in the xylene product were observed. Zeolite catalysts have also been tested for alkylation of benzene with propylene to produce cumene [7] and cymene from toluene

by alkylation with propylene [8]. Conditions of reaction were optimised with rare-earth-modified zeolites to give 75–80% cumene yields.

Medium pore zeolites exhibiting channels with dimensions of about 0.55 nm have led to shape selectivity in the processing of alkyl aromatics, particularly with respect to the *para* isomers of dialkyl aromatic hydrocarbons, such as *p*-xylene, *p*-ethyltoluene and *p*-diethylbenzene. Large pore zeolites of the type Y, Beta and MCM-22 do not exhibit *para* selectivity, but are advantageously used in the synthesis of monoalkyl benzenes like ethylbenzene and cumene.

Mn is accepted as a possible candidate for isomorphous substitution into micro porous aluminophosphates. The incorporation of transition metal ions into framework sites of aluminophosphate molecular sieves [9] is of particular interest for the design of novel catalysts. Paramagnetic species are often introduced into molecular sieves to generate a catalytically reactive species or site.

In the present paper, a more detailed study of the *para* selectivity compared to *meta* and *ortho* in heterogeneous catalysis over MnAPO-5 and MnAPO-11 is undertaken. Ethylation of benzene, ethylation of ethylbenzene,

* Corresponding author. Tel.: +91 4424768820; fax: +91 442352870.
E-mail address: vijju@vsnl.com (V.R. Vijayaraghavan).
[1] Research Scientist, University Grants Commission, New Delhi, India.

isopropylation of benzene, isopropylation of ethylbenzene, methylation of toluene and *t*-butylation of ethylbenzene were used as model reactions for the study. The effects of coking on the catalytic activity, pore size of the catalyst and the dimensions of products and reactants are also discussed.

The effect of temperature, feed ratio and space velocity for various reactions over MnAPO-5 and the conversion and yield data have been discussed elsewhere [12–15] and are beyond the scope of this paper.

2. Experimental procedure

The catalysts MnAPO-5 and MnAPO-11 were synthesised and characterised using XRD, ICP-MS, SEM, BET, acidity, Al and P MAS-NMR. The synthesis, calcination and characterisation procedures are reported elsewhere [10–14].

2.1. Molecular size computation

Quantum chemical computations were performed on the reactant and product molecules in order to find their molecular dimensions. The systems were examined by Hybrid Hartree-Fock—Density Functional Theory (DFT) calculations with Becke's three parameter hybrid-exchange functional and the gradient-corrected nonlocal correlation functional of Becke and Lee et al. (B3LYP) [16,17] using the Gaussian 03 software. We performed all electron cal-

culations using the split valence basis set, which includes polarisation and diffuse functions on the heavy atoms, at B3LYP/6-31 + G* level [18]. The molecular geometries of the systems with the highest symmetries were obtained by complete structural optimisation. At the optimised geometries, vibrational frequencies were calculated to ascertain that the structures correspond to potential minima. The dimensions of the molecules were obtained from their optimised geometries and the results are shown in Figs. 2–4.

2.2. Coke content measurement

The amount of coke formed in the reactions was measured ex situ. The coke content was measured after 1 h run and at the end of run. The spent catalyst was calcined at 500 °C for 2 h, in a stream of air, under atmospheric pressure. The weight loss was measured, and from the difference in weight, wt% of coke content was calculated. The results obtained by this method match with the results obtained by TGA method. The coke contents of the catalysts for different reactions are given in Tables 1–5.

