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Transalkylation of ethyl benzene with triethylbenzene over ZSM-5 zeolite catalyst

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ABSTRACT

Transalkylation of 1,3,5-triethylbenzene (TEB) with ethylbenzene (EB) has been studied over ZSM-5 zeolite using a riser simulator reactor with respect to optimizing DEB yield. The reaction temperature was varied from 350 to 500 °C with contact time ranging from 3 to 15 s to report on the effect of reaction conditions on TEB conversion, DEB selectivity and isomerization of TEB. The transalkylation of TEB with EB was compared with the reactions of pure 1,3,5-TEB and EB (disproportionation, isomerization and cracking). A synergistic effect was observed on the conversion of 1,3,5-TEB and DEB yield. The 1,3,5-TEB conversion increased from 40% to 50% with simultaneous increase in the DEB selectivity from 17% to 36% in transalkylation reaction (EB + 1,3,5-TEB) as compared with the reaction of pure 1,3,5-TEB. It was found that pure 1,3,5-TEB underwent cracking reaction to produce DEB and EB. The isomerization of 1,3,5-TEB was more active at low temperature while cracking was more active at high temperature. The temperature of 350 °C was observed as the optimum for production of maximum amount of DEB. Kinetic parameters for the disappearance of 1,3,5-TEB during its transformation reaction via cracking and isomerization pathways were calculated using the catalyst activity decay function based on time-on-stream (TOS). The apparent activation energies decrease in order $E_{\text{secondary cracking}} > E_{\text{primary racking}} > E_{\text{isomerization}}$ for ZSM-5 catalysts.

1. Introduction

Reactions of aromatic hydrocarbons represent the most important part of petrochemistry and zeolites are indispensable catalysts for these applications [1]. Alkylations [2] disproportionations [3,4] isomerizations [5], and transalkylation reactions [6,7] are of the primary interest for upgrading of less-valuable aromatics.

Considerable industrial demand recently appeared for selective production of diethylbenzene. The *para*-diethylbenzene (*p*-DEB) is a high value adsorbent commonly for *p*-xylene adsorptive separation in processes UOP Parex and IFP eluxyl [8–11]. The *p*-DEB is key starting material for production of *p*-divinyl benzene an important monomer for the production of copolymers, such as ion-exchange resin and viscosity modifiers of lubricant oil. In contrast and similarly to the situation with xylene isomers, *o*-DEB and *m*-DEB have lower market value. Due to the fact that all three isomers of DEB posses similar physical properties their separation is a difficult task and direct highly selective preparation of *p*-DEB is still rather challenging.

Recently, two processes of production of *p*-DEB, i.e. EB alkylation with either ethanol [12,13] or ethylene [14] and shape selective EB disproportionation were reported [15–17]. Initially, Karge et al. [18,19] used EB disproportionation to characterize acid forms of zeolites. Large-pore zeolites exhibited an induction period but their selectivities to *p*-diethylbenzene were close to thermodynamic ones. On the other hand, significant increase in *p*-DEB selectivity was observed for ZSM-5 zeolite. Following this pioneer work, numerous studies were carried out over USY, Beta, MCM-22, ZSM-5 [20–22]. The composition of the diethylbenzene isomers in the reaction mixtures was usually limited by thermodynamics leading to an equilibrium composition with relative low amount of the *p*-DEB compared with the *m*-DEB. This resulted in the conclusion that the mechanism of zeolite-catalyzed ethylbenzene disproportionation is very similar to toluene disproportionation i.e. differences in diffusion coefficients among *para*, *meta*, and *ortho* diethylbenzenes play an important role [23]. Further on, proper deactivation of the external surface of zeolite crystals by Mg or P compounds enhances the selectivity up to 98–99% [23].

Detailed mechanistic study by Huang et al. [24,25] using solid state ^{13}C NMR evidenced that zeolite acidity and pore size strongly

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Nomenclature

C_i	concentration of specie i in the riser simulator (mol/m^3)
CL	confidence limit
E_i	apparent activation energy of ith reaction (kJ/mol) [E_1 is the activation energy for 1,3,5-TEB cracking reaction; E_2 is the activation energy for 1,3,5-TEB isomerization reaction; $E3$ is the activation energy for DEB cracking reaction]
k_i	apparent kinetic rate constant (m^3/kgcat s) [k_1 is the rate constant for 1,3,5-TEB cracking reaction; k_2 is the rate constant for 1,3,5-TEB isomerization reaction; k_3 is the rate constant for DEB cracking reaction] = $k_{0i}\exp[-(E_i/R)(1/T-1/T_0)]$
k_{0i}	pre-exponential factor in Arrhenius equation defined at an average temperature (m^3/kgcat s), units based on first-order reaction
MW_i	molecular weight of specie i
R	universal gas constant (kJ/kmol K)
t	reaction time (s)
T	reaction temperature (K)
T_0	average temperature of the experiment
V	volume of the riser (45 cm^3)
W_c	mass of the catalysts (0.81 gcat)
W_{hc}	total mass of hydrocarbons injected in the riser (0.162 g)
y_i	mass fraction of ith component (wt%)

Greek letter

α	apparent deactivation constant (s^{-1}) (TOS model)

affect their catalytic behavior in EB disproportionation. It was observed that EB disproportionation occurred at low reaction temperatures over large-pore zeolite H-Y in contrast to medium-pore ZSM-5 zeolites. This can be the effect of diffusion as ZSM-5 zeolite as acid sites in ZSM-5 are of much higher acid strength. Generally, ethylbenzene disproportionation proceeds via alkylcarbenium mechanism resulting in secondary reactions leading to coke formation.

Recently Al-Khattaf et. al. [26] performed catalytic study of EB disproportionation over ZSM-5 zeolite using a novel riser simulator reactor system. It was observed that disproportionation was a dominant reaction at temperatures 350–400 °C while cracking reaction became more significant above 400 °C. Two reaction mechanisms leading to different product distributions proceeding at low and high temperatures were postulated. The DEBs can also be produced by transalkylation of triethylbenzene (TEB) with ethylbenzene (EB), however, very rare literature data are available [1]. Al-Khattaf et al. [27] reported on a similar reaction of transalkylation of toluene and trimethylbenzene. Transalkylation proceeded with a higher reaction rate resulting into the production of larger amount of xylene as compared with transformation of pure toluene or trimethylbenzene. Consequently, Akhtar and Al-Khattaf [28] performed transalkylation of EB, toluene and benzene with 1,3,5-TEB over USY steamed zeolite. Conversion of TEB was observed to depend upon the nature of alkyl substituent on the benzene ring of the partner reactant. With increasing length of the chain on the benzene ring the conversion of TEB increased.

The objection of this investigation was the transalkylation of 1,3,5-TEB with EB over ZSM-5 zeolite in a fluidized-bed reactor along with its kinetic study. The study focuses on the effect of contact time and reaction temperature related to the DEB yields and isomer distributions of DEB and TEB. Based on the experimental data, kinetic model of TEB transalkylation with EB is also proposed.

