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Kinetics modeling of disproportionation and ethylation of ethylbenzene over HZSM-5: Effects of SiO_2/Al_2O_3 ratio

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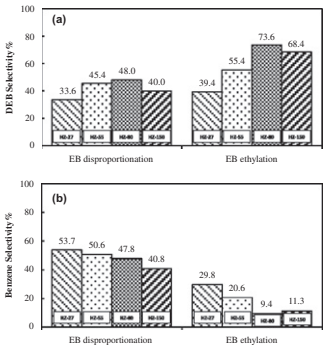
HIGHLIGHTS

- Effects of SiO_2/Al_2O_3 ratio of HZSM-5 in disproportionation/ethylation EB are studied.
- Main product is DEB and benzene.
- At low temperature ethylation is favorable than disproportionation to produce DEB.
- HZSM-5 with Si/Al = 80 gives highest EB conversion and selectivity of DEB.
- Activation energy for DEB formation on Si/Al = 80 is smaller than other HZSM-5 samples.

GRAPHICAL ABSTRACT



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ABSTRACT

This article deals with the effects of SiO_2/Al_2O_3 ratio of HZSM-5 catalysts in disproportionation and ethylation of ethylbenzene to produce para-diethylbenzene (p-DEB). The physicochemical characterization of the catalyst samples shows that the variation of SiO_2/Al_2O_3 has minimal impact on the crystallinity of HZSM-5 samples. On the other hand, the acidity of the materials decreased while specific surface area increased with increasing the SiO_2/Al_2O_3 ratios. The catalytic experiment in the CREC Riser Simulator shows that low temperature favors the EB ethylation reaction while higher temperature is favorable for disproportionation. The DEB selectivity is found to be significantly higher in ethylation of EB with ethanol than disproportionation. Among the five HZSM-5 catalysts, the sample with SiO_2/Al_2O_3 = 80 gives highest EB conversion and is more selective to DEB although the p-DEB/m-DEB for the catalysts are comparable with other samples. The value of the activation energy for EB cracking is comparable to the activation energy of EB disproportionation which is consistent to the high benzene selectivity in this route. During the EB ethylation with ethanol, a small amount of benzene was formed via the cracking of EB, which is reflected by higher activation energy of the EB cracking reaction. The kinetics analysis also confirms that during EB ethylation, the disproportionation and cracking of EB is negligible. In EB ethylation, the HZSM-5 catalyst with SiO_2/Al_2O_3 = 80 requires lowest amount of activation energy to form DEB which is reflected in higher DEB selectivity of the catalyst.

1. Introduction

p-Diethylbenzene (p-DEB), the most desirable among the three DEB isomers, have found wide range of applications in the chemical and petrochemical industries. It is commonly utilized as monomer for the production of ion exchange resin and viscosity modifiers for lubricating oil [1]. A significant amount of the produced p-DEB goes in producing divinylbenzene (DVB), an intermediate used as a cross-linking agent in the manufacture of certain plastics [2]. p-DEB is employed as a desorbent in UOP para-ex and IFP-eluxyl desorption processes [1,3]. It also works as an

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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 the *i*th reaction (kJ/mol)
k_i	apparent rate constant for the *i*th reaction (m^3/kg of catalysts)
k_{oi}	pre-exponential factor for the *i*th reaction after re-parameterization (m^3/kg of catalysts)
MW_i	molecular weight of specie *i*
r_i	rate of reaction for species *i*
R	universal gas constant (kJ/kmol K)
t	reaction time (s)
T	reaction temperature (K)
T_o	average temperature of the experiment
V	volume of the riser (45 cm^3)
W_c	mass of the catalyst (0.81 g)
W_{hc}	total mass of the hydrocarbon injected the riser (0.162 g)
y_i	mass fraction of *i*th component

Greek letters

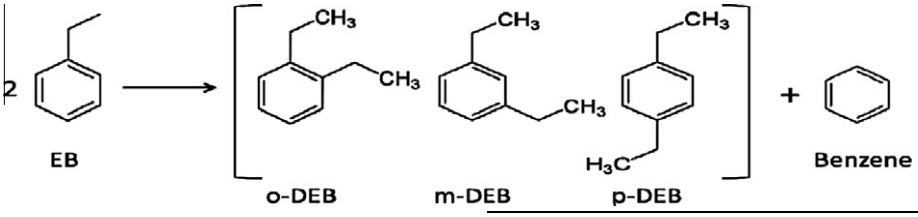
α	apparent deactivation function
λ	catalyst deactivation constant (RC model)

Abbreviations

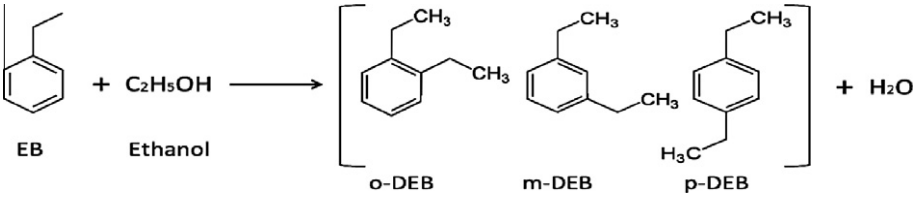
BZ	benzene
EB	ethylbenzene
DEB	diethylbenzene
p-DEB	para-diethylbenzene
m-DEB	meta-diethylbenzene
o-DEB	ortho-diethylbenzene

additive in industrial heat transfer fluids. Accounting for all the after mentioned applications, current worldwide demand for p-DEB is estimated to 12,000 tons per years, which is expected to grow further [2]. With the present market prices of $4000/per metric ton, the annual sales volume is approximately around US$ 48 million dollars [2]. Considering the attractive price and increasing demand, in recent years there are significant initiatives to increase the p-DEB productions. Conventionally, p-DEB is produced by reduction of diacetophenone. The other alternative routes are, disproportionation of ethylbenzene (EB) and/or alkylation of EB with ethanol, ethylene, or ethyl chloride [1,3–5] according to the following reactions:

- Disproportionation of ethylbenzene:



- Alkylation of ethylbenzene with ethanol:



One can see from the above alternative routes; alkylation of each mole of EB gives one mole of DEB while the disproportionation of EB requires two moles of EB to produce one mole of DEB. Also, disproportionation gives one mole of benzene per mole of DEB produced. Therefore, the alkylation with an appropriate agent appears to be more preferable. Among the after mentioned alkylation agents, ethanol is considered to be the most economical due to its ample availability and relatively cheaper prices. From the technical view point, ethanol is also desirable given that the water produced during alkylation with ethanol helps suppressing the coke formation, resulting sustained catalyst activity for longer period of time. To apprehend the advantages of EB alkylation with ethanol there are significant research initiatives that have been under taken around the world to develop industrial scale EB alkylation technology.

The majority of those literature articles are focused on the catalyst development and establishing the possible reaction mechanisms. Most of the previous studied catalysts are based on various types of zeolites, such as mordenite, USY, Beta, MCM-22 and ZSM-5 [4,6]. These catalysts show good catalytic activity and stability in EB disproportionation/alkylation using different types of reactor and reaction conditions. The main limitations of these catalysts is the low selectivity of p-DEB due to the thermodynamic equilibrium with other DEB isomers (para:meta:ortho = 30:54:16) [1,6]. Cracking of EB on the acidic sites is the other important issue related to the zeolite base catalysts. It not only consumes the EB feed to produce undesired products (mainly benzene) but also responsible for catalyst deactivation by coke formation. Modification of the catalyst is one of the most widely accepted ways to increase the selectivity of p-DEB. There are two possible alternatives of modifying the zeolite based catalysts: (i) passivation of the external acidic sites, minimizing the secondary isomerization of p-DEB (to form the m- or o-DEB) and cracking reaction and (ii) modifying the structure of the zeolite to facilitate the

distinguishing diffusivities among p-DEB, m-DEB and o-DEB [6–9]. Na, Fe, Mn, Al, La_2O_3 and CeO_2 are commonly used agents/metals to modify the zeolites for EB alkylation [9,13]. Nitridation of parent HZSM-5 zeolites with flowing pure ammonia at high temperature can suppress the isomerization of para-DEB and leading to enhancement of para selectivity due to the absence of strong acid sites [8]. There are several studies reported the disproportionation and alkylation of EB on different HZSM-5 catalysts, most of them deals with effects of conversion of EB and p-DEB selective with various modified forms of HZSM-5. No attention has been paid to systematic evaluation of HZSM-5 with various Si/Al ratios. Regarding the structure modification, there are several alternatives controlling the pore sizes/structures of the zeolites [14]. Pre-coking is usually helpful of adjusting the pore opening size to increase the p-DEB selectivity [10]. However, studies show in addition to the positive impacts on the catalysts, both the passivation and shape adjustments may affect the active sites in zeolite channels [14]. Therefore, both these techniques remain interesting topics for researchers to develop a highly active and p-DEB selective catalyst. Further, the Si-CVD surface treatment is an acid catalysis reaction during which the rate of deposition depends strongly on the acidity of zeolites. The external acidity can be eliminated without significantly changing the internal acidity by Si-CVD technique [15,16].