2.3. Catalytic studies

The reactions were carried out in a fixed-bed continuous downflow glass reactor of 40 cm length and 1 cm internal diameter. About 1 g of the catalyst was employed in the

Table 1
Effect of time on stream over MnAPO-5; temperature = 400 °C; WHSV = 2 h^{-1}; feed ratio = 1:1 (benzene:ethanol)

Time (h)	Conversion (wt%)	Product yield (wt%)				Selectivity (%)				Coke (wt%)
		EB	PDEB	MDEB	PAB	EB	PDEB	MDEB	PAB	
1	47.00	14.60	12.30	6.30	13.80	31.06	26.17	13.41	29.36	2.2
2	23.00	7.70	6.10	2.85	6.30	33.48	26.52	12.61	27.39	–
3	9.10	3.40	2.60	1.20	1.90	37.36	28.57	13.19	20.88	–
4	1.30	0.80	0.20	0.10	0.20	61.54	15.40	7.68	15.38	10.6

Table 2
Effect of time on stream over MnAPO-5; temperature = 350 °C; WHSV = 2 h^{-1}; feed ratio = 1:3 (ethylbenzene:ethanol)

Time (h)	Conversion (wt%)	Product yield (wt%)				Selectivity (%)			Coke (wt%)
		PDEB	MDEB	ODEB	PAB	PDEB	MDEB	PAB	
1	20.0	8.3	3.6	1.1	6.9	41.5	18.0	34.5	3.2
2	11.4	5.0	2.2	0.6	3.6	43.9	19.3	31.6	–
3	5.9	2.6	1.4	0.3	1.6	44.1	23.7	27.1	–
4	3.3	1.8	0.8	0.1	0.6	54.6	24.2	18.2	9.6

Table 3
Effect of time on stream over MnAPO-5; temperature = 350 °C; WHSV = 2 h^{-1}; feed ratio = 1:3 (benzene:2-propanol)

Time (h)	Conversion (wt%)	Product yield (wt%)			Selectivity (%)			Coke (wt%)
		Cumene	*p*-DIPB	*m*-DIPB	Cumene	*p*-DIPB	*m*-DIPB	
1	19.77	11.95	4.89	2.93	60.4	24.7	14.9	3.4
2	5.53	3.83	1.20	0.50	69.3	21.7	9.0	–
3	1.34	0.98	0.27	0.09	73.1	20.2	6.7	–
4	1.05	0.86	0.14	0.05	81.9	13.3	4.8	10.8

Table 4
Effect of time on stream over MnAPO-5; temperature = 350 °C; WHSV = 2 h^{-1}; feed ratio = 1:3 (ethylbenzene:2-propanol)

Catalysts	Time (h)	Conversion (wt%)	Product yield (wt%)		Selectivity (%)		Coke (wt%)
			p-IPEB	m-IPEB	p-IPEB	m-IPEB	
MnAPO-5	1	16.7	10.9	5.8	65.27	34.73	3.8
	2	6.1	3.3	2.8	54.09	45.91	–
	3	1.4	0.8	0.6	57.14	42.86	11.1

Table 5
Product distribution for poly alkyl benzene (PAB) for ethylation of benzene

Time	PAB (wt%)	PAB distribution (wt%)		
		1,2,4-Isomer	1,3,5-Isomer	TEB
1	13.8	11.04	0.55	2.21
2	6.3	5.30	0.13	0.87
3	1.9	1.68	0.02	0.20
4	0.2	0.19	–	0.01

Temperature = 400 °C; feed ratio (benzene:ethanol) = 1:1; WHSV = 2 h^{-1}.

study. The temperature was measured using a thermocouple inserted in the reactor at the bottom of the catalyst. The reaction mixture was fed into the reactor by a motor driven syringe pump at different flow rates. After each run, the catalyst was regenerated in situ by passing CO_2-free, dry air through the reactor at 500 °C for 6 h in order to remove the deposited coke and to restore the original activity of the catalyst.

2.4. Gas chromatography

The reactant effluent was analysed by gas chromatography (Shimadzu GC with FID) with a CP-Sil 19CB column (30 m, 0.5 mm i.d., staionary phase thickness 0.25 μm), applying temperature programming (10 °C/min) from 80 to 250 °C (10 min at the final temperature). The identification of the organic extract was carried out by GC–MS (Shimadzu GCMS-QP5000), using a HP-5MS column (30 m, 0.25 mm i.d., (5% phenyl)-methyl polysiloxane, stationary phase thickness 0.25 μm). The following temperature programme was applied: 10 °C/min from 50 to 250 °C (10 min at the final temperature). Injected volume was 0.4 μl, using an injector split ratio 1:100. These results were identified from MS library.