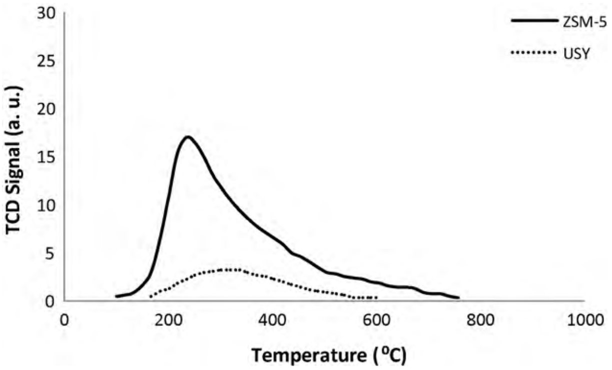


Fig. 1. Temperature programmed desorption (TPD) of ammonia for ZSM-5 and USY catalysts.

2. Experimental

2.1. Catalysts

The ZSM-5 zeolite used in this study was obtained from Davison Grace while ultrastable Y zeolite (USY) from Tosoh. The protonic forms of both zeolites were prepared by ion-exchange with NH_4NO_3 to replace the sodium cations followed by calcination. Finally, the H-ZSM-5 and H-Y zeolites were spray-dried using kaolin as the filler and silica sol as the binder. The resulting catalyst particles of size 60 μm have the composition: 30 wt% zeolite, 50 wt% kaolin, and 20 wt% silica sol. Sodium was removed also for the pelletized catalysts. Finally, the catalyst was calcined for 2 h at 600 °C. The calcined USY zeolite was further treated with 100% steam at 760 °C for 5 h to produce USY-steamed catalyst (labeled as FCC-SY).

Analytical grade (99% purity) pure ethylbenzene (EB), and 1,3,5-triethylbenzene (TEB) were obtained from Sigma–Aldrich. All chemicals were used as received without any further purification.

2.2. Catalyst characterization

Textural and acidic properties of both catalysts were studied as follows. The BET surface area was determined using a NOVA 1200 (Quantachrome). The acidic properties of the catalysts were evaluated using NH_3 temperature-programmed desorption (NH_3-TPD). In all experiments, 50 mg of sample was out-gassed at 400 °C for 30 min in a stream of helium and then cooled to 150 °C. At that temperature NH_3 was adsorbed on the sample by injecting pulses of 2 ml/pulse. After the adsorption of NH_3, the zeolite sample was flushed at 150 °C for 1 h with helium to remove an excess of NH_3 and then temperature was raised with a ramp of 30 °C/min up to 1000 °C in a helium stream of 30 ml/min. A thermal conductivity detector was used to monitor the desorbed NH_3 (Fig. 1).

Acidic and textural properties of catalysts under study are summarized in Table 1. It is evidenced that the concentration of acid sites in ZSM-5 (0.233 mmol/g) is much higher than for USY (0.033 mmol/g). Also, from Fig. 1, it looks that the acid strength of ZSM-5 sites is higher than for USY.

Table 1
Characterization of zeolite catalysts under study.

Catalyst	Acidity (mmol/g)	BET surface area (m^2/g)	Total pore volume (cm^3/g)
ZSM-5	0.233	70	0.325
FCC-USY	0.033	155	0.23

Table 2
Product distribution (mol%) at various reaction conditions for pure 1,3,5-TEB using ZSM-5 catalyst.

Temp (°C)/time (s)	Gases	Benzene	Toluene	EB	DEB			1,2,4-TEB	1,2,3-TEB	1,3,5-TEB	Coke C (wt%)
					m-DEB	*p*-DEB	*o*-DEB				
500											
3	8.15	0.97	0.25	1.20	1.12	0.21	0.23	1.60	0.09	86.19	
5	11.28	1.50	0.37	1.72	1.70	0.29	0.36	2.77	0.11	79.91	
7	14.82	2.01	0.44	2.27	2.23	0.37	0.47	3.57	0.16	73.67	
10	18.29	2.78	0.58	2.66	2.67	0.37	0.61	4.79	0.19	67.07	
15	22.19	3.40	0.68	3.19	3.03	0.43	0.71	5.92	0.26	60.19	0.148
450											
3	6.32	0.47	0.00	1.07	1.23	0.25	0.25	2.08	0.00	88.33	
5	7.90	0.72	0.20	1.50	1.70	0.33	0.50	3.32	0.12	83.71	
7	9.20	0.86	0.21	1.75	1.95	0.38	0.44	4.19	0.16	80.87	
10	11.73	1.20	0.27	2.27	2.52	0.46	0.58	5.81	0.22	74.95	
15	13.76	1.60	0.34	2.82	3.00	0.53	0.73	7.63	0.30	69.29	0.100
400											
3	2.95	0.25	0.00	0.55	0.90	0.22	0.19	2.22	0.07	92.65	
5	4.38	0.26	0.00	0.86	1.46	0.32	0.15	4.14	0.14	88.29	
7	4.48	0.26	0.00	0.93	1.61	0.37	0.36	5.05	0.16	86.76	
10	6.15	0.30	0.00	1.33	2.14	0.49	0.49	6.59	0.23	82.29	
15	7.96	0.37	0.00	1.78	2.78	0.61	0.66	8.80	0.30	76.73	0.128

2.3. *The riser simulator reactor*

All experiments were carried out in the riser simulator reactor. This reactor is novel bench scale equipment with internal recycle unit invented by de-Lasa and the details of the riser simulator were published elsewhere [29].

Catalytic experiments were performed at a catalyst/reactant ratio of 5 (weight of catalyst = 0.81 g) for different residence times of 3, 5, 7, 10, 13, and 15 s and at reaction temperatures of 350, 400, 450 and 500 °C. The equimolar reactant mixture of EB and 1,3,5-TEB was used, which is equivalent to 40:60 wt% of EB: 1,3,5-TEB respectively. The transformation of pure 1,3,5-TEB was also performed to have a comparison with transalkylation reaction. The reproducibility in the conversion and selectivities was in the range of ±2%.

The reaction mixture was analyzed in an Agilent 6890N gas chromatograph with a flame ionization detector and a capillary column INNOWAX (length – 60 m, i.d. 0.32 mm).

After each kinetic run, Argon was fed to the reactor bed and the reactor was cooled down. Then the reactor was opened and the spent catalyst removed and the amount of coke was determined by a combustion method using a carbon analyzer multi EA 2000 (Analytikjena). A small amount of the spent catalyst (0.35 g) was used for the analysis while oxygen is supplied to the unit directly. The

Table 3
Product distribution (mol%) at various reaction conditions for 40 wt% EB and 60 wt% TEB using ZSM-5 zeolite catalyst.