In addition to catalyst modification the contact time between the catalyst and the reactant/product also have significant influence on the selectivity of p-DEB. Short contact time fluidized bed reactors are favorable to improve the p-DEB selectivity using ZSM-based catalysts [1,3,17]. In fact, the alkylation of EB in fluidized bed offers three important advantages over the fixed bed operations: (i) short contact time to minimize the further isomerization of p-DEB and reduces cracking reactions maximizing the p-DEB selectivity, (ii) proper temperature control on the catalyst particles and (iii) continuous catalyst regeneration. The present research group recently investigated a series of zeolite based fluidizable catalysts aiming superior performance in catalytic alkylation of EB to DEB [1,3,17].

Considering the significance of the adjustment of the surface acidity of the catalyst and the contact time between the catalyst and reactant/product, the present research is focused on the study of effects of acidity and contact time on the conversion of EB and p-DEB selectivity for both the disproportionation and ethanol alkylation of EB. It was envisioned that for short reaction time, the potential of isomerization of p-DEB (to m-, o-DEB) and the side reactions taking place will be limited. The HZSM-5 with various SiO_2/Al_2O_3 ratios (27, 55, 80, 150 and 280) are considered. The main reason of selection of HZSM-5 is its unique combination of stability and shape selectivity and possibility of modifying the surface acidity. The contact time of the reaction is adjusted by changing the reaction time in a fluidized bed CREC Riser Simulator. Kinetic modeling of both the EB alkylation and EB disproportionation are also carried out using the catalyst activity decay function based on time on stream. The kinetics parameters are estimated by least-squares fittings of the model equation using experimental data implemented in MATLAB. The estimated parameters are evaluated based on their physical significances and various statistical indicators.

2. Experimental methods

2.1. Materials

The commercial zeolites used in this study was supplied by Zeolyst; ZSM-5 (CBV3024E, Nominal SiO_2/Al_2O_3 = 27, NH4-form; CBV5524G, Nominal SiO_2/Al_2O_3 = 55, NH4-form; CBV8014, Nominal SiO_2/Al_2O_3 = 80, NH4-form; and CBV28014, Nominal SiO_2/Al_2O_3 = 280, NH4-form). HZSM-5 of nominal SiO_2/Al_2O_3 = 150 (CT 412) was supplied by Catal. International Ltd. (UK). Prior to testing, the as-received NH4-form zeolites were calcined in standing air at 550 °C for 5 h (ramping rate of 3 °C min^{-1}), in order to get the H-form. These zeolites are hereafter referred as HZ-27, HZ-55, HZ-80, HZ-150, and HZ-280, where the number represents the nominal SiO_2/Al_2O_3 ratio.

2.2. Catalyst synthesis

All the Na-ZSM-5samples were ion-exchanged with NH_4NO_3 to replace the Na^+ with NH_4^+. The samples were converted into the proton-exchanged form by calcination for 2 h at 600 °C.

2.3. Catalyst characterization

2.3.1. Atomic absorbance

The chemical compositions were determined by atomic absorption spectroscopy, using the Perkin–Elmer equipment (Model AAS 1100B).

2.3.2. Brunauer–Emmett–Teller (BET) surface area measurements

The textural properties of all zeolite samples were characterized by N_2 adsorption measurements at 77 K, using Quantachrome Autosorb 1-C adsorption analyzer. Samples were outgassed at 220 °C under vacuum (10–5 Torr) for 3 h before N_2 physisorption. The BET specific surface areas were determined from the desorption data in the relative pressure (P/P0) range from 0.06 to 0.3, assuming a value of 0.164 nm 2 for the cross-section of the nitrogen molecule.

2.3.3. X-ray diffraction

The high-angle powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu powder diffraction system using Cu Kα radiation (λKα1 = 1.54051 Å, 45 kV and 35 mA). The XRD patterns were recorded in the static scanning mode from 1.2° to 60° (2θ) at a detector angular speed of 0.01°/s and step size of 0.02°.

2.3.4. NH_3-temperature-programmed desorption

Temperature-programmed desorption of NH_3 (NH_3-TPD) was carried out using Quantachrome Autosorb 1-C/TCD equipped with a mass spectrometry detector (Cirrus 2, mks, spectra products). Samples were pretreated at 450 °C in a flow of helium (25 ml min^{-1}) for 2 h. This was followed by the adsorption of ammonia (5 vol.% in helium) at 100 °C for 30 min. Samples were then purged in a He stream for 2 h at 100 °C in order to remove loosely bound ammonia (i.e. physisorbed and H-bonded ammonia). Then, the samples were heated again from 100 to 700 °C at a heating rate of 10 °C/min in a flow of helium (25 ml min^{-1}) while monitoring the evolved ammonia using TCD.

2.3.5. FTIR spectroscopy

Infrared spectroscopy of adsorbed pyridine was used to determine the types of available acid sites (i.e. Brönsted and/or Lewis acid sites). The measurements were carried out using a Fourier transform infrared using Nicolet FTIR spectrometer (Magna 500 model). The samples in the form of a self-supporting wafer (*ca.* 60 mg in weight and 20 mm in diameter) were obtained by compressing a uniform layer of powder. The wafer was then placed in an infrared vacuum cell equipped with KBr windows (Makuhari Rikagaku Garasu Inc., JAPAN), and pretreated under vacuum (*ca.* 10^{-3} Torr) at 450 °C for 2 h. The adsorption temperature of pyridine was 150 °C. For a quantitative characterization of acid sites, the following bands and absorption coefficients were used: pyridine (PyH^+) band at 1545 cm^{-1}, ε = 0.078 cm/μmol^{-1}; pyridine (PyL) bands at 1461 and 1454 cm^{-1}, ε = 0.165 cm/μmol^{-1} [18,19].

2.4. Disproportionation/ethylation of ethylbenzene in fluidized CREC Riser Simulator

The catalytic disproportionation and ethylation of EB experiments were conducted by using a fluidized CREC Riser Simulator operated under expected conditions of a commercial scale reactor unit. The CREC Riser Simulator is a bench scale mini-fluidized bed reactor, invented at CREC-UWO [20]. This reactor can be operated in batch mode under turbulent fluidized bed conditions and predetermined contact times simulating various locations of riser/downer type reactor units. The reactor details and the experimental procedure can be found elsewhere [20–22].

The disproportionation/ethylation of ethylbenzene experiments were conducted using 0.80 g of catalysts with particle size of 60 μm. For the disproportionation reaction, pure ethylbenzene was injected as feed while 1:1 ethylbenzene to ethanol molar feed ratio was used as feed for the ethylation experiments. Before the actual runs, the catalyst was thermally activated at 620 °C for 15 min in the presence of Ar. The experiments were performed at different temperature levels ranging between 200 and 400 °C and atmospheric pressure. After the injection, reactor pressure increased given the system is operated in batch mode. The reaction time (contact time) was varied from 5 to 20 s. After each run the product gas samples were analyzed three times by automatic injection into a GC. The standard deviations at each run were found in the range of ±2%. The GC analyzed data were further processed to calculate the conversion and selectivity using the following equations:

$$\text{Conversion of EB, } X_{EB} = \frac{\text{wt of ethylbenzene converted}}{\text{wt of ethylbenzene fed}} \times 100\%$$

$$\text{Selctivity of product } i, S_i = \frac{\text{wt of product } i}{\text{ethylbenzene conversion}} \times 100\%$$

$$\text{p-DEB selectivity} = \frac{\text{wt p} - \text{DEB produced}}{\text{wt total} - \text{DEB produced}} \times 100\%$$

3. Results and discussions

3.1. Physicochemical properties of the catalysts

The specific surface area and pore volume determined by nitrogen physisorption for the HZSM-5 with different SiO_2/Al_2O_3 samples are listed in Table 1. The BET surface area of the samples compared well with the value given by the supplier. After ion-exchange, the surface area of all the samples significantly varied with the variation of the SiO_2/Al_2O_3 ratios. The specific surface area of HZSM-5 samples increased with the increase of SiO_2/Al_2O_3 ratios (Table 1). The pore volumes of the samples were calculated to be 0.25, 0.25, 0.28, 0.26 and 0.23 for the SiO_2/Al_2O_3 ratio of 27, 55, 80, 150 and 280, respectively. Min and Hong [23] also reported similar behavior of HZSM-5 samples with SiO_2/Al_2O_3 varied between 21 and 36.

Table 1
Textural properties of MFI microporous aluminosilicate of different Si/Al ratios.

Samples	SiO_2/Al_2O_3[a]	S_{BET} ($m^2\,g^{-1}$)	S_{meso} ($m^2\,g^{-1}$)	V_{micro} (cm^3/g)[b]	$V_{meso,N2}$ (cm^3/g)[c]
HZ-27	25	357	44.0	0.15	0.10
HZ-55	52	376	74.0	0.15	0.10
HZ-80	82	451	51.0	0.19	0.09
HZ-150	131	435	69.0	0.17	0.09
HZ-280	283	443	23.0	0.21	0.02

[a] By Atomic Absorbance Spectroscopy (AAS).
[b] Obtained from *t*–plot.
[c] Pore volume in the range of 4–100 nm derived from N_2 adsorption.