2.5. MnAPO-5 and MnAPO-11

The MnAPO-5 [19] molecular sieve is composed of 4-ring, 6-ring and 12-ring straight channels, which are interconnected by 6-ring windows. The main channels of this structure type are nearly circular and have a diameter of 7.3 Å. In MnAPO-11 [20] the main channels are formed from 10 rings with an elliptical dimension of 6.3 and 3.9 Å. Fig. 1 shows the pore diameter of MnAPO-5 and MnAPO-11.
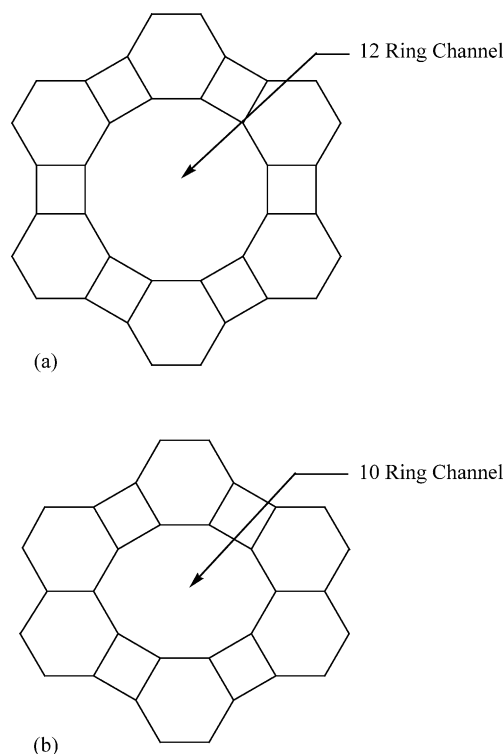

Fig. 1. Simplified structure of (a) MnAPO-5 and (b) MnAPO-11.

3. Results and discussion

3.1. Monoalkyl benzene selectivity

The results for ethylation and isopropylation of benzene (Tables 1 and 3) and the projections of molecules (Fig. 2) show that ethylbenzene and cumene have been formed in greater selectivity than the other products. It may be due to the small size of ethylbenzene and cumene than the other products shown in Fig. 3.

3.2. para-, meta- and ortho-Dialkyl benzene selectivity

The results are presented in Tables 1–4 show the distribution of the reaction products for para, meta and ortho isomers. This is strongly influenced by the channel geometry and the transport of individual isomers into channel structure.

