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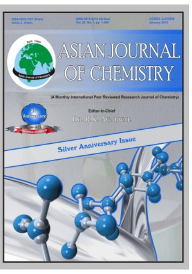

Vapour Phase Ethylation of Benzene Over ZSM-5 Synthesized in Fluoride Medium

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ZSM-5 zeolite (Si/Al ratio 50, 75 and 100) was hydrothermally synthesized in fluoride medium. Their crystal size and crystallinity were high. SEM images of synthesized material showed large elongated prismatic crystals. Their catalytic activity was examined for vapour phase ethylation of benzene between 200 and 400 ºC. The ethylbenzene conversion was high at 300 ºC compared with other temperatures. The selectivity of ethylbenzene was high at low ethanol content in the feed, but decreased with an increase in ethanol content. Among the diethyl benzene isomers the selectivity of *p*-diethyl benzene was higher than others. High selectivity of *p*-diethyl benzene was due to large crystal size and high crystallinity. Hence synthesis of ZSM-5 in fluoride medium could catalyze *para* selective ethylation of ethylbenzene. The same catalyst could also be applied to other selective alkylations.

Key Words: ZSM-5, Fluoride media, Benzene, Ethylation.

INTRODUCTION

ZSM-5 zeolite is the largely exploited catalyst in the petrochemical industries. Medium pore size, thermal and hydrothermal stabilities and strong acidity are some of the important characteristics for their main catalytic applications. The acidity can be tuned to desired extents altering by Si/Al ratios. This zeolite has been synthesized in alkaline medium and subjected to ion exchange to get H-form. Alkaline medium was reported to yield reduced crystallinity and surface area[1]. In contrast, synthesis of ZSM-5 in fluoride medium was reported to yield large crystal size and high crystallinity[2]. High crystallinity precludes external acid sites which are commonly observed over ZSM-5, synthesized in alkaline medium.

Generally ZSM-5 zeolite with external acid sites promotes isomerization of *p*-diethyl benzene to *meta*-diethyl benzne (*m*-DEB) at high temperatures. Hence it could be logical that ZSM-5 synthesized in fluoride medium, can be ideal for *para* selective ethylation of benzene to *p*-diethyl benzene suppressing its isomerization. ZSM-5 synthesized in fluoride medium was also reported to possess weak and medium acid sites without strong acid sites. It is an advantage such acid sites might not promote much isomerization. Hence in the present study, ethylation of benzene was carried out in the vapour phase with this interest of acquiring high selectivity to *p*-diethyl benzene using ethanol as alkylating agent. Olah *et al.*[3] reported alkylation and trans alkylation of benzenes over graphite-intercalated Lewis acid halides and per fluorinated resign sulphonic acid (nafion-H) catalyst. The reaction was studied between 125 and 210 ºC. The lifetime of aluminum halide catalysts was limited due to their leaching cause a sharp decline in the catalytic activity with time. But sulphonic acid resign catalyst showed better stability and good activity.

Vijaya ragavan *et al.*[4] also reported AlPO-5, MAPO-5, ZnAPO-5 and MnAPO-5 catalyst were used the products of ethyl benzene, *p*-diethyl benzene, *m*-diethyl benzene and poly alkyl benzene. Mn-AOP$_5$ was more effective catalyst than others. Conversion was maximum (47 %) at 400 ºC. ZSM-5 has been used in the mobile Badger process for the vapour phase alkylation of benzene with ethylene[5-7]. The same reaction was also studied over MCM-22[8,9]. However such reactions could not much importance in *para* selective product, but ZSM-5 synthesized in fluoride medium can be avoid further isomerization.

EXPERIMENTAL

Tetraethylorthosilicate (TEOS), aluminium sulphate, ammonium fluoride and phosphoric acid were purchased from Merck. Structural directing agent (tetrapropylammonium bromide) was purchased from Sigma Aldrich.

The gel-composition used for the synthesis of ZSM-5 is given below:

$0.07\,C_{12}H_{28}NBr: 1.0\,SiO_2: 0.01Al_2O_3:0.01P_2O_5:1.6\,NH_4F: 80\,H_2O$

ZSM-5 (50, 75 and 100) samples were synthesized in hydrothermal fluoride medium, but only difference is by their aluminium ratios alteration. The ZSM-5 (50) zeolite synthesized procedure as follows: 39 g of water was taken in a 100 mL of beaker, weighed accurately 0.08 g of phosphoric acid in it. 0.66 g of structural directing agent was added and allowed to constant stirred for an hour. The pH was raised to 5.5 ± 0.1 used 1:1 ammonia solution. The solution was kept an hour for aging, then follow by the additions 7.3 g of tetraethyl orthosilicate and 2.1 g of ammonium fluoride added in it. The gel was transferred into 75 mL Teflon lined auto clave at 170 ºC in a hot over for 3 days hydrothermal process. A complete crystalline material was obtained after filtration followed by dried in an oven at 110 °C for 12 h.