The XRD patterns of all the HZSM-5 zeolite samples with different SiO_2/Al_2O_3 indicate that the structure of the zeolite remained intact even with the significant variation of the SiO_2/Al_2O_3 ratios (Fig. 1). Thus, the variation of the SiO_2/Al_2O_3 of the HZSM-5 zeolites affects only the acidity of the zeolite, without destroying the parent HZSM-5 structure.

The NH_3-TPD experiments show that the HZSM-5 samples contain both low and high temperature peaks, corresponding to weak and strong acid sites, respectively (Fig. 2a). The range of weak and medium strength acid sites were set at 200–300 °C, 300–450 °C, respectively. The acid sites appeared above 450 °C is considered as strong acid sites [24]. Table 2 summarizes the amount and percentage of various types of acid sites. One can see in Table 2, with increasing SiO_2/Al_2O_3 ratios the total acidity of HZSM-5 samples decreased while the percentage of strong acidic sites (>450 °C) increased. The presence of Brönsted and Lewis acid sites were confirmed by the pyridine FTIR characterization (Fig. 2b). The amount and percentages of each of Brönsted and Lewis type acid sites are also presented in Table 2. As it can be noticed that up to $SiO_2/Al_2O_3 = 80$, the Brönsted acidic sites were decreased with increasing the SiO_2/Al_2O_3 ratio after that it started increasing slightly. On the other hand the Lewis acid sites were increased then decreased again with increasing the SiO_2/Al_2O_3 ratio. It is interesting to note that among the HZSM-5 samples, the sample with SiO_2/Al_2O_3 ratio of 80 shows a good balance between Brönsted and Lewis acid sites. An appropriate balance between the strong acidic sites with keeping the Brönsted acidic sites in the higher level is desirable for EB transformation reaction [25–27].

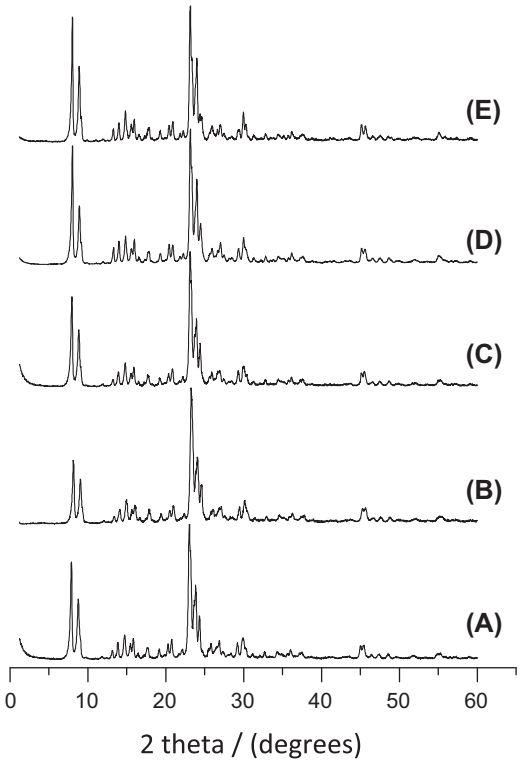


Fig. 1. XRD patterns of MFI microporous aluminosilicate of different SiO_2/Al_2O_3; (A) 27, (B) 55, (C) 80, (D) 150, and (E) 280.

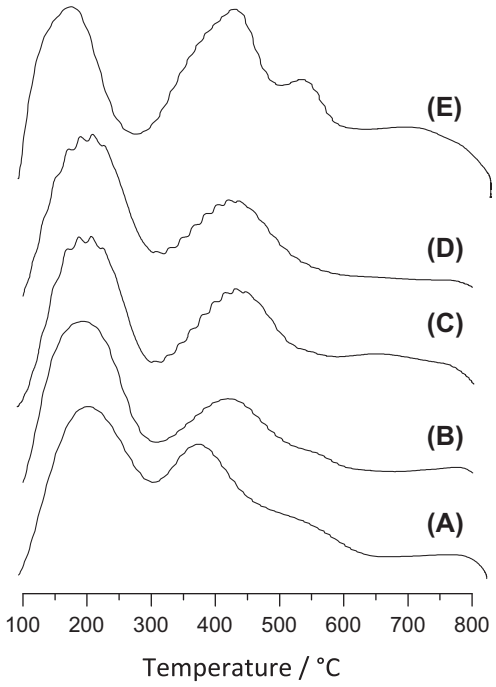


Fig. 2a. NH_3 TPD profiles of MFI microporous aluminosilicate of different SiO_2/Al_2O_3; (A) 27, (B) 55, (C) 80, (D) 150, and (E) 280.

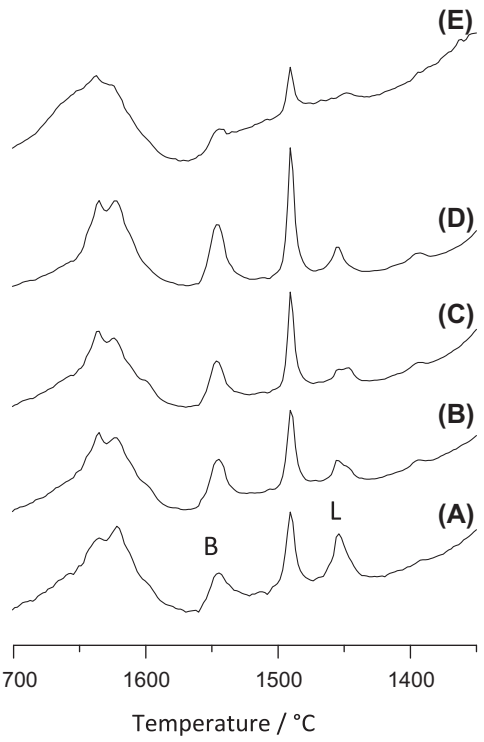


Fig. 2b. FTIR of chemisorbed pyridine of MFI microporous aluminosilicate of different SiO_2/Al_2O_3; (A) 27, (B) 55, (C) 80, (D) 150, and (E) 280 (B: Brönsted, L: Lewis acid sites).

3.2. Disproportionation versus ethylation of ethylbenzene

As mentioned in the experimental section, both the disproportionation and ethylation of EB experiments were conducted in a CREC Riser Simulator under fluidized bed conditions. In order to compare products compositions between disproportionation and ethylation, all the catalytic runs were carried out using same amount of EB feed. Table 3 presents the product analysis results of the disproportionation of EB over the HZSM-5 samples after 20 s of reaction at three levels of reaction temperatures (250, 300 and 350 °C). One can see that at all temperature levels diethylbenzene (DEB) and benzene are the main products. Among the DEB isomers p-DEB and m-DEB are dominant while a small amount of o-DEB is also detected under the present experimental conditions. The gaseous product predominantly ethylene but their overall composition is very low. The other hydrocarbon products such as triethylbenzene, toluene and gaseous hydro-carbons are negligible.

In disproportionation of EB the origin of benzene could be both disproportionation and cracking reactions [1,3]. In this study at all temperature levels the HZSM-5 catalysts samples produced highest amount of benzene. This observation might lead one to speculate about the possibility of cracking, especially for catalyst with high acidic site concentration. One way to confirm the occurrence of cracking is the product gas analysis which is also originated from the cracking reaction. As it can be seen in Table 3, the amount of product gas is minimal even at high EB conversion. This suggests that the benzene is mainly produced via the disproportionation reaction. Previously, the present research group demonstrated that higher reaction temperature (>400 °C) favors the cracking reaction that produces undesired product benzene [3,17] using a USY catalyst. In the present study the catalytic runs were conducted well below 400 °C, as a result the cracking reaction is limited.

Table 4 reports the product distribution for ethylation of EB with ethanol over HZSM-5 samples being investigated in this study. The ethylation experiments were conducted using 1:1 EB to ethanol molar ratio and at different reaction temperatures and contact times. The analysis shows that the products are still the same as observed during disproportionation, only the conversion of EB and the product compositions are significantly changed in

Table 2
Acid sites characteristics of MFI microporous aluminosilicate of different Si/Al ratios.

Zeolites	NH_3-TPD (mmol g^{-1})[a]				FTIR-chemisorbed pyr. (mmol g^{-1})		
	T[b]	L.T. (weak)	H.T. (medium–strong)		T[b]	B	L
		200–300 °C	300–450 °C[c]	460–575 °C[c]			
HZ-27	0.73	0.48 (67%)[d]	0.23 (31%)	0.02 (2%)	0.75	0.65 (87%)	0.10 (13%)
HZ-55	0.46	0.26 (57%)	0.18 (39%)	0.02 (4%)	0.30	0.29 (97%)	0.01 (3%)
HZ-80	0.35	0.19 (55%)	0.12 (34%)	0.04 (11%)	0.14	0.08 (56%)	0.06 (44%)
HZ-150	0.21	0.04 (19%)	0.12 (57%)	0.05 (24%)	0.13	0.08 (61%)	0.05 (39%)
HZ-280	0.09	0.03 (27%)	0.02 (20%)	0.05 (53%)	0.02	0.01 (69%)	0.01 (31%)

[a] L.T. and H.T. correspond to low- and high-temperature NH_3 desorption peak, respectively.
[b] Total number of acid sites.
[c] Strong acid sites of Brönsted and Lewis nature, respectively [X].
[d] Number in parenthesis corresponds to % of acid sites.