Fig. 3 shows the projections of various para and meta isomers. The critical diameter of p-isomer is smaller than meta-, and the formation of p-isomer with greater selectivity
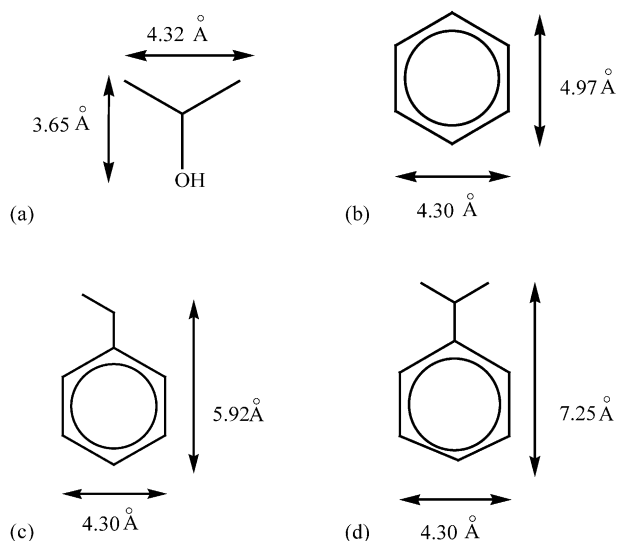
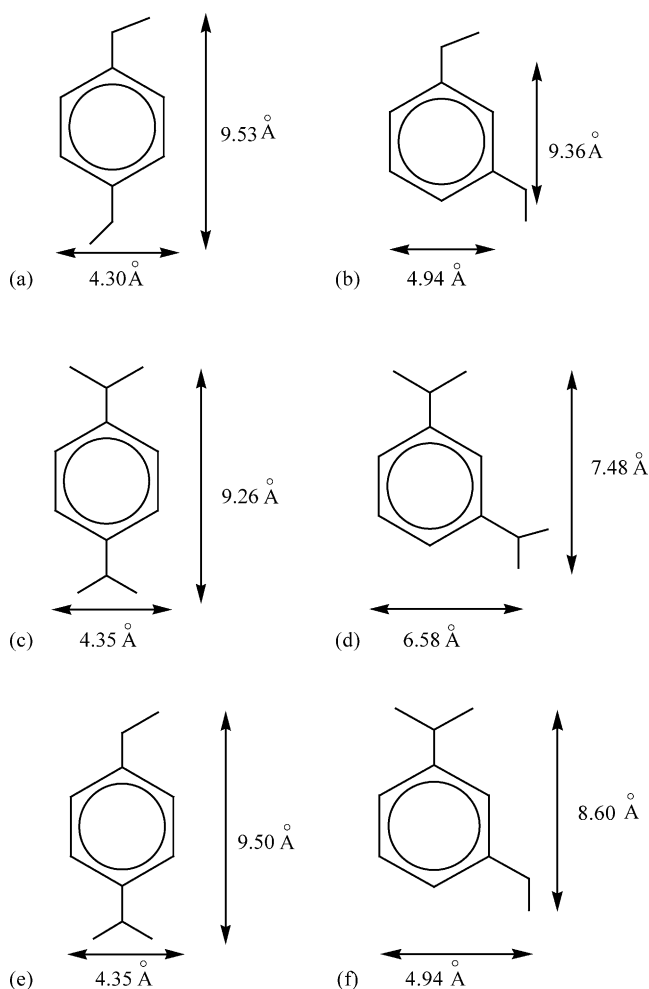Fig. 2. Projection of molecules (a) 2-propanol, (b) benzene, (c) ethylbenzene and (d) cumene.

Fig. 3. Projection of dialkylbenzenes (a) *p*-diethylbenzene, (b) *m*-diethylbenzene, (c) *p*-diisopropylbenzene, (d) *m*-diisopropylbenzene, (e) *p*-isopropylethylbenzene and (f) *m*-isopropylethylbenzene.

Table 6
Product distribution for poly alkyl benzene (PAB) for ethylation of ethylbenzene

Time	PAB (wt%)	PAB distribution (wt%)		
		1,2,4-Isomer	1,3,5-Isomer	TEB
1	6.9	5.76	0.24	0.90
4	3.6	3.24	0.07	0.29
5	1.6	1.44	–	0.16
4	0.6	0.56	–	0.04

Temperature = 350 °C; feed ratio (ethylbenzene:ethanol) = 1:3; WHSV = 2 h^{-1}.

suggesting that (i) *para* isomers diffuse out of the pores faster, (ii) the bulky *meta* isomers take longer path to diffuse out of the molecular sieves whose spatial constraints may force isomerisation to the *para* isomer leading to greater *para* selectivity and (iii) reaction is taking place on the acid sites inside the catalyst channels.

The results obtained for the first hour run of the various reactions (Tables 1–4) show that increase in *meta* selectivity was observed with bulkiness of the reactants. The order of *meta* isomer selectivity for various reactions studied is found to be ethylation of benzene (13.4%) < isopropylation of benzene (14.9%) < ethylation of ethylbenzene (18%) < isopropylation of ethylbenzene (34.7%). This may be attributed to dimer, trimer, etc., blocking the active sites hence both the reactants (aromatics and alcohol) are adsorbed on the same site, which resulting in increased formation of *m*-isomer.

The *ortho* isomer is not formed in significant amount in ethylation and isopropylation reactions over MnAPO-5 (Tables 1–4), possibly due to (i) steric hindrance and (ii) low density of acid sites on external surface and alkylation occurring inside the aluminophosphate molecular sieve channels.