Detection methods: X-ray diffraction spectra of ZSM-5 catalysts were recorded on X-ray diffractometer (PAN alytical X' pert Pro) with CuK$_\alpha$ radiation source (λ = 1.54 Å) used liquid nitrogen-cooled germanium solid state detector. The diffractograms were recorded in the 2θ range 5-80º in step of 1.2º with count time of 10 sec at each point.

The surface morphology of the catalysts was viewed under high resolution scanning electron microscope (SEM-S-3400 N HITACHI) with an ion-sputter gold coated particles approximately 50-20 µm thick. Elemental composition was obtained with EDX of the same instrument. .

Vapour phase ethylation of benzene was carried out in down-flow vertical fixed bed reactor. 0.3 g of catalyst was placed in mid of the glass reactor and the catalyst supported by glass wool. Equal proportions of the reactants were fed into the reactor using infusion pump with proper flow time interval. The products were confirmed by GC-MS (gas chromatograph/mass spectrometer) (Perkin-Elmer Clarus 500).

RESULTS AND DISCUSSION

The XRD patterns of ZSM-5 (50, 75 and 100), 3 days synthesized samples are shown in Fig. 1. All these synthesized materials were showed, their resultant peaks similar with reported[10], but their relative intensity of crystallinity was higher than alkaline medium synthesized[1]. The high crystallinity was due to more silica and alumina can complete soluble in acidic pH of between 4 and 6. Hence, more atom transport to the gel composition for high crystallinity.

The SEM images of ZSM-5 (50, 75 and 100) zeolites are shown in Fig.2. All of them seem to be apt elongated prismatic crystals, but few tiny crystals were also present in it. These tiny crystals are commonly available during the ZSM-5 synthesis[11]. The relative tiny crystals very low compared with alkaline medium synthesized, and these tiny crystals were also established the optimum limitation of Si/Al ratio.

Catalytic activity

Effect of temperature: Ethylation of benzene was carried out over ZSM-5 (50, 75 and 100) at 200, 250, 300, 350 and 400 ºC with the feed ratio 1:1 (benzene : ethanol) and WHSV 2.775 h^{-1}. The products were mainly ethyl benzene with the minor products of *o*-diethyl benzene (*o*-DEB) and *m*-diethyl benzene. The results of ethyl benzene conversion and product selectivity are presented in Table-1. The benzene conversion over ZSM-5 (50) increased with the increase in temperature from 200 to 300 ºC and then decreased. The decrease in conversion was due to coke formation. The formation of coke was verified by physical observation. The following reaction