Temp (°C)/time (s)	Gases	Benzene	Toluene	EB	DEB			1,2,4-TEB	1,2,3-TEB	1,3, 5-TEB	Coke C (wt%)
					m-DEB	*p*-DEB	*o*-DEB				
500											
3	8.61	3.75	0.34	44.06	1.67	0.42	0.24	0.81	0.03	40.06	
5	12.40	5.45	0.45	41.18	2.32	0.63	0.38	1.26	0.06	35.87	
7	15.35	6.78	0.53	38.54	2.94	0.85	0.50	1.78	0.08	32.65	
10	18.58	8.62	0.67	35.60	3.19	0.87	0.57	2.08	0.09	29.74	
13	21.30	10.62	0.79	32.74	3.63	1.02	0.67	2.67	0.12	26.44	
15	23.74	11.60	0.87	30.90	3.70	1.00	0.71	2.76	0.12	24.60	0.189
450											
3	6.52	2.87	0.26	46.04	1.94	0.60	0.29	1.06	0.04	40.38	
5	8.83	3.99	0.33	43.47	2.65	0.87	0.43	1.62	0.07	37.73	
7	11.32	5.62	0.43	43.81	2.96	0.99	0.50	1.97	0.08	32.31	
10	13.26	6.37	0.47	39.13	3.78	1.33	0.67	2.82	0.12	32.06	
13	13.27	6.78	0.48	37.84	4.62	1.79	0.83	3.72	0.15	30.52	
15	17.18	8.42	0.61	35.24	4.55	1.62	0.87	3.69	0.15	27.67	0.208
400											
3	2.51	1.12	0.10	48.49	1.80	0.63	0.25	1.01	0.04	44.05	
5	3.51	1.74	0.14	46.76	2.46	0.95	0.38	1.69	0.06	42.33	
7	4.53	2.35	0.17	45.23	3.22	1.33	0.52	2.45	0.09	40.11	
10	5.78	3.22	0.22	43.52	4.09	1.77	0.69	3.30	0.12	37.29	
13	7.31	4.28	0.28	41.10	4.85	2.16	0.84	4.18	0.16	34.84	
15	8.51	5.28	0.36	38.75	5.09	2.28	0.90	4.39	0.17	34.27	0.356
350											
3	0.70	0.46	0.00	50.69	1.56	0.52	0.20	0.88	0.00	44.99	
5	0.85	0.69	0.00	49.20	2.35	0.93	0.36	1.71	0.05	43.87	
7	1.01	0.90	0.00	48.66	2.71	1.15	0.51	2.22	0.07	42.76	
10	1.39	1.29	0.00	48.06	3.61	1.64	0.60	3.06	0.10	40.25	
13	1.98	1.76	0.09	45.75	4.50	2.14	0.77	4.08	0.13	38.80	
15	2.58	2.37	0.12	44.04	5.17	2.55	0.90	4.77	0.15	37.34	0.507

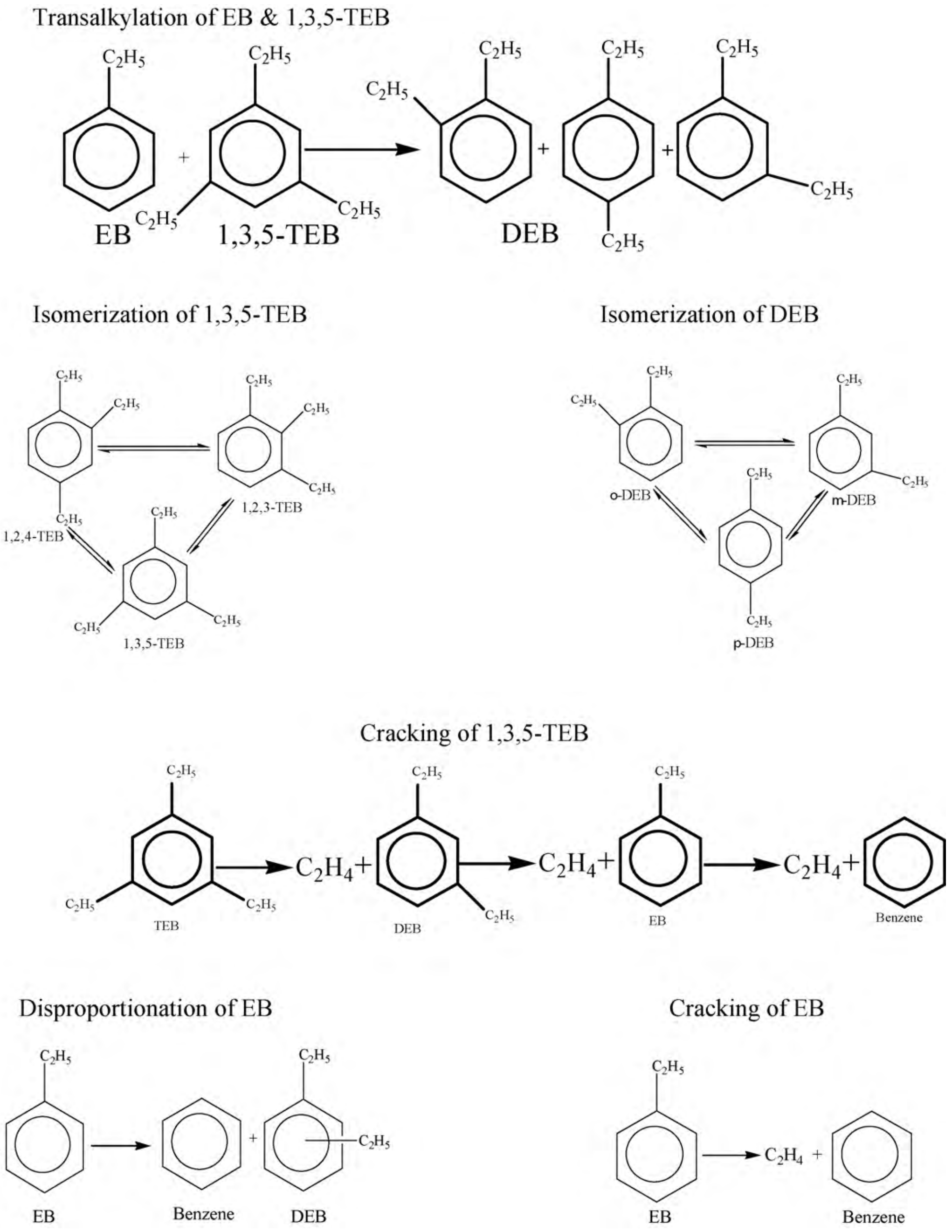


Fig. 2. Reactions occurring during transalkylation reaction of ethylbenzene (EB) and 1,3,5-triethylbenzene (TEB).

coke formed on the sample during the reaction was burned completely converting the carbonaceous deposits into carbon dioxide, which was determined.

3. Results and discussion

The transalkylation of 1,3,5-TEB with EB at different reaction temperatures and contact times using ZSM-5 zeolite was studied and results were compared with the transformation of pure 1,3,5-TEB and EB under identical reaction conditions (cf. Tables 2 and 3). The transalkylation of 1,3,5-TEB with EB was carried out at a molar ratio of EB:TEB, 1:1 (equivalent to 40:60 wt%, respectively). The results of transalkylation reaction has shown that the main transalkylation reaction of EB with 1,3,5-TEB producing DEB is accompanied by several side reactions as summarized in Fig. 2. It has been noticed that reactivity of 1,3,5-TEB increases with increasing reaction temperature. Simultaneously, 1,3,5-TEB undergoes isomerization to produce 1,2,4-TEB and 1,2,3-TEB.