3.3. Polyalkylbenzene selectivity

Polyalkylbenzenes [1,2,4- and 1,3,5- triethylbenzene and 1,2,4,5-tetraethylbenzene (TEB)] are formed as major byproducts in the ethylation of benzene and ethylbenzene. The product distribution is shown in Tables 5 and 6. The projections of the molecules are shown in Fig. 4. The pore size of MnAPO-5 is 7.3 Å while the critical diameter of 1,2,4-isomer is 4.94 Å, 1,3,5-isomer is 7.87 Å and TEB is 6.86 Å.

A perusal of the data reveals that the critical diameter follows the order 1,3,5-isomer > TEB > 1,2,4-isomer. The 1,2,4-isomer possesses a lower critical diameter than the pore size of MnAPO-5 (Fig. 1) which permits it to diffuse out of the pore at a relatively faster rate than the other products. This explains the higher concentration of the 1,2,4-isomer in the product distribution. The 1,3,5-isomer, being a bulkier isomer, is formed in lower amounts due to its slower diffusion rate. It may undergo further alkylation or rearrange to form a smaller molecule or cracking to form coke. The very formation of 1,3,5-isomer may be due to lattice vibration which
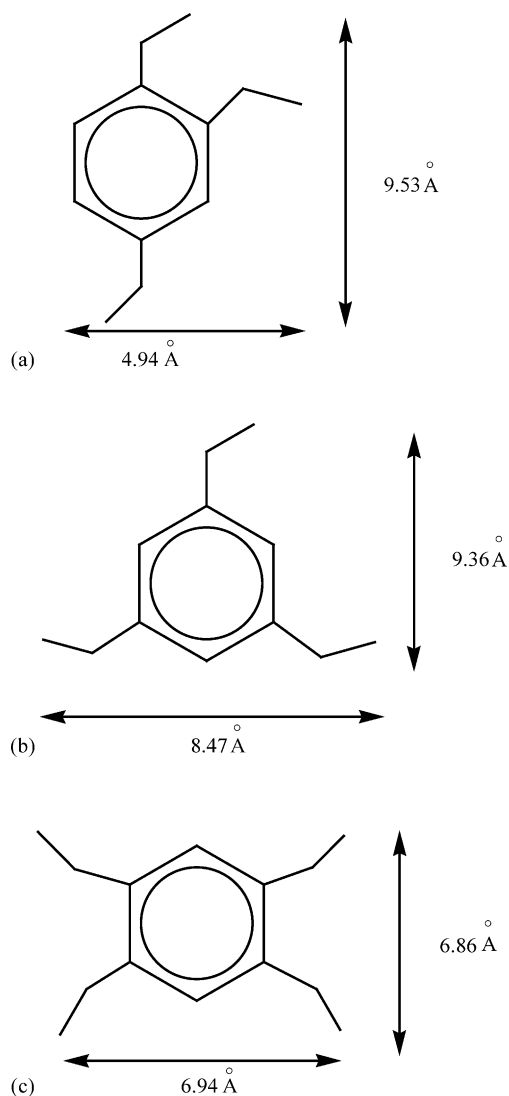
Fig. 4. Projection of poly alkyl benzenes (a) 1,2,4-triethyl benzene, (b) 1,3,5-triethyl benzene and (c) 1,2,4,5-tetraethyl benzene.

Fig. 5. Projection of molecules (a) methanol, (b) ethanol, (c) *p*-xylene, (d) *o*-xylene, (e) *m*-xylene and (f) *p*-ethyl toluene.

enlarge the size of the pores of the catalyst. The critical diameter of TEB is closer to the pore size suggesting restricted movement in the pore relative to 1,2,4-isomer. However, its diffusion rate is higher than 1,3,5-isomer and it is formed in significant amounts.

3.4. Time on stream and regeneration of the catalyst

Figs. 2–5 shows the dimensions of the reactants and products. It indicates that increase in bulkiness of the reactants cause poor diffusion, results in higher retention of reactants inside the pores of the catalyst, which may result in faster deactivation of the catalyst.