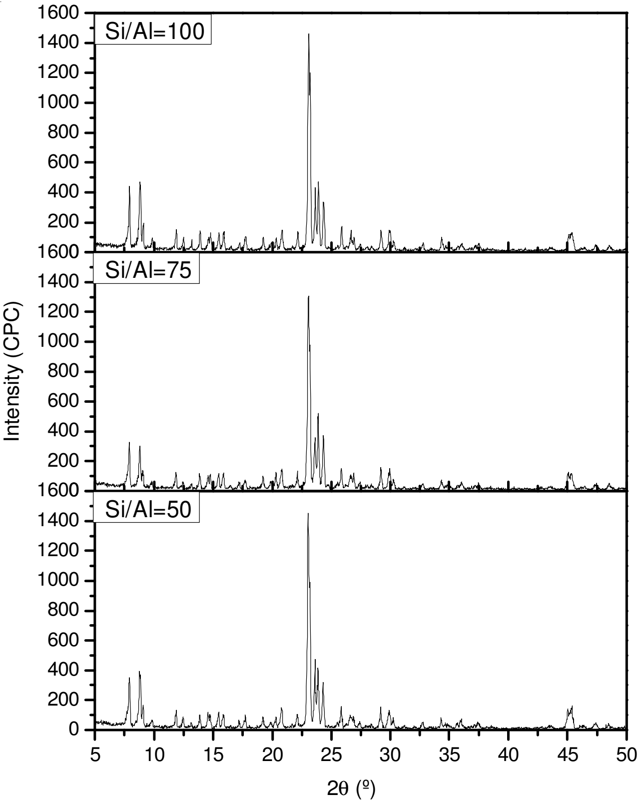


Fig. 1. XRD patterns of ZSM-5 Zeolites

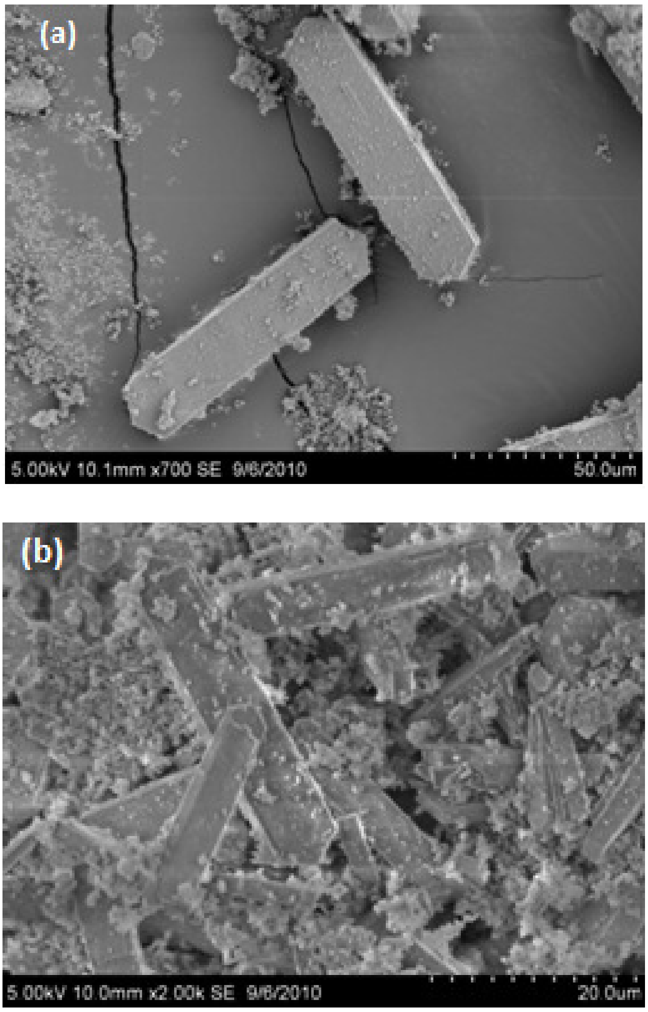


Fig. 2. SEM pictures of ZSM-5 (a) Si/Al = 50; (b) Si/Al = 75; (c) Si/Al = 100

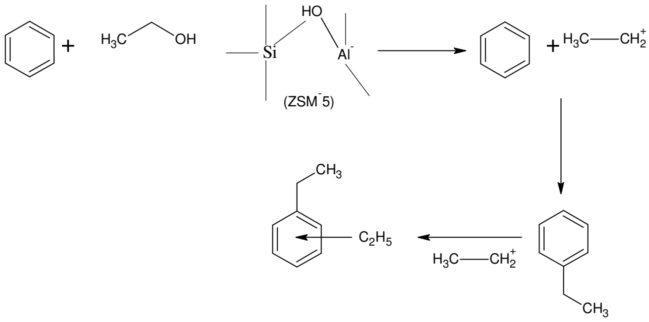
TABLE-1
EFFECT OF TEMPERATURE. REACTION CONDITION: FEED RATIO 1:1, Wt OF THE CATALYST 0.3 g, WHSV = 0.2775 h^{-1}

Catalysts	Temp. (°C)	Conv. (%)	Product selectivity (%)				
			EB	*p*-DEB	*m*-DEB	*o*-DEB	Others
ZSM-5 (50)	200	31	87	1	6	2	4
	250	34	89	2	6	1	2
	300	39	91	2	5	2	0
	350	31	82	3	7	1	7
	400	25	78	3	9	1	9
ZSM-5 (75)	200	23	89	1	8	1	1
	250	28	90	2	5	2	1
	300	35	91	3	4	1	1
	350	29	87	4	6	1	2
	400	20	85	4	8	1	2
ZSM-5 (100)	200	11	89	1	9	1	0
	250	13	93	0	6	1	0
	300	19	94	0	6	0	0
	350	16	89	3	7	0	1
	400	10	87	4	7	0	2

EB = Ethyl benzene, DEB = Diethyl benzene.

Scheme-I illustrates ethylation of benzene. Ethanol is chemisorbed on Bronsted acid sites to form ethyl cation which make electrophilic attack on benzene to form mono and diethyl benzenes. Although in the channel intersection of the zeolite (9 Å), all the three diethyl benzene isomers could be formed but EB was the major product since the alcohol content 1:1 feed ratio. The selectivity of the products showed a higher value for ethyl benzene than the diethyl benzene isomers. The selectivity of ethyl benzene increased with an increase in temperature slowly but at 350 and 400 °C it decreased steadily. The decrease was due to its conversion of di and poly alkyl benzene. Consecutive alkylation of ethyl benzene to diethyl benzene is also on endothermic process[12]. Formation of di and poly alkyl benzene was favour at high temperature.