3.1. Transformation reaction of pure ethylbenzene (EB)

Disproportionation reaction of pure ethylbenzene over ZSM-5 catalyst has been reported in our earlier publication [26]. We observed that the increase in the reaction temperature favored cracking reaction. The ratio of *p*-DEB/*m*-DEB varied from 0.70 to 0.88. The kinetic parameters for EB disproportionation were also calculated using catalyst activity decay function based on time-on-stream (TOS). The apparent activation energy for cracking reaction was observed to be higher than that of disproportionation reaction.

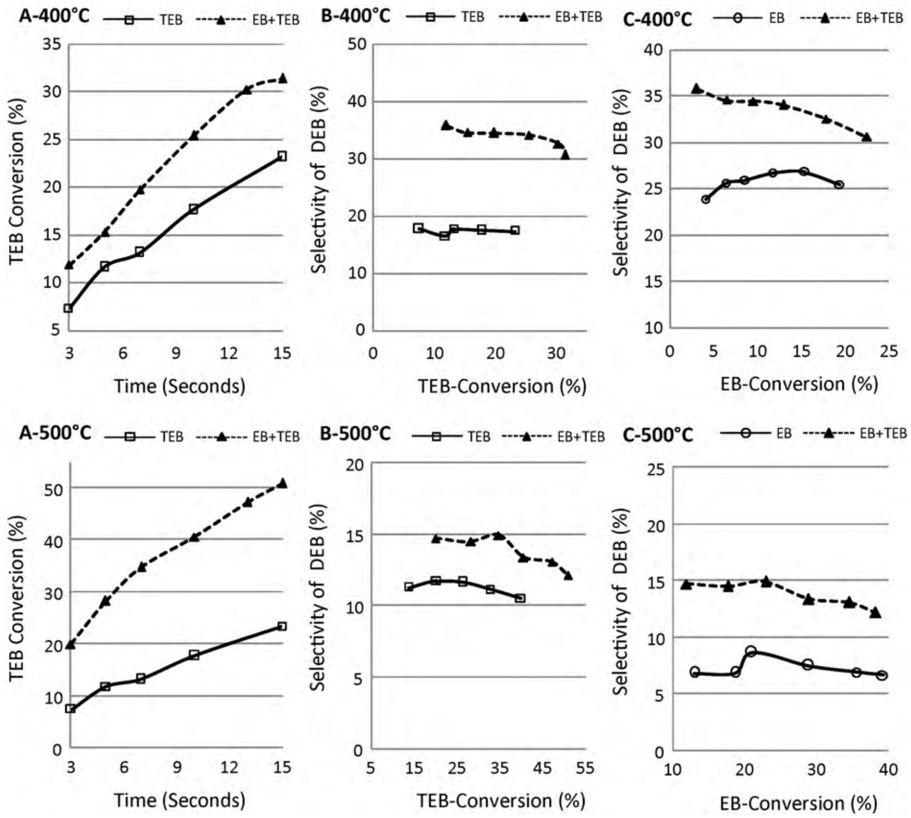


Fig. 3. (A) The conversion of TEB vs. contact time for the pure 1,3,5-TEB and the mixture of EB and 1,3,5-TEB. (B) The selectivity (%) of DEB with respect to the TEB-conversion (%) for the pure 1,3,5-TEB and the mixture of EB and 1,3,5-TEB. (C) The selectivity (%) of DEB with respect to the EB-conversion (%) for the pure EB and the mixture of EB and 1,3,5-TEB at 400 and 500 °C using ZSM-5 catalyst. The data of pure EB (for comparison) has been taken from Ref. [26].

3.2. Transformation of pure 1,3,5-triethylbenzene

The experimental results from transformation of pure 1,3,5-TEB at different reaction temperatures and different contact times using ZSM-5 catalysts are presented in Table 2. It was observed that maximum TEB conversion (40%) occurred using contact time of 15 s at a reaction temperature of 500 °C. The product distribution has shown that maximum amounts of DEB (4.2%), EB (2.3%), benzene (3.4%) and gases (22.2%) were formed at contact time of 15 s at reaction temperature of 500 °C. This indicates that 1,3,5-TEB undergoes cracking stepwise reaction. In the first step it produces DEB while in second step EB is formed and in third step even benzene. It is important to note that tetraethylbenzenes were not detected in any appreciable amount indicating that TEB does not particularly undergo any disproportionation reaction. It might be connected with easy dealkylation producing ethylene from original ethyl group of TEB. In addition, 1,3,5-TEB isomerizes to 1,2,4-TEB and 1,2,3-TEB isomers. The amount of 9.1% of 1,2,4-TEB and 1,2,3-TEB from 1,3,5-TEB was achieved after 15 s at 400 °C. These results indicate that low temperature favors isomerization of 1,3,5-TEB while higher temperature favors cracking reaction. Similar results were obtained for trimethylbenzene over different zeolites by Čejka et al. [30].

3.3. Transalkylation of 1,3,5-TEB with EB vs. results of transformations of pure 1,3,5-TEB and EB

3.3.1. Reactivity

The conversion of 1,3,5-TEB during transalkylation of 1,3,5-TEB with EB as well as of pure 1,3,5-TEB at 400 and 500 °C for different contact times is depicted in Fig. 3. Conversion of 1,3,5-TEB increases when EB has been added to the reaction mixture indicating a synergistic effect due to transalkylation of EB with TEB. It is not clear if this transalkylation proceeds via bimolecular or dealkylation/alkylation mechanism. The conversion of 1,3,5-TEB increases with prolongation of the contact time and increasing temperature. The maximum conversion of 1,3,5-TEB (50.8%) was observed at 500 °C after 15 s when using a mixture of 1,3,5-TEB and EB.

3.3.2. The production of diethylbenzene (DEB)

The selectivity to DEB in transalkylation of 1,3,5-TEB with EB as well as of pure EB and pure 1,3,5-TEB is given for different conversions of EB and TEB in Fig. 3 at reaction temperatures of 400 and 500 °C. Fig. 3 shows an increase in the conversion of TEB when EB has been added to the 1,3,5-TEB. However, the EB conversion decreases for the mixture EB and TEB at 500 °C as compared with the pure EB. A lower conversion of EB in the reaction mixture of EB and TEB can be due to some dealkylation of TEB to DEB and finally to EB. Fig. 3 clearly shows that selectivity to DEB decreases with increasing reaction temperature for pure EB feed and for the mixture of EB and 1,3,5-TEB. In contrast, it is almost stable for pure 1,3,5-TEB. The behavior of 1,3,5-TEB can be explained in terms of the production of DEBs. As for pure 1,3,5-TEB, cracking reaction leads to a mixture of DEBs [26,30,31] while DEBs are produced by disproportionation reaction of EB or by transalkylation from the mixture of EB and TEB. Therefore, the increase in the rate of the cracking reaction at higher temperatures causes a relative decrease in the rate of disproportionation and transalkylation. This results in a decrease in the selectivity to DEB for pure EB and mixture of EB and TEB, respectively. The overall selectivity to DEBs is much higher for the reaction mixture of the EB and 1,3,5-TEB than for pure EB and pure TEB. It indicates a synergistic effect of transalkylation of EB and TEB. The maximum selectivity of DEB (52.7%) was observed during transalkylation of EB and TEB at 350 °C at contact time of 3 s