The regeneration time required by the catalyst (e.g., MnAPO-5) for various reactions studied are shown in Table 7. The catalyst can be regenerated with air in a conventional manner to remove the coke deposits and restore the lost activity.
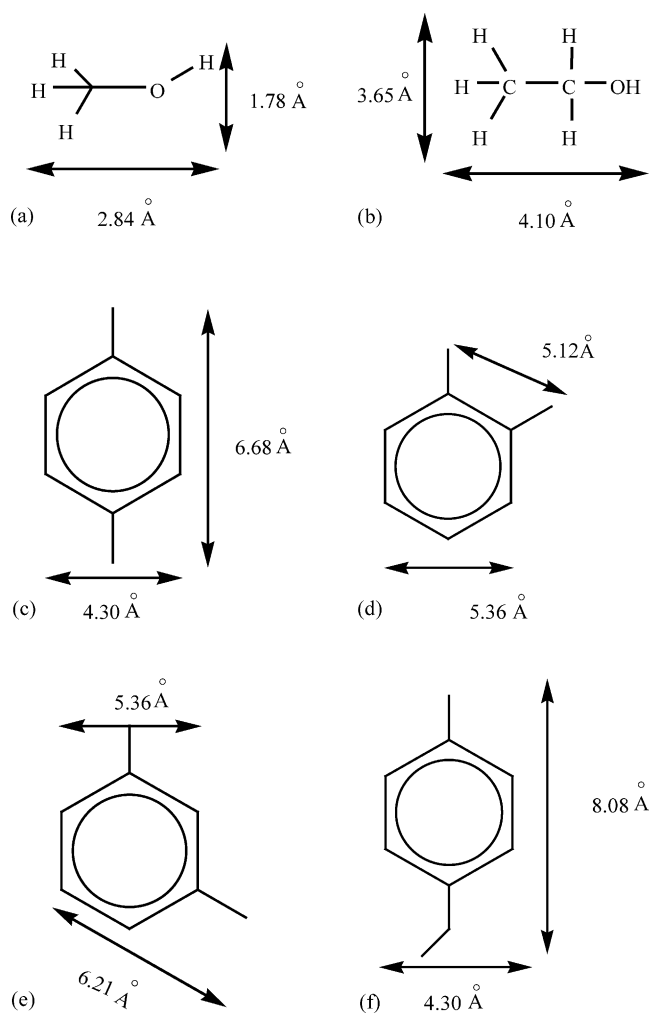
Synthesis of mono- and dialkyl benzenes by alkylation of benzene, EB and toluene with C_1–C_3 alcohols are catalysed by Brönsted acid sites. These reactions are accompanied by side reactions leading to high molecular weight products, resulting in catalyst coking. Alkylation results indicate that a strong deactivation of the catalyst can occur with TOS (Tables 1–4 and 8). It might be due to (i) the microporous nature of the catalysts, which offers diffusional constraint for the products formed and (ii) the formation of dimers, trimers, etc., of ethylene and propylene, leading eventually to undemanded bulky coke products.

3.5. Coke content and comparison of reactions

The coke content is measured after 1 h run and at the end of run. The results are presented in Tables 1–4.

When coke contents are compared for ethyaltion of benzene and ethylbenzene, ethyaltion of ethylbenzene showed a lower coke content (9.6%) than ethyaltion of benzene (10.6%) which shows that catalyst is still active for ethylation of ethylbenzene and it may be displaying extended life.

Table 7
Regeneration time for MnAPO-5 for various reactions

Reaction	Regeneration time (h)
Ethylation of benzene	2
Isopopylation of benzene	2.5
Ethylation of ethylbenzene	3
Isopropylation of ethylbenzene	4
t-Butylation of ethylbenzene	6

TOS = 1 h; temperature = 350 °C.

These variations in coke content and difference in activity is mainly due to the temperatures at which the reactions are being carried out.

When isopropylation of benzene and ethylbenzene are compared, isopropylation of ethylbenzene showed lower conversion than benzene at the end of first hour. The concentration of 2-propanol adsorbed over the catalyst may be less in case of isopropylation of ethylbenzene than isopropylation of benzene reaction. Though the reactions are carried out at same conditions like temperature, WHSV and feed ratio, isopropylation of ethylbenzene showed faster deactivation of the catalyst (catalyst deactivated at the end of 3 h). It may be attributed to the bulkiness of the reactants. At 350 °C, ethylbenzene may also undergo oxidation to give styrene and 2-propanol dehydrated to give propylene which may deactivate the catalyst by forming dimer, trimer, etc., leading to high molecular weight products resulting in catalyst coking. Therefore, in isopropylation of ethylbenzene both the reactants compete for the deactivation of the catalyst whereas in the isopropylation of benzene only 2-propanol accounts for the deactivation of catalyst.