The same reaction was also studied over ZSM-5 (75 and 100) and the results are presented in the same Table. These catalysts also showed an increase in conversion with an increased in temperature from 200 to 300 °C and then decreased thereafter. The product selectivity also followed the same trend that of ZSM-5 (50): the selectivity of *p*-diethyl benzene was higher than diethyl benzene isomers due to high crystallinity and large crystal size.



Scheme-I: Ethylation of benzene and ethyl benzene isomers

Effect of feed ratio: The effect of feed ratios (benzene: ethanol) was studied at 300 °C over ZSM-5 (50). The results are presented in Table-2. The ethyl benzene conversion increased from 1:1 to 1:2, but decreased at 1:3 and 1:4. The high conversion at 1:2 was due to increase the number of ethyl cations for ethylation. The decreased at 1:3 and 1:4 was due to dilution of benzene. Decrease in conversion with an increase in the content of alkylating agent was also reported in the literature[13]. The selectivity of ethylbenzene decreased with increase in alcohol content of the feed established consecutive alkylation. The selectivity of *m*-diethyl benzene was very low due to large crystal size and high crystallinity. The observation suggested that the route of converting benzene to diethyl benzene directly. The high selectivity of ethylbenzene compared to all other products even at high alcohol content in the feed.

TABLE-2
EFFECT OF FEED RATIOS. REACTION CONDITIONS: CATALYST = ZSM-5 (50); CATALYST 0.3 g; TEMP. = 300 °C

Catalysts	Feed ratios	Conv. (%)	Product selectivity (%)				
			EB	*p*-DEB	*m*-DEB	*o*-DEB	Others
ZSM-5 (50)	1:1	39	91	5	2	2	0
	1:2	46	76	16	4	2	2
	1:3	38	69	26	3	1	1
	1:4	29	61	33	2	2	2

EB = Ethyl benzene; DEB = Diethyl benzene

Effect of weight hourly space velocity (WHSV): The effect of weight hourly space velocity on the ethylbenzene conversion and product selectivity was studied at 2.832, 5.455, 8.183 and 10.917 h^{-1} and the results are presented in Table-3. With increase in weight hourly space velocity the conversion was decreased. The selectivity of the ethyl benzene gradually increased due to suppression of consecutive alkylation. It was also confirmed by decreased in the selectivity of *p*-diethyl benzene and *m*-diethyl benzene.

TABLE-3
EFFECT OF WEIGHT HOURLY SPACE VELOCITY. REACTION CONDITIONS: CATALYST = ZSM-5(50); CATALYST Wt = 0.3 g; TEMP. = 300 °C; FEED RATIO 1:2

Feed ratios	Conversion (%)	Product selectivity (%)				
		EB	*p*-DEB	*m*-DEB	*o*-DEB	Others
2.832	46	76	16	4	2	2
5.455	33	79	15	3	1	2
8.183	29	83	13	2	1	1
10.970	23	89	10	1	0	0

EB = Ethyl benzene; DEB = Diethyl benzene

Effect of time on stream: The effect of time on stream at 6 h with feed ratio 1:1 and WHSV 2.74 h^{-1} at 300 °C was studied. The results are presented in Table-4. With increased in time on stream a slight decrease conversion was noted at the end of 6 h. Hence coke might be form at very slow rate. The selectivity of EB remained the same throughout the time on stream. Similarly the selectivity of *m* and *p*-diethyl benzene also remained the same. Hence as said above the reaction did not promote coke formation.

TABLE-4
EFFECT OF TIME ON STREAM. REACTION CONDITIONS: CATALYST: ZSM-5(50); CATALYST Wt. = 0.3 g; WHSV: 2.74 h^{-1}; TEMP. = 300 °C; FEED RATIO 1:1

Time on Stream (h^{-1})	Conversion (%)	EB	*p*-DEB	*m*-DEB	*o*-DEB	Others
1	41	76	16	4	2	2
2	43	75	20	3	1	1
3	42	76	21	2	1	0
4	42	76	18	3	2	1
5	40	77	17	3	1	2
6	38	79	17	3	1	0

EB = Ethyl benzene; DEB = Diethyl benzene

Conclusion

Hence ethylation of benzene could be made to give ethylbenzene to high selectivity with the feed ratio 1:2. The selectivity of diethyl benzene could also be enhanced by increase the alcohol content in the feed. Suppression of *o*-diethyl benzene and *m*-diethyl benzene was essentially due to high crystallinity and large crystal size. Hence the same catalyst could be very active for *para* selective ethylation of ethylbenzene. Even for *para* selective alkylation of other alkyl aromatics this catalyst could be convenient.

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