Table 3
Product distribution (wt%) of ethylbenzene disproportionation on HZSM-5 with different Si/Al ratio at 20 s reaction time.

Catalysts	Temp. (°C)	EB conv. (%)	Product yield (%)					
			Benzene	*p*-DEB	*m*-DEB	*o*-DEB	Total-DEB	Others[a]
HZ-27	200	7.07	4.42	1.18	1.44	0.07	2.69	–
	250	15.8	8.95	2.73	3.64	0.18	6.55	0.36
	300	41.01	22.2	3.73	6.44	0.46	10.6	4.18
	350	47.57	27.9	1.94	3.48	0.35	5.77	7.33
HZ-55	200	4.35	2.54	0.48	0.88	0	1.4	–
	250	14.7	7.3	2	3.93	0.17	6.1	–
	300	38.4	19.8	4.22	9.2	0.9	14.3	–
	350	48.5	27.35	2.66	5.75	0.77	9.2	–
HZ-80	200	2.40	1.73	0.28	0.36	0.00	0.64	–
	250	9.37	5.18	1.34	2.56	0.10	4	–
	300	27.53	13.04	4.13	8.40	0.90	13.43	0.35
	350	42.17	20.45	4.95	10.44	1.23	16.62	1.12
HZ-150	200	1.41	0.92	0.20	0.29	0.00	0.49	–
	250	5.83	3.11	0.92	1.65	0.0	2.57	–
	300	26.06	12.3	4.03	7.92	0.53	12.48	0.48
	350	35.91	18.15	3.94	8.10	0.69	12.73	1.3
HZ-280	200	0.30	0.16	0.14	0.00	0.00	0.14	–
	250	0.78	0.49	0.19	0.00	0.00	0.19	–
	300	3.97	1.94	1.08	0.46	0.00	1.54	0.30
	350	18.78	8.41	5.01	3.60	0.00	8.62	0.97

[a] Xylenes, toluene and ethyltoluenes.

Table 4
Product distribution (wt%) of ethylbenzene ethylation reaction on HZSM-5 with different Si/Al ratio at 20 s reaction time.

Catalysts	Temp. (°C)	EB conv. (%)	Product Yield (%)					
			Benzene	p-DEB	m-DEB	o-DEB	Total-DEB	Others[a]
HZ-27	200	7.47	1.48	3.58	2.37	0.13	6.08	0.64
	250	21.14	5.26	5.68	5.49	0.34	11.51	2.27
	300	34.80	10.25	5.32	6.04	0.34	11.71	6.09
	350	35.72	13.92	3.06	4.42	0.36	7.85	8.04
HZ-55	200	15.21	1.05	5.14	10.72	0.71	16.58	0.94
	250	28.80	4.25	6.40	12.86	0.94	20.20	2.91
	300	38.30	8.52	5.03	10.66	1.13	16.82	5.59
	350	44.08	15.10	2.39	4.88	0.96	8.23	9.07
HZ-80	200	17.41	0.59	6.24	9.60	0.69	16.54	0.52
	250	29.25	2.02	8.07	15.44	1.21	24.72	1.45
	300	40.57	4.86	8.90	18.13	1.80	28.83	2.98
	350	43.76	6.88	7.95	16.90	2.02	26.87	4.20
HZ-150	200	11.57	0.29	5.31	4.54	0.33	10.17	0.43
	250	26.30	1.61	8.20	13.09	0.70	21.99	1.41
	300	36.15	4.49	8.02	15.09	1.02	24.13	3.37
	350	34.11	9.59	3.86	8.19	0.96	13.01	6.16
HZ-280	200	1.30	0.00	1.06	0.11	0.00	1.17	–
	250	5.00	0.00	3.22	0.71	0.00	3.94	–
	300	14.71	0.61	12.28	4.80	0.00	17.08	0.59
	350	27.20	3.51	8.32	6.84	0.19	15.35	2.28

[a] Xylenes, toluene and ethyltoluenes.

case of the EB ethylation with ethanol. A small amount of triethylbenzene was found in disproportionation runs. No such product was detected in the EB ethylation with ethanol. The following sections present the effects of SiO_2/Al_2O_3 ratios along with temperature and contact time on conversion and product selectivity during both the disproportionation and ethylation of EB.

3.2.1. Conversion of ethylbenzene (EB)

Fig. 3 compares the EB conversions over various SiO_2/Al_2O_3 containing HZSM-5 catalysts at 250 °C in the CREC Riser Simulator. One can see that both in ethylation and disproportionation, the EB conversion on HZ-280 catalyst was much lower compared to the other catalyst samples which is mainly due to the very low acidity of this catalyst sample. For all the five HZSM-5 samples the EB conversion in ethylation was much higher than disproportionation.

When the EB conversions were plotted against temperature, it clearly shows that with increasing reaction temperature the conversion of EB increased (Fig. 4). At temperatures higher than 300 °C the EB conversion in both the disproportionation and ethylation are comparable. This suggests that above 300 °C temperature higher amount of EB adsorbs on the on the Brönsted acid sites which favors the disproportionation [25,26]. As a result, the overall conversion of EB in the disproportionation is increased and reached to the level of EB ethylation. For the same reason the HZSM-5 samples with higher acidity (lower SiO_2/Al_2O_3 ratios) displayed higher EB conversion in the disproportionation reaction runs than those of the lower acidic catalyst samples. The

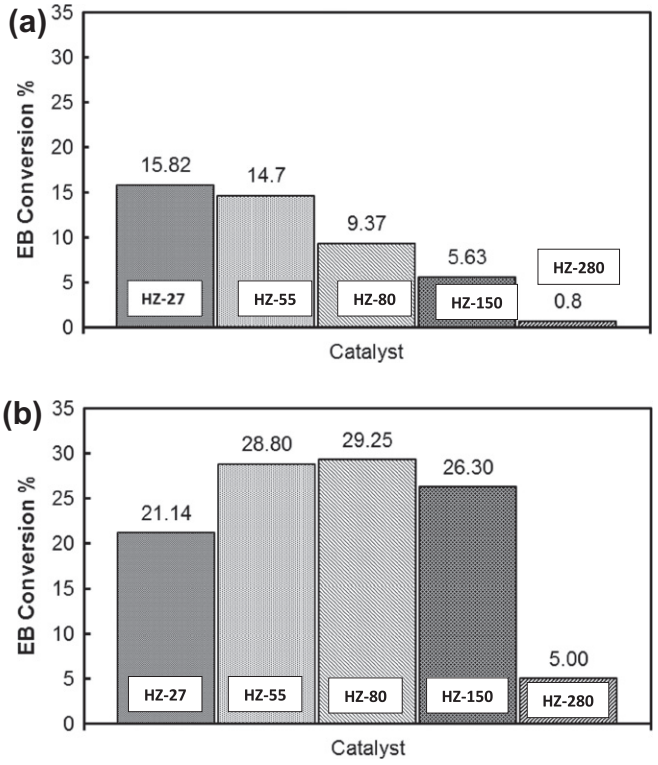


Fig. 3. EB conversion at temperature of 250 °C and 20 s contact time for (a) EB disproportionation and (b) EB ethylation over different catalysts.

proportional relationship between the temperature and the EB conversion also suggests that under the studied range both disproportionation and ethylation reactions were away from the thermodynamic equilibrium.

Fig. 5 displays the comparison of the EB conversions at different reaction times and at constant temperature of 300 °C. As expected, both the disproportionation and ethanol alkylation reactions, show increasing trend with increasing the contact time. When compared among the different HZSM-5 catalysts, the higher acidic catalysts (SiO_2/Al_2O_3 = 27 and 55) display higher EB conversions in disproportionation reaction compare to the lower acid catalysts, while for ethylation reaction the EB conversion for high acid catalyst is lower than low acidic catalysts. Excessive acid sites and the absence of the competition for active sites between ethanol and EB favor this higher EB conversion during disproportionation. Again, due to very low acidity, the HZ-280 sample shows very low EB conversion.

When compared the performance of three HZSM-5 catalysts in ethylation, the sample with SiO_2/Al_2O_3 = 80 displays superior activity. This is possibly due to the appropriate balance between the availability of strong acidic sites (11%) along with the total acidity (0.354 mmol/g) as found in the NH_3-TPD study (Table 2). The sample, SiO_2/Al_2O_3 = 27 with higher total acidity (0.73 mmol/g) contains only small percentage of strong acidic sites (2%), while with SiO_2/Al_2O_3 = 280 sample, 53% of the total sites are strong acidic sites but the total acidity is very low (0.094 mmol/g). Consequently, SiO_2/Al_2O_3 = 80 catalyst shows better performance as compared to the other HZSM-5 samples considered in this investigation.