When ethyaltion of ethylbenzene and isopropylation of ethylbenzene are compared, catalyst is deactivated at the end of third hour in case of isopropylation of ethylbenzene whereas ethyaltion of ethylbenzene showed a deactivation at the end of fourth hour. A coke content of 11.1% is obtained at the end of third hour for isopropylation of ethylbenzene and 9.6% is obtained at the end of fourth hour for ethyaltion of ethylbenzene. This suggests deactivation is much faster in isopropylation of ethylbenzene than ethyaltion of ethylbenzene.

3.6. Ethylation and methylation of toluene over MnAPO-11

The objective of performing ethylation of ethylbenzene and toluene over medium pore MnAPO-11 is to get greater *para* isomer than over the large pore MnAPO-5.

When ethylation performed over MnAPO-11 and/or ZAPO-11 at various experimental conditions showed no change and/or less than 0.2% conversion, methylation of toluene showed good conversion (Table 8).

AlPO$_4$-11 is a crystalline aluminophosphate with pores consisting of channels with a diameter of 0.39 nm × 0.63 nm (Fig. 1). A projection of ethanol, methanol, toluene, isomers of xylene and *p*-ethyltoluene is shown in Fig. 5. Methanol molecules pass through the channels of MnAPO-11 more easily than ethanol. The formation of *o*-xylene in higher concentration than *m*-xylene should be due to the free diffusion of *o*-xylene.

The observations at temperature 400 °C (Table 8) suggest that the pore size of the catalyst may expand to some extent and allow xylene isomers to pass through the pores whereas the larger size of *p*-ethyltoluene faces a restricted transition state selectivity.

3.7. t-Butylation of ethylbenzene with t-butanol over MnAPO-5

t-Butylation of EB was performed for exploring the possibilities of synthesising *para-t*-butyl EB. At 350 and 400 °C the expected *para* product is not formed and instead cracked products like cumene, ethyltoluene, *p*-isopropylethylbenzene and *iso*-butene were formed leading to rapid catalyst deactivation in 1 h. At 300 °C the expected *para* product was formed to 1.5% and other products were formed to the extent of less than 1%. At 300 °C also deactivation of the catalyst was fast (<2 h). At 250 °C, the conversion was very low (<1%), indicating that the catalyst is not active at 250 °C. The catalyst deactivation at 300 °C may be due to the formation of dimers, trimers, etc., of butene. These dimers, trimers, etc., should have blocked the active sites of the catalyst by way of coke deposition.

t-Butylation of EB was also performed in liquid phase at 200 °C and 15 kg/cm^2 pressure yielding *p-tertiary* butyl ethylbenzene (6%) and other products (cumene, methyethylbenzene, toluene and *m-tertiary* butyl ethylbenzene) at less than 1.3%. It shows a *para* selectivity of 82%. The catalyst was found to be active for 24 h while thereafter a decrease in conversion was observed. After 24 h the catalyst was unpacked from the reactor. The spent catalyst was found to be grey in colour and not black which suggesting that catalyst deactivation is only partial and regeneration to original activity is possible in 3 h.

Table 8
Effect of time on stream over MnAPO-11; temperature = 400 °C; WHSV = 2 h^{-1}; feed ratio = 1:2 (toluene:methanol)

Time (h)	Conversion	Product yield (wt%)				Selectivity (%)			Coke (wt%)
		p-Xylene	*m*-Xylene	*o*-Xylene	Heavies	*p*-Xylene	*m*-Xylene	*o*-Xylene	
1	20.32	11.9	3.1	4.2	1.12	58.6	15.3	20.7	1.8
2	13.93	8.7	1.8	2.9	0.53	62.5	12.9	20.8	–
3	8.14	5.2	0.8	1.8	0.34	63.9	9.8	22.1	–
4	4.23	2.8	0.4	0.9	0.13	66.2	9.5	21.2	8.6

3.8. Dodecylation of benzene with dodecene over MnAPO-5

The vapour phase long chain alkylation is carried out with benzene and dodecene under various experimental conditions over MnAPO-5, gave a poor conversion of 0.3% and the catalyst is completely carbonised in less than 30 min and regeneration of catalyst required a long time (12 h).