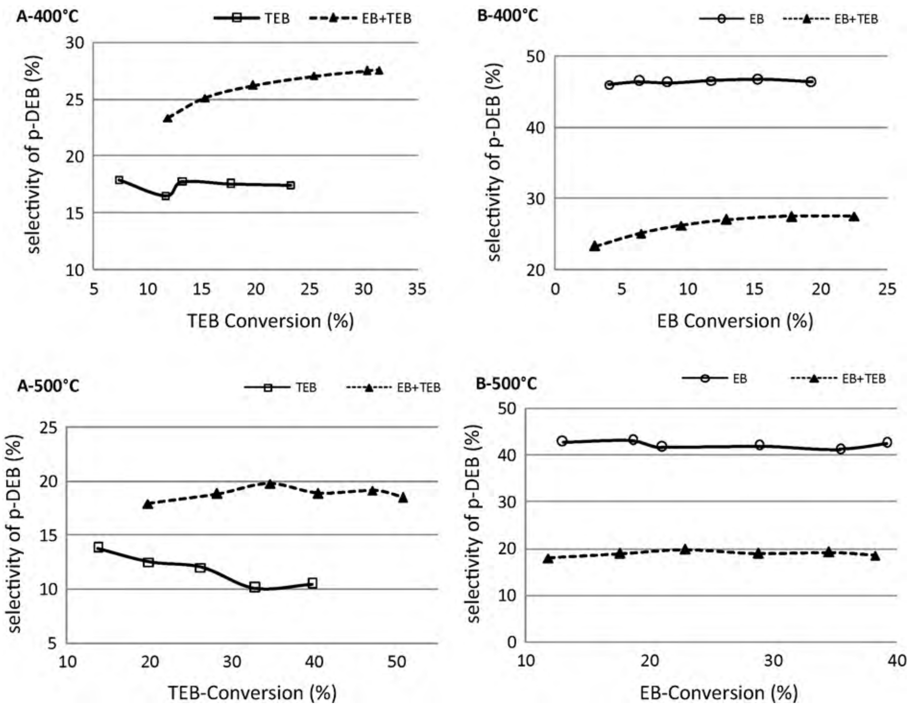


Fig. 4. The selectivity to *p*-DEB (%) with respect to the (A) TEB-conversion (%) and (B) EB-conversion (%) at 400 and 500 °C for pure EB, pure 1,3,5-TEB and the mixture of EB and 1,3,5-TEB using ZSM-5 catalyst. The data of pure EB (for comparison purpose) has been taken from Ref. [26].

at a TEB conversion of only 10%. Therefore, we can conclude that at 350 °C with a contact time of 3 s the transalkylation reaction is most favorable resulting into maximum selectivity to DEB.

Selectivity to *p*-DEB in DEB during the transalkylation of 1,3,5-TEB with EB as well as in the reaction of EB and 1,3,5-TEB for different conversions of EB and TEB is provided in Fig. 4. It is observed that selectivity to *p*-DEB is the highest (∼47%) in the reaction of EB while it is the lowest (∼15%) for 1,3,5-TEB. The mixture of EB and 1,3,5-TEB provides selectivity to *p*-DEB of ∼27% at 400 °C. It has been reported in the literature [32] that the thermodynamic equilibrium selectivity to *p*-DEB is ∼30%. Since the feed is 1,3,5-TEB, dealkylation of any ethyl group results in the formation of *m*-DEB. *m*-DEB then undergoes isomerization to *ortho* and *para* DEB isomers. 1,3,5-TEB can also isomerize to 1,2,4-TEB and 1,2,3-TEB. In the case of EB, the DEB is produced by disproportionation reaction and formation of *p*-DEB can be favored from steric reasons inside the zeolite channel system. Therefore, the disproportionation of EB occurring mainly inside the channels of ZSM-5 zeolite might not lead to the formation of thermodynamic equilibrium of DEB isomers but already some preference for *p*-DEB can be expected [22]. The diffusion rate of DEB isomers follows the order *p*-DEB ≫ *o*-DEB > *m*-DEB, hence *p*-DEB diffuse out of the pores more rapidly. A similar behavior has been observed in xylene isomerization by Mirth et al. [33]. The diffusion coefficients of *p*-xylene: *m*-xylene has been reported to be 1000:1. It is important to note that in the reaction of TEB the ratio of *m*-DEB:*p*-DEB:*o*-DEB obtained is 5:1:1. For the mixture of EB and 1,3,5-TEB the ratio is 6:3:1 and for EB the *o*-DEB isomer was not detected at all and *m*-DEB: *p*-DEB ratio was ∼1:1. Literature data reports the thermodynamic ratio of *m*-DEB:*p*-DEB:*o*-DEB around 6:3:1 [28,34]. It is very clear that in the case of pure EB, DEB isomers do not follow the thermodynamic equilibrium due to the product shape selectivity of ZSM-5 zeolite. Therefore it can be concluded that a mixture of EB and TEB results into thermodynamic distribution of all three isomers of DEB. Whereas for pure EB and TEB the thermodynamic equilibrium is not followed due to kinetic (in the case of EB disproportionation) and diffusion effects.

3.3.3. Isomerization of TEB

The 1,3,5-TEB can isomerize to 1,2,4-TEB and 1,2,3-TEB. The selectivity to 1,2,4-TEB and 1,2,3-TEB formed during the transalkylation of 1,3,5-TEB with EB as well as of pure 1,3,5-TEB is provided for different conversions of 1,3,5-TEB in Fig. 5. It has been observed

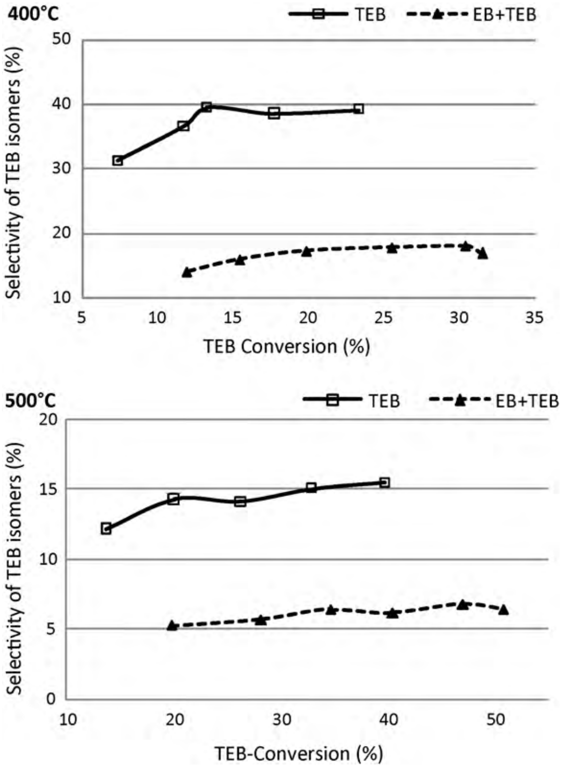


Fig. 5. The selectivity to 1,3,5-TEB-isomers (1,2,4-TEB and 1,2,3-TEB) with respect to the TEB conversion at 400 and 500 °C for pure 1,3,5-TEB and the mixture of EB and 1,3,5-TEB.