3.2.2. Selectivity of DEB and BZ

Fig. 6 displays the selectivity of total DEB for both the disproportionation and ethylation of EB reactions using three HZSM-5 catalysts at constant 25% EB conversion and 300 °C temperature. HZ-280 sample is not included in Fig. 6 given very low conversion

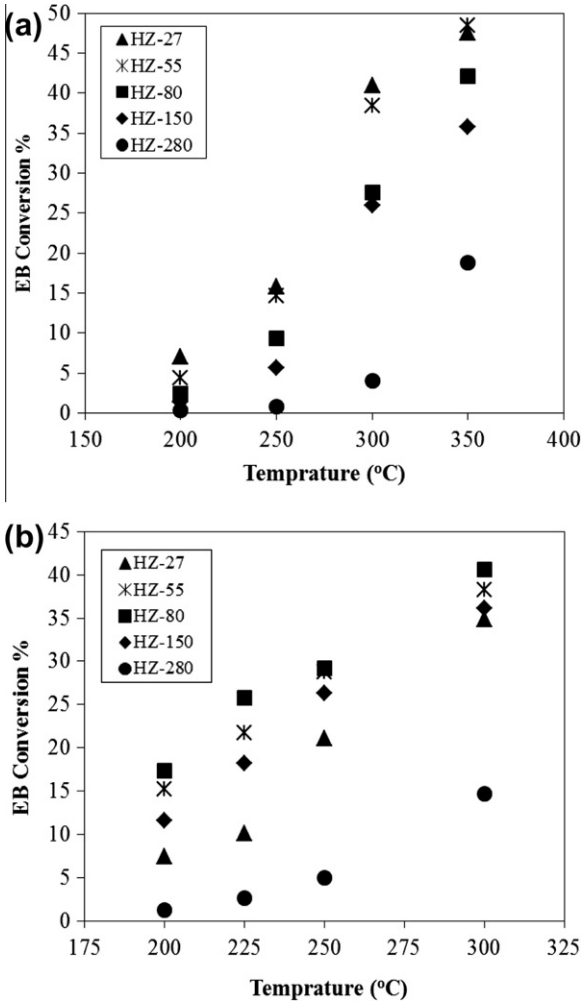


Fig. 4. Variation of EB conversion with temperature at 20 s contact time, comparison between different catalysts for (a) EB disproportionation reaction and (b) EB ethylation reaction.

(much less than 25%) and negligible product yields. One can see that the DEB selectivity with all the catalysts for the ethylation reaction is almost double the selectivity in the disproportionation reaction. Among the four catalysts, the HZ-80 shows highest DEB selectivity while HZ-27 shows lowest DEB selectivity. This observation indicates that the surface acidity for the HZ-80 catalyst is suitable as compare to the other three catalysts. Fig. 7 shows the DEB selectivity as function of temperature. For all catalysts the total DEB selectivity increased with increasing reaction temperature. This trend was expected given all the experiments were conducted relatively at lower temperature (350 °C maximum). Previous studies demonstrated that at high reaction temperature (above 400 °C) the selectivity of DEB start to decrease due to the secondary cracking of product DEB. Al-Khattaf [28] showed that with increasing reaction temperature the selectivity of DEB reaches to maximum point then starts to decrease. The decrease in selectivity of DEB at high temperature was due to the increasing role of other reactions such as cracking and transalkylation at higher temperatures. Similar behaviors for DEB selectivity with temperature was reported by Halgeri and Jagannath [29] and Sharnappa et al. [11,12]. As reaction temperature increases, EB conversion and benzene selectivity increase while DEB selectivity decreases. This finding can be further confirmed by comparing the benzene (BZ) selectivity during the disproportionation and ethylation of EB. Expectedly, the benzene selectivity was drastically decreased in

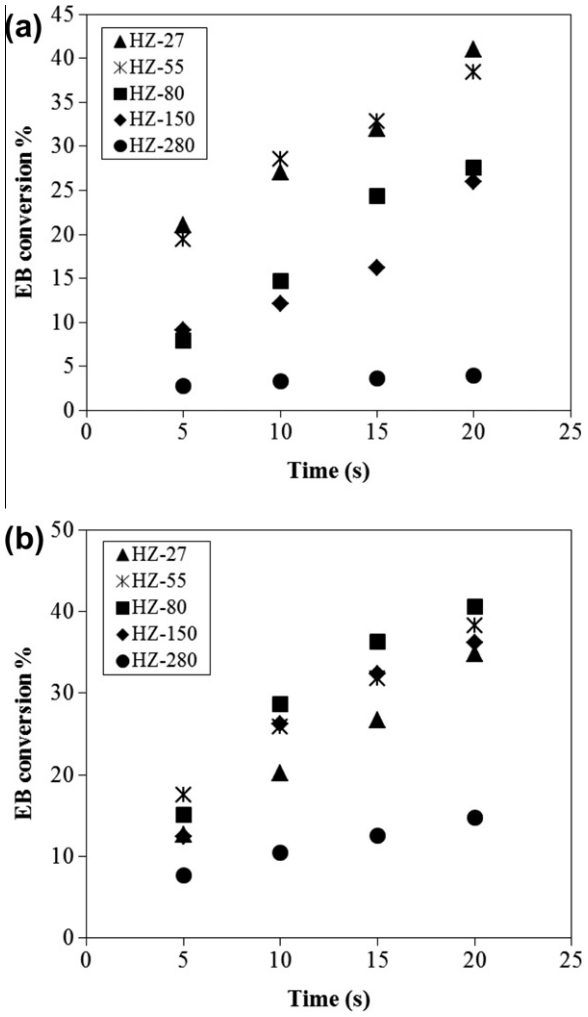


Fig. 5. Variation of EB conversion with contact time at 300 °C, comparison between different catalysts for (a) EB disproportionation reaction and (b) EB ethylation reaction.

presence of ethanol during the ethylation of EB as the benzene selectivity was very high in the disproportionation reaction. Therefore, ethylation, is more favored, due to the nature of the disproportionation reaction where 2 mol of EB disproportionate to give 1 mol each of DEB and Benzene. Effects of contact time on the DEB selectivity is reported in Fig. 8. For all catalysts the DEB selectivity increased with the increase of contact time. However, increments with the SiO_2/Al_2O_3 = 80 catalyst is significantly higher than the other HZSM-5 catalyst samples.

When the DEB/BZ ratios were calculated for different temperature and 20 s contact time, it was noticed that depending on the reaction temperature the DEB/BZ ratios varies between 0.4 and 0.7. The lowest value was found for the HZSM-5 sample containing highest acidity (Si/Al = 27). Although, ideally the DEB/BZ molar ratio should be equal to 1, the discrepancy is mainly due to the cracking reaction which produces excess benzene as reflected by the lowest value for the catalyst with highest acidity. Also, the presence of some minor side products (such as toluene, xylene, and triethylbenzene) that are not included in the ratio contributed to the error.

3.2.3. Selectivity of p-DEB

Fig. 9 shows the p-DEB selectivity (% p-DEB/total DEB) for different HZSM-5 samples at various EB conversions and 300 °C temperature. The selectivity of HZ-280 sample was not included in Fig. 9 given its very low product yields and low EB conversions at 300 °C. One can see in this figure especially at high temperature (also in Tables 3 and 4) that the distribution of DEB isomers m-DEB/p-DEB/o-DEB is approximately 6:3:1, respectively. Arsonova et al. [30–32] reported similar observations using a H-Y zeolite catalyst. It is interesting to see that low acidity catalysts HZ-55, HZ-80 and HZ-150, regardless of disproportionation and ethylation of EB the p-DEB selectivity is almost constant at all conversion level. The stable p-DEB selectivity was also due to the lack of excessive acid sites with these catalysts. It is hypothesized that the available acid sites are just sufficient to produce p-DEB (which is the first product) and there are no further isomerization or cracking over this catalysts especially with low temperature and small contact time. For HZ-280 catalyst high p-DEB selectivity was observed (Tables 3 and 4) because of its low acidity lead to minimize the isomerization of p-DEB to m-DEB. On the contrary, the p-DEB selectivity for high acid catalyst (HZ-27) decreases with increase the conversion in both disproportionation and ethylation of EB. The main reason for the decreasing p-DEB selectivity is the isomerization of the para isomer to meta isomer at high conversion. Also, the secondary cracking of p-DEB to produce benzene could be another reason for the decreasing p-DEB selectivity. In the case of disproportionation with the high acidic HZ-27 catalyst, availability of abundant acidic sites at the outer surface of the catalyst helps for isomerization of p-DEB as well as cracking of both the reactant EB and product DEB. As a result, the p-DEB selectivity decreased with conversion. However, in the case of ethylation with ethanol, the isomerization of the p-DEB is most likely the main reason for decreasing the p-DEB selectivity using the HZ-27 catalyst given the fact the benzene selectivity is very low indicating minimal cracking of feed and product. This result further indicates the significance of the ethyl group transfer.