Dodecylation of benzene with dodecene was carried out in liquid phase at $200\,^{\circ}$C and at $15\,kg/cm^2$ pressure giving a conversion of 5.5% with a 2-phenyl dodecane selectivity of 70%. The other products were 3- and 4-phenyl dodecane. The conversion was steady upto 20 h, with gradual decrease thereafter.

4. Conclusion

The vapour phase alkylation reactions show that increase in carbon chain and bulkiness of the alkylating agents lead to rapid deactivation of the catalyst. *Para* selectivity was observed with TOS for all the reactions. *Meta* selectivity was increased with bulky alkylating agents. At higher temperatures (e.g., 350 and $400\,^{\circ}$C) the catalyst was very active, while at the same time deactivation was also faster. In a molecular sieve catalyst molecular dimensions have significant effects on diffusivity, isomerisation and selective diffusion, highly favouring the fast diffusing species and thus influencing the primary product distribution at the catalytic sites. The liquid phase *t*-butylation of ethylbenzene and dodecylation of benzene at $200\,^{\circ}$C showed good conversion and greater *para* and 2-phenylalkane selectivity. The catalyst also showed extended life. All these studies suggest that MnAPO-5 is a good catalyst for short chain and long chain alkylation.

References

[1] T. Yashima, H. Ahmad, K. Yamazoki, M. Katsuata, N. Hara, J. Catal. 16 (1970) 273.
[2] T. Yashima, K. Yamazoki, H. Ahmad, M. Katsuata, N. Hara, J. Catal. 17 (1970) 151.
[3] N.Y. Chen, W.W. Kaeding, E.G. Dwyer, J. Am. Chem. Soc. 101 (1979) 6783.
[4] W.W. Kaeding, C. Chu, L.B. Young, B. Wescstein, S.A. Butter, J. Catal. 67 (1981) 159.
[5] W.W. Kaeding, C. Chu, L.B. Young, B. Wescstein, S.A. Butter, J. Catal. 69 (1981) 392.
[6] L.B. Young, S.A. Butter, W.W. Kaeding, J. Catal. 76 (1982) 418.
[7] Y.C. Yen, Stanford. Res. Inst. Econ. Rep. 22A (1972);
Y.C. Yen, Stanford. Res. Inst. Econ. Rep. 22B (1977).
[8] Y.C. Yen, Stanford Res. Inst. Econ. Rep. 49 (1969).
[9] M. Hartmann, L. Kevan, Chem. Rev. 99 (1999) 636.
[10] S.P. Elangovan, V. Krishnamurthy, V. Murugesan, Hungarian J. Ind. Chem. 23 (1995) 119.
[11] S.P. Elangovan, V. Krishnamurthy, V. Murugesan, Catal. Lett. 36 (1996) 271.
[12] V.R. Vijayaraghavan, K. Joseph Antony Raj, J. Mol. Catal. A 207 (2004) 41.
[13] K. Joseph Antony Raj, V.R. Vijayaraghavan, Proc. Indian Acad. Sci. (Chem. Sci.) 116 (2004) 1.
[14] K. Joseph Antony Raj, V.R. Vijayaraghavan, Catal. Lett. 96 (2004) 67.
[15] K. Joseph Antony Raj, V.R. Vijayaraghavan, Indian J. Chem. 43A (2004) 254.
[16] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[17] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[18] J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Srtucture Methods, Gaussian Inc., Pittsburgh, PA, 1996.
[19] N. Azuma, M. Hartmann, L. Kevan, J. Phys. Chem. 99 (1995) 6670.
[20] N. Azuma, L. Kevan, J. Phys. Chem. 99 (1995) 5083.