that the rate of isomerization of pure 1,3,5-TEB is much higher when compared with the transalkylation of 1,3,5-TEB with EB. The maximum selectivity to 1,2,4-TEB and 1,2,3-TEB obtained is 39% after 15 s at 400 °C. It is also observed that the selectivity to 1,2,4-TEB and 1,2,3-TEB decreases with increasing reaction temperature. The selectivity drops from 39% to 17% at 400 °C with a contact time of 15 s when EB was added to the feedstock of 1,3,5-TEB. The decrease in the rate of isomerization can be explained as follows. For 1,3,5-TEB only, cracking and isomerization reactions take place while for a mixture of EB and TEB transalkylation proceed with a large extent decreasing the isomerization reaction of 1,3,5-TEB. Large extent of transalkylation reaction was recently reported also for the reaction of 1,2,4-trimethylbenzene with toluene in the same temperature range [35].

The ratio of 1,2,4-TEB:1,2,3-TEB around 30 was observed for pure TEB as well as a mixture of EB and TEB at 400 °C. A similar value has been reported by Akhtar and Al-Khattaf [28] during transalkylation of EB with TEB using FCC-Y zeolite. In contrast, the reported ratio of 1,2,4-trimethylbenzene:1,2,3-trimethylbenzene isomers is only about 10 [28,34]. The higher ratio of 1,2,4-TEB:1,2,3-TEB as compared with that of 1,2,4-TMB:1,2,3-TMB is probably due to the fact that ethyl group is bulkier than that of methyl group. Thus, the presence of three ethyl groups on three adjacent carbon atoms on a benzene ring in 1,2,3-TEB is less likely as compared with 1,2,3-TMB due to steric hindrance. Moreover, the 1,2,4-TEB is produced by shifting of only one ethyl group on the same benzene ring of 1,3,5-TEB, while in case of 1,2,3-TEB two ethyl groups have to shift their positions.

3.3.4. *Formation of benzene and gaseous products*

The amount of light gases and benzene (mol%) produced during transalkylation of 1,3,5-TEB with EB as well as of pure 1,3,5-TEB is provided in Tables 2 and 3.

The amount of gaseous products is higher in the case of mixture of EB and 1,3,5-TEB as compared with that of pure EB and pure 1,3,5-TEB. The gases are produced during cracking reaction. Generally, the rate of cracking reaction increases with increasing reaction temperature [26,30,31].

The amount of benzene produced from pure EB is much higher compared with pure 1,3,5-TEB or mixture of EB and 1,3,5-TEB. The maximum amount of benzene produced during EB reaction is 21% with a contact time of 15 s at 500 °C. Benzene formed in the reaction of pure EB consists of benzene formed via disproportionation and via cracking. As for the reaction of 1,3,5-TEB, the selectivity to benzene is much less than for pure EB or EB and TEB reaction system. This indicates that cracking of 1,3,5-TEB is stepwise reaction. The first and the second step are prominent to produce DEB and EB while the third step of cracking to produce benzene is rather limited. This observation is supported by the fact that rate of cracking reaction decreases with decreasing number of alkyl groups on the benzene ring.

In our previous study of transalkylation reaction of EB and 1,3,5-TEB over FCC-USY zeolite [28] benzene was formed ∼2% whereas in the present study we achieved ∼12%. The production of larger amount of benzene can be explained in terms of differences in acidity of ZSM-5 and FCC-USY zeolites. The concentration of acidic site in ZSM-5 zeolite (0.233 m mol/g) is much higher than for USY zeolite (0.033 m mol/g). In addition to that the acid strength of Bronsted sites (Si–OH–Al groups) in ZSM-5 zeolite is significantly higher than in USY. Therefore ZSM-5 favors more cracking reaction increasing the selectivity to benzene.

3.3.5. *Comparison of performance of ZSM-5 and FCC-USY zeolite catalysts*

We have already reported on the transalkylation of a mixture of EB and 1,3,5-TEB using FCC-SY zeolite [28]. In this section we compare the performance of ZSM-5 and FCC-USY zeolite catalyst as for TEB conversion and DEB selectivity, cf. Fig. 6. It is observed that the conversion of 1,3,5-TEB is almost comparable for both catalysts and it increases with increasing reaction temperature and contact time. In addition, the DEB selectivity is higher for FCC-USY catalyst when compared with ZSM-5 at all reaction temperatures. It has been observed that DEB selectivity decreases with increasing TEB conversion over ZSM-5 zeolite while it is very stable over USY based catalyst. It seems that both acidity as well as pore size of these zeolites play a significant role. The DEB can be produced either by cracking of TEB or via transalkylation of EB and 1,3,5-TEB. It has been reported earlier [36] that cracking of alkylbenzenes proceeds more easily over ZSM-5 zeolite than over FCC-SY. Since cracking of TEB does not stop after one step it continues further to produce EB and then benzene. Consequently, over ZSM-5 zeolite the amount of DEB produced decreases at higher TEB conversion due to increase in cracking of DEB itself.

4. Kinetic modeling of 1,3,5-TEB transformation reactions

4.1. *Model formulation*

The transformation reaction of 1,3,5-TEB over zeolites occurs through two main reaction pathways as shown in Scheme 1 below and discussed in Section 3.2.

The first reaction pathway is *cracking* of TEB resulting in the formation of DEB as primary reaction products and light hydrocarbons mainly ethylene. The second reaction pathway is *isomerization* leading to 1,2,4-TEB and 1,2,3-TEB. Third possible mechanism includes 1,3,5-TMB disproportionation, although tetraethylbenzenes were not detected under our reaction conditions.

The results in Table 2 were modeled using steady state approximations and considering catalyst decay to be a function of time-on-stream. The following set of species balances and catalytic reactions were utilized.

Rate of 1,3,5-TEB disappearance:

$$\frac{V}{W_c}\frac{dC_{TEB}}{dt} = -[k_1 C_{TEB} + k_2 C_{TEB}]\exp(-\alpha t) \tag{1}$$

Rate of formation of diethylbenzene (DEB):

$$\frac{V}{W_c}\frac{dC_{DEB}}{dt} = [k_1 C_{TEB} - k_3 C_{DEB}]\exp(-\alpha t) \tag{2}$$

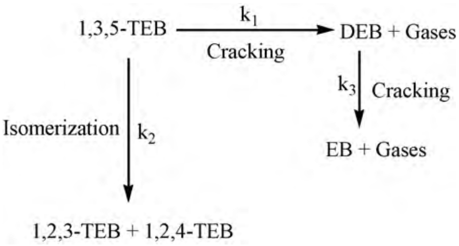
Rate of formation of ethylbenzene (EB):

$$\frac{V}{W_c}\frac{dC_{EB}}{dt} = [k_3 C_{DEB}]\exp(-\alpha t) \tag{3}$$

Rate of formation of isomerization products (1,2,4- and 1,2,3-TEBs):

$$\frac{V}{W_c}\frac{dC_{iso}}{dt} = [k_2 C_{TEB}]\exp(-\alpha t) \tag{4}$$

where C_{TEB}, triethylbenzene concentration in the riser simulator; C_{DEB}, diethylbenzene concentration in the riser simulator; C_{EB},



Scheme 1. Transformation reactions of 1,3,5-TEB.