According to previous studies acidity, and MFI crystal size are two important parameters that influence p-DEB selectivity over HZSM-5 catalysts [33]. Generally, low acidity and larger crystal sizes (longer diffusion length) favor the p-DEB selectivity. In the context of the present study the HZSM-5 samples were modified to vary the acidity keeping the crystal size almost same. Therefore, the low acidic catalysts showed better and stable p-DEB selectivity. Mishin et al. [13] showed that formation of very strong acid sites caused by an increasing contribution from isolated Al atoms in the framework seems to be the reason for the enhanced catalytic activity of dealuminated zeolite samples. Chen et al. [14] reported the effects of surface modification on the para-selectivity of modified HZSM-5 samples. They concluded that during the disproportionation of EB a substantial inactivation of surface active sites is inevitable in provoking substantial relative increase in para-DEB selectivity. Guan et al. [8] also reported improved and stable p-DEB selectivity with modified (acidity) HZSM-5 samples. It was showed that very high selectivity to p-DEB (>90%) can be achieved by controlling the concentration of very strong acid sites [34,35].

4. Kinetic modeling

Reaction kinetics of both ethylbenzene transformation and ethylation reactions are presented in this section. Mathematical models representing the rates of chemical reactions are developed based on the main product distributions observed for both reactions. As seen in Section 3.2, under the reaction conditions in the context of the present study both the disproportionation and ethylation of EB in the CREC Riser Simulator gives DEB and BZ as major products containing the aromatic ring. The gaseous product predominantly ethylene but their overall composition is very low.

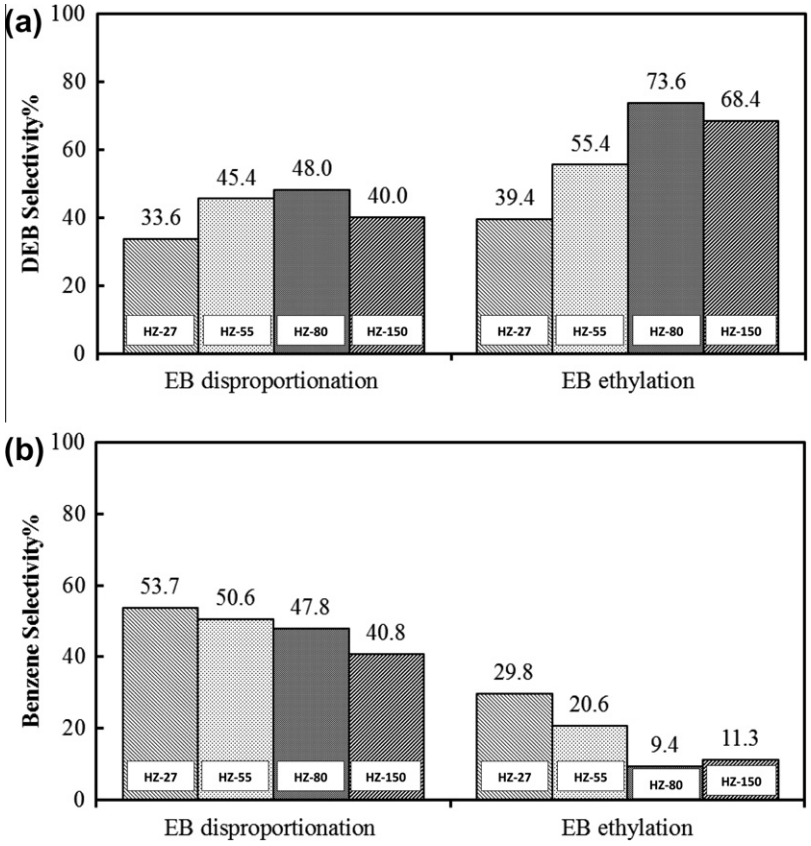


Fig. 6. (a) DEB selectivity and (b) BZ selectivity for different catalysts at 25% EB conversion and 300 °C, comparison between EB disproportionation reaction and EB ethylation reaction.

Considering all the facts the developed model equations are based on proposed reaction Schemes 1 and 2 for ethylbenzene transformation and ethylation reactions, respectively.

In formulating the kinetic models, we assumed the ethylation reaction follows a simple second-order kinetics and a pseudo-first order reaction kinetic was assumed for disproportionation and cracking reactions. Catalyst deactivation is assumed to be a function of time on stream (TOS) and a single deactivation function was defined for all reactions. Isothermal operating conditions can also be assumed given the design of the riser simulator unit and the relatively small amount of reacting species. It is important to mention here that in model formulation each of the DEB isomers is considered as separate products. However, given its very low yields (Tables 3 and 4) the contribution of o-DEB has been neglected. This assumption is consistent to the published literature articles, especially when the disproportionation and ethylation of EB reactions are conducted at low temperature (below 350 °C) [1,3,31].

4.1. Model development for ethylbenzene transformation

Based on the observed product distribution, reaction Scheme 1 is proposed to represent the main reacting species of the transformation reaction. Using power law model, the rate of reaction for each reacting species can be written as:

Rate of reaction for ethylbenzene

$$-\frac{V}{W_c}\frac{dC_{EB}}{dt} = (k_1 C_{EB} + k_3 C_{EB})\ \exp(-at) \tag{1}$$

Rate of reaction for benzene

$$\frac{V}{W_c}\frac{dC_B}{dt} = (k_1 C_{EB} + k_3 C_{EB})\ \exp(-at) \tag{2}$$

Rate of reaction for p-DEB

$$\frac{V}{W_c}\frac{dC_P}{dt} = (k_1 C_{EB} - k_2 C_P + k_{-2} C_m)\ \exp(-at) \tag{3}$$

Rate of reaction for m-DEB

$$\frac{V}{W_c}\frac{dC_m}{dt} = (k_2 C_P - k_{-2} C_m)\ \exp(-at) \tag{4}$$

where C_i is molar concentration of each species in the system, V is the volume of the reactor, W_c is the mass of the catalyst, t is time in seconds, k_i is the rate constant of each species, while α is the catalyst deactivation constant.

4.2. Model development for ethylation of ethylbenzene

Reaction Scheme 2 takes into consideration the main products of the alkylation of ethylbenzene with ethanol. The reaction network is used to develop the model equations for the kinetics of the reaction. Thus, we have:

Rate of reaction for ethylbenzene

$$-\frac{V}{W_c}\frac{dC_{EB}}{dt} = (k_1 C_{EB} C_E + k_3 C_{EB})\ \exp(-at) \tag{5}$$

Rate of reaction for p-DEB

$$\frac{V}{W_c}\frac{dC_P}{dt} = (k_1 C_{EB} C_E - k_2 C_p + k_{-2} C_m)\ \exp(-at) \tag{6}$$

Rate of reaction for m-DEB

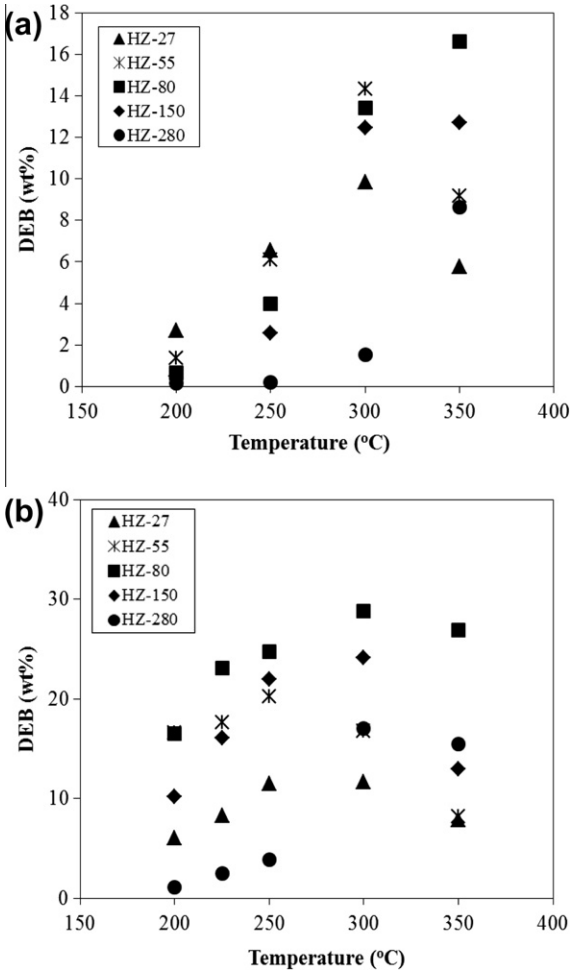


Fig. 7. Variation of DEB yield with temperatures for (a) EB disproportionation and (b) EB ethylation at 20 s, comparison between different catalysts.