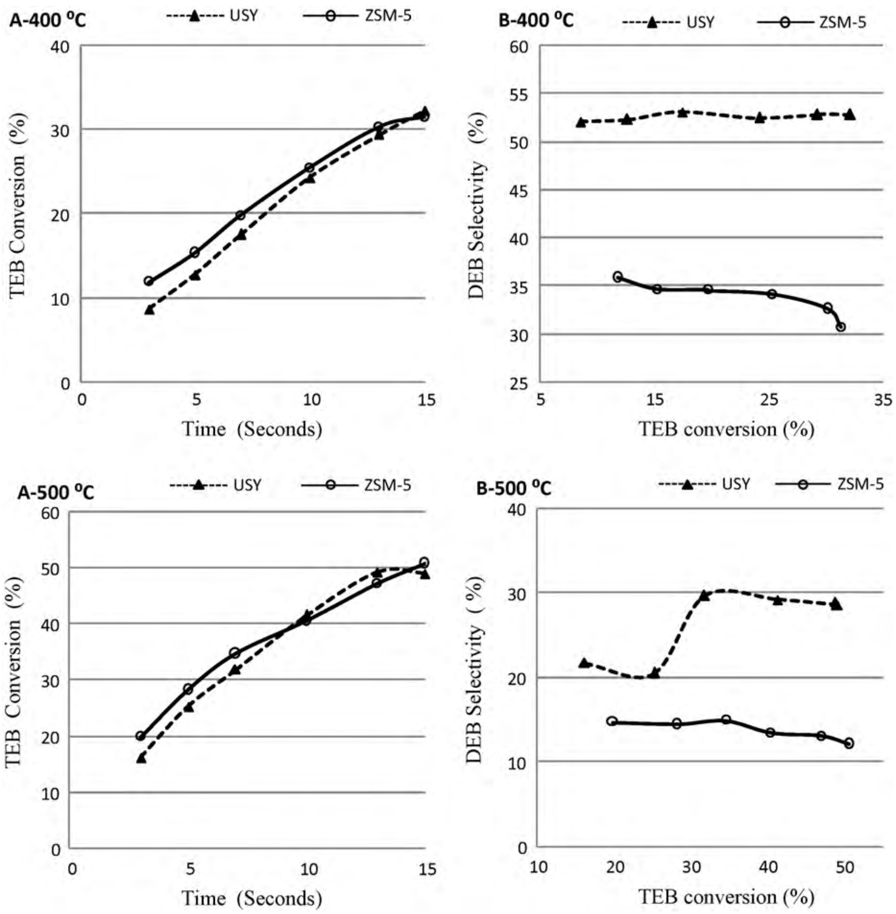


Fig. 6. (A) The conversion of TEB vs. contact time for mixture of EB and 1,3,5-TEB. (B) The selectivity of DEB's (%) with respect to the TEB conversion at 400 and 500 °C for the mixture of EB and 1,3,5-TEB, using ZSM-5 and USY zeolite based catalysts. The data of USY zeolite (for comparison) has been taken from Ref. [28].

ethylbenzene concentration in the riser simulator; C_{iso}, isomerization products concentration in the riser simulator; V, volume of the riser (45 cm^3); W_c, mass of the catalysts (0.81 g); t, time (s); α, deactivation constant; k, rate constant (cm^3/gcat s).

It should be noted that the following assumptions were made in deriving the reaction network:

(a) Both cracking and isomerization reactions follow simple *first-order.*
(b) An irreversible reaction path is assumed for both the cracking and isomerization reaction pathways.
(c) The model assumes catalytic reactions only and neglects thermal conversion.
(d) A single deactivation function defined for all the reactions taking place.
(e) The reactor operates under isothermal conditions, justified by the negligible temperature change observed during the reactions.

Using similar derivation procedures as outlined in Ref. [26], Eqs. (1)–(4) can be expressed in terms of weight fractions which are the measurable variables from GC analysis as:

$$\frac{dy_{TEB}}{dt} = -\left[k_1 y_{TEB}\frac{W_c}{V} + k_2 y_{TEB}\frac{W_c}{V}\right]\exp(-\alpha t) \qquad (5)$$

$$\frac{dy_{DEB}}{dt} = \left[k_1 y_{TEB}\frac{MW_{DEB}W_c}{MW_{TEB}V} - k_2 y_{DEB}\frac{W_c}{V}\right]\exp(-\alpha t) \qquad (6)$$

$$\frac{dy_{EB}}{dt} = k_3 y_{DEB}\frac{W_c MW_{EB}}{VMW_{DEB}}\exp(-\alpha t) \qquad (7)$$

$$\frac{dy_{iso}}{dt} = k_2 y_{TEB}\frac{W_c}{V}\exp(-\alpha t) \qquad (8)$$

where

$$Cx = \frac{y_x W_{hc}}{VMW_X}$$

W_{hc} = total mass of hydrocarbons inside the riser (0.162 g), MW_X = molecular weight of X molecule.

Kinetic constants for the cracking and isomerization reactions can be expressed using the Arrhenius equation, and a centering temperature, T_0 be the average reaction temperature introduced to reduce parameter interaction.

$$k_i = k_{0i}\exp\left(-\frac{E_i}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \qquad (9)$$

4.2. Model parameter determination

The kinetic parameters k_{0i}, E_i, and α, for the reactions were determined by fitting experimental data to Eqs. (5)–(8) through non-linear regression analysis using the MATLAB package. Tables 4 and 5 show the values of the estimated parameters over ZSM-5 and FCC-SY, respectively along with their corresponding 95% confidence limits. Correlation matrices of the regression analysis were computed and presented in Tables 6 and 7. A comparison between experimental results and model predictions is given in Fig. 7 for ZSM-5 and FCC-USY catalysts.

Table 4
Estimated kinetic parameters based on time-on-stream (TOS model) for ZSM-5.

Parameters	Values		
	k_1	k_2	k_3
E_i (kJ/mol)	26.81	8.66	32.37
95% CL	10.31	8.45	25.22
k_{0i}[a] (10^3 m^3/kg of catalyst s)	0.767	0.706	8.98
95% CL × 10^3	0.115	0.10	3.16
$\alpha = 0.069$ (0.025)			

[a] Pre-exponential factor as in the Arrhenius equation form with T_0.

Table 5
Estimated kinetic parameters based on time on stream (TOS model) for FCC-USY.

Parameters	Values		
	k_1	k_2	k_3
E_i (kJ/mol)	22.01	5.99	32.06
95% CL	6.95	4.12	27.90
k_{0i}[a] (10^3 m^3/kg of catalyst s)	1.038	0.338	4.11
95% CL × 10^3	0.138	0.065	1.20
$\alpha = 0.01$ (0.01)			

[a] Pre-exponential factor as in the Arrhenius equation form with T_0.