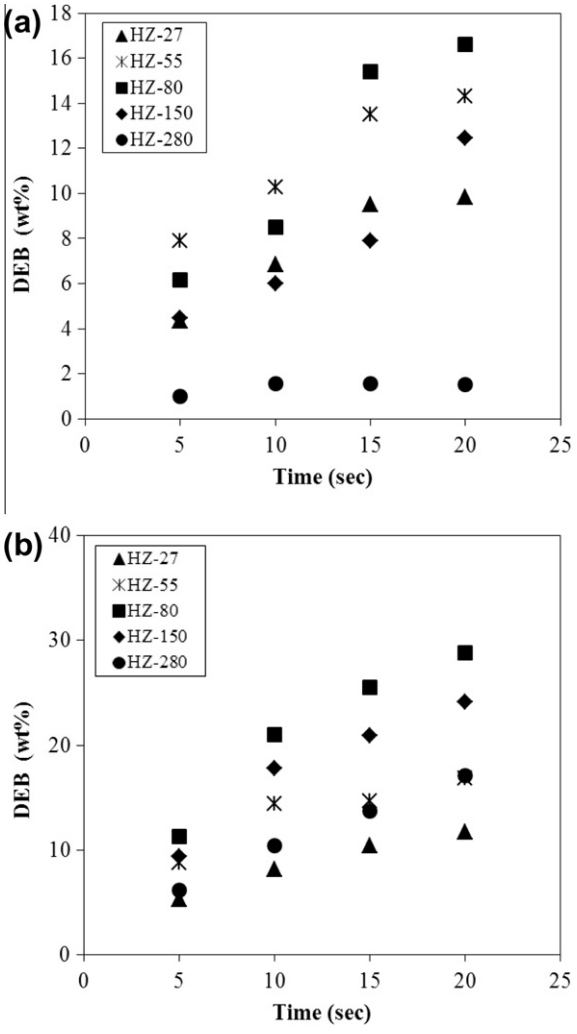


Fig. 8. Variation of DEB yield with contact time at 300 °C for (a) EB disproportionation and (b) EB ethylation, comparison between different catalysts.

$$\frac{V}{W_c}\frac{dC_m}{dt} = (k_2 C_P - k_{-2} C_m)\ \exp(-at) \tag{7}$$

Rate of reaction for benzene

$$\frac{V}{W_c}\frac{dC_B}{dt} = (k_3 C_{EB})\ \exp(-at) \tag{8}$$

Due to the negligible amount of benzene in the reaction product on HZ-80 and HZ-150, k_2 and $k_3 \approx 0$.

The molar concentration C_i can be expressed in terms of weight fraction of each species y_i, which are the measurable variables from the chromatographic analysis, hence,

$$C_i = \frac{y_i W_{hc}}{MW_i V} \tag{9}$$

where W_{hc} is the weight of feedstock injected into the reactor, MW_i is the molecular weights of the species.

The rate constant was represented with the temperature dependence form of the Arrhenius equation given as:

$$k_i = k_{i0}\ \exp\left[-\frac{E_i}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{10}$$

where k_{i0} and E_i are the pre-exponential factor and activation energy of the reaction i respectively. T_0 is referred to as the centering temperature which is the average of all the temperatures for the experiment in order to reduce parameter interaction.

In order to ensure thermodynamic consistency at equilibrium, the rate constant for the isomerization reaction (p-DEB to m-DEB) in the above equation are expressed as follows:

$$K_2 = \frac{k_2}{k_{-2}} = \left(\frac{C_M}{C_P}\right)_{eq} \tag{11}$$

where K_2 are temperature-dependent equilibrium constant for the isomerization reaction. However, an average value was computed for K_2, because the thermodynamic equilibrium concentrations of the DEBs remain fairly constant within the temperature range of this work.

The above models were evaluated considering that the both the disproportionation and ethylation of ethylbenzene over HZSM-5 catalyst samples were free from transport limitations. This assumption is reasonable given the fact the HZSM-5 sample has small crystallite sizes of 0.5×10^{-6} m to 2×10^{-6} m [36]. For this crystal size ranges, one can expect that the value of effectiveness factor should be close to one. Considering this fact, the effect of diffusion has not been incorporated in the kinetics analysis. Recently, Marin and his co-workers [37] also reported the kinetic modeling of ethylbenzene dealkylation over Pt promoted H-ZSM-5 zeolite catalysts by considering negligible contribution of the diffusion resistance.

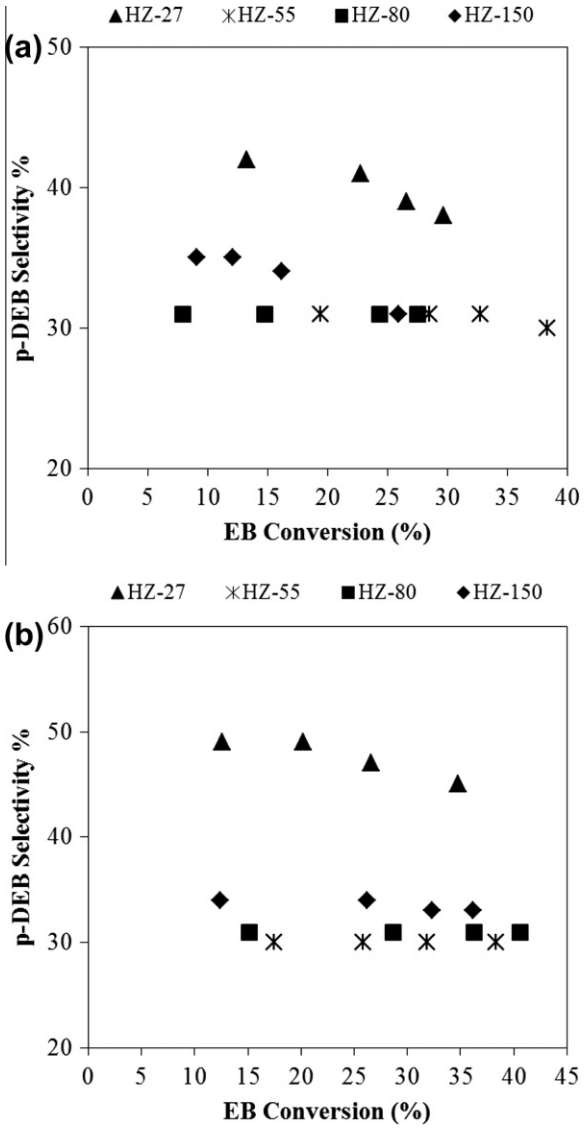
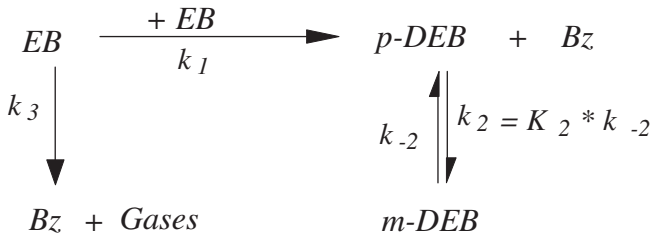


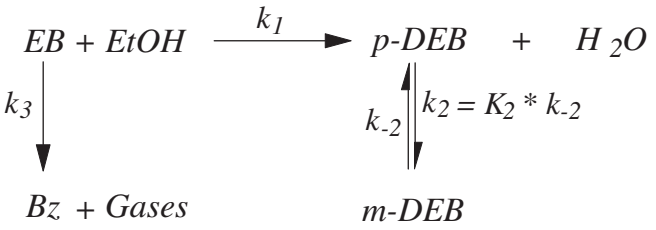
Fig. 9. Variation of p-DEB selectivity with EB conversion at 300 °C for (a) EB disproportionation and (b) EB ethylation, comparison between different catalysts.



Scheme 1. Reaction network of ethylbenzene transformation.

4.3. Model parameter evaluation

The mole balance equations (Eqs. (1)–(9)) incorporating the Arrhenius relation (Eq. (10)) were evaluated by a least square fitting of the kinetic parameters using the experimental for both the disproportionation and ethylation of EB reactions data obtained from the CREC Riser Simulator. The data points were taken at various reaction times ranging from 5 to 20 s at different temperature levels. The models were evaluated by using MATLAB



Scheme 2. Reaction network of ethylation of ethylbenzene with ethanol.

(ODE 45-4th order Runge–Kutta method and LSQCURVEFIT) least square fitting of the kinetic parameters. The centering temperature in the Arrhenius was taken equal to 275 °C. The optimization criteria are that all the rate constants had to be positive, the activation energies for reaction positive, all consistent with physical principles.

The parameters were determined at 95% confidence limit. Total one hundred and twelve (112) for disproportionation and one hundred and twelve (112) for ethylation of EB reactions data points were taken for parameter estimation. Thus, total seven parameters, the degree of freedom for the model exceeded 103 and 104 (number of data points – number of parameters to be estimated), respectively. This shows that considerable experimental data were used to optimize the model parameters.

The models were discriminated based on their coefficient of determination (R^2), lower SSR (sum of the squares of the residuals, Lower cross-correlation coefficient (γ), and smaller individual confidence intervals for the model parameters. The values of the model parameters along with their corresponding 95% confidence limits (CLs) are shown in Table 5. One should remember that the power law model as developed in Eqs. (1)–(8) are not based on the mechanism of the surface reaction. Therefore, the estimated activation energies are apparent activation energies which have combined effects various steps (adsorption of reactant-surface reaction-desorption of products) involved in the catalytic reaction.