4.3. Discussion of kinetic modeling results

From the results of the kinetic parameter modeling presented in Table 4 for ZSM-5, it is seen that the apparent activation energy of 26.81 kJ/mol was obtained for 1,3,5-TEB cracking to DEB. The secondary cracking reaction of DEB to EB has higher activation energy of 32.37 kJ/mol. For 1,3,5-TEB isomerization the determined activation energy was 8.66 kJ/mol being substantially lower compared with cracking.

Kinetic parameters determined over FCC-SY are presented in Table 5. It is observed that catalyst deactivation was found to be very small ($\alpha \approx 0.01$), indicating a low coke formation under the present reaction conditions. Apparent activation energies of 22.01 and 32.06 kJ/mol were obtained for the primary and secondary cracking reactions of 1,3,5-TEB, respectively. The activation energy for the isomerization reaction was determined as 5.99 kJ/mol.

The higher activation energy for the primary cracking reaction to produce DEB over ZSM-5 compared with FCC-USY catalysts our experimental results showing the production of more DEB in case of FCC-USY than over ZSM-5 zeolite catalyst. Furthermore, over the two zeolites, the apparent activation energies were found to decrease: $E_{secondary\ cracking} > E_{primary\ racking} > E_{isomerization}$. Comparison between experimental results and model predictions given in Fig. 7 shows a close match except for the TEB isomers (1,2,3- and 1,2,4-TEB) over FCC-USY.

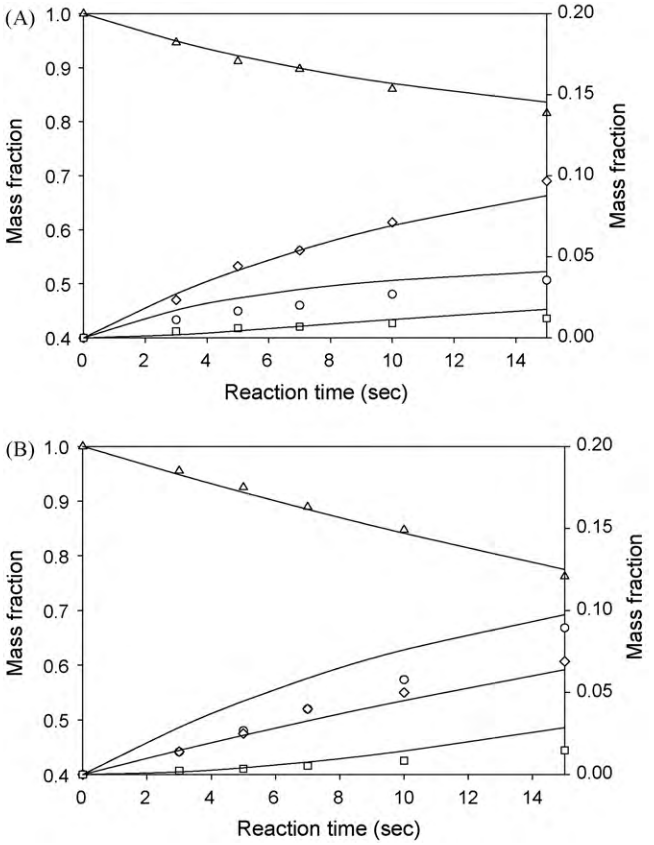


Fig. 7. Comparison between experimental results and numerical simulations (—) based on 1,3,5-TEB transformation reaction (Scheme 1) over (A) ZSM-5; (B) FCC-SY at $T = 673$ K: (△) 1,3,5-TEB; (◊) DEB; (○) 1,2,4-TEB + 1,2,3-TEB; (□) EB.

Table 6
Correlation matrix for parameters – TOS model for ZSM-5.

	k_1	E_1	k_2	E_2	k_3	E_3	α
k_1	1.0000	−0.2432	0.4280	0.0787	0.4471	−0.1199	0.7659
E_1	−0.2432	1.0000	0.0777	−0.5557	0.1751	−0.2629	0.0002
k_2	0.4280	0.0777	1.0000	−0.0503	0.2249	0.0557	0.8251
E_2	0.0787	−0.5557	−0.0503	1.0000	0.0790	−0.1461	−0.0110
k_3	0.4471	−0.1751	0.2249	0.0790	1.0000	−0.5208	0.3706
E_3	−0.1199	0.2629	0.0557	−0.1461	−0.5208	1.0000	0.0038
α	0.7659	0.0002	0.8251	−0.0110	0.3706	0.0038	1.0000

Table 7
Correlation matrix for parameters – TOS model for FCC-SY.

	k_1	E_1	k_2	E_2	k_3	E_3	α
k_1	1.0000	−0.1408	0.3367	0.0325	0.5434	−0.0777	0.8735
E_1	−0.1408	1.0000	0.0690	−0.5404	−0.1755	0.3280	−0.0044
k_2	0.3367	0.0690	1.0000	−0.0185	0.1452	0.0875	0.6230
E_2	0.0325	−0.5404	−0.0185	1.0000	0.0750	−0.1901	−0.0134
k_3	0.5434	−0.1755	0.1452	0.0750	1.0000	−0.4946	0.4543
E_3	−0.0777	0.3280	0.0875	−0.1901	−0.4946	1.0000	0.0215
α	0.8735	−0.0044	0.6230	−0.0134	0.4543	0.0215	1.0000

5. Conclusions

The following conclusions can be drawn from the transalkylation reaction of ethylbenzene (EB) with 1,3,5-triethylbenzene (TEB) over ZSM-5 zeolite catalyst and subsequent comparison with the reactions of pure ethylbenzene and 1,3,5-triethylbenzene under similar conditions.

- A synergistic effect in the reaction of 1,3,5-TEB has been observed during the transalkylation reaction with ethylbenzene as compared with the transformation reaction of pure 1,3,5-TEB.
- The selectivity to DEB (%) produced during transalkylation of EB and 1,3,5-TEB is much higher than that of pure 1,3,5-TEB or pure EB indicating a synergistic effect.
- The selectivity to *p*-DEB is much higher for pure EB as compared with that of pure 1,3,5-TEB or the mixture of EB and 1,3,5-TEB
- The isomerization of 1,3,5-TEB proceeds with a higher rate than for pure 1,3,5-TEB as compared with the mixture of EB and 1,3,5-TEB. The 1,2,4-TEB is preferentially formed over 1,2,3-TEB.
- The conversion of 1,3,5-TEB is comparable on both FCC-USY and ZSM-5 zeolite catalysts. However DEB selectivity is higher in case of FCC-USY zeolite than that of ZSM-5 zeolite due to a lower acidity.
- Kinetic parameters for the transformation of 1,3,5-TEB over ZSM-5 and FCC-USY zeolite catalysts have been calculated using the catalyst activity decay function, based on the time-on-stream (TOS). The apparent activation energies were found to decrease as follows:

$$E_{secondarycracking} > E_{primary\ cracking} > E_{isomerization}.$$

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