It is noticed from Table 5, that in EB transformation the estimated activation energies for the cracking reaction forming benzene over all the HZSM-5 catalyst are found to be slightly higher than those for the formation of the desired product p-DEB. This result indicates that in EB transformation using HZSM-5 catalysts the cracking reaction is comparable with the desired disproportionation reaction having slight edge. This observation is consistent to the experimental selectivity data as obtained from the fluidized bed reaction runs, which shows that all the HZSM-5 catalysts are equally favors both the cracking and disproportionation to produce benzene and the desired product p-DEB. Among the three catalysts being considered for the kinetics investigation the estimated activation energy for HZ-27 is the lowest which is in line with the highest benzene selectivity as shown in Table 3. When compared

Table 5
Estimated kinetic parameters (at 95% confidence limit) for disproportionation and ethylation of EB over HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios.

Parameters	EB disproportionation			EB ethylation with ethanol		
	HZ-27	HZ-80	HZ-150	HZ-27	HZ-80	HZ-150
k_{01}[a]	2.5 ± 0.2	2.1 ± 0.1	2.3 ± 0.1	2.6 ± 0.3	4.9 ± 0.6	4.8 ± 0.4
k_{02}	330 ± 16	530 ± 98	470 ± 17	2.2 ± 0.6	146 ± 22	8.6 ± 0.4
k_{03}	0.87 ± 0.2	0.36 ± 0.1	0.38 ± 0.1	0.01 ± 0.002	–	–
E_1	19.5 ± 7.0	38 ± 4.5	43 ± 5.3	25.6 ± 3.8	22.5 ± 4.4	38.4 ± 3.3
E_3	40 ± 4.4	40 ± 4.0	50 ± 8.0	78.8 ± 12.8	–	–

k_{01}, k_{02}, k_{03}: 1×10^3 m^3/kg cat s.
E_1, E_1, E_1: kJ/mol.
[a] (for ethylation: k_{01}: 1×10^2 m^6/kg cat s)×.

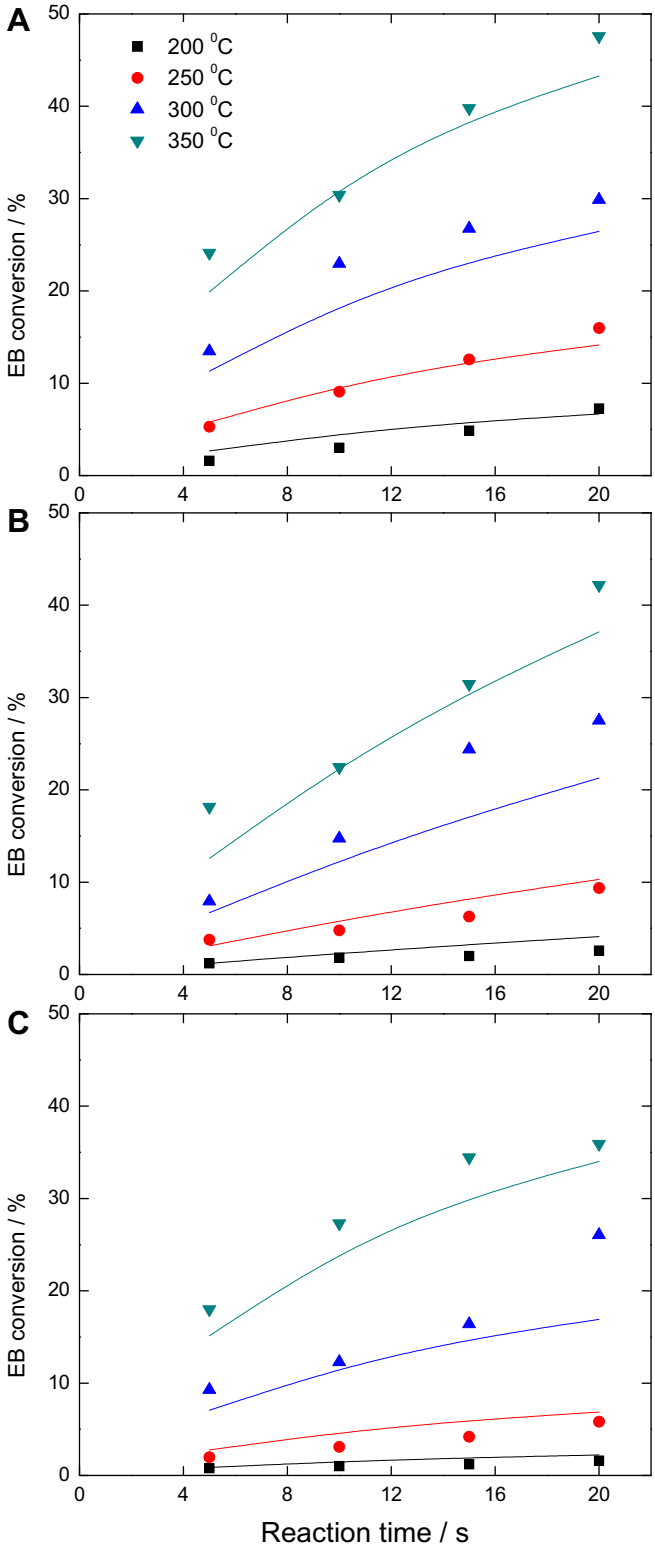


Fig. 10. EB disproportionation reaction: Influence of reaction temperature and time on ethylbenzene conversion on HZSM-5 samples with: (A) $SiO_3/Al_2O_3 = 27$, (B) $SiO_3/Al_2O_3 = 80$ and (C) $SiO_3/Al_2O_3 = 150$. Experimental data: data points, model prediction: continuous line.

the activation energy for the disproportionation forming p-DEB, the HZ-27 catalyst requires the least amount of activation energy as compare to the other HZ-80 and HZ-150. This is also consistent as the acidity of this catalyst is highest among the five HZSM-5 catalysts being investigated.

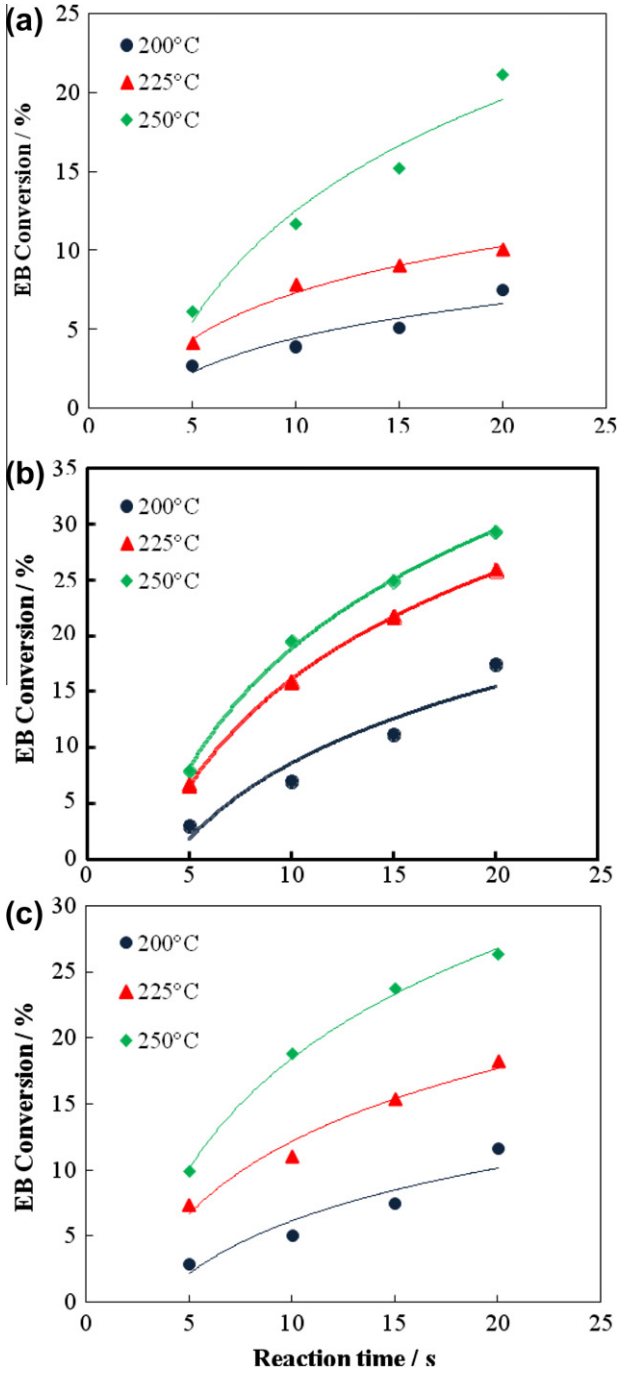


Fig. 11. EB ethylation reaction: Influence of reaction temperature and time on ethylbenzene conversion on HZSM-5 samples with: (A) $SiO_3/Al_2O_3 = 27$, (B) $SiO_3/Al_2O_3 = 80$ and (C) $SiO_3/Al_2O_3 = 150$. Experimental data: data points, model prediction: continuous line.

The scenario is completely different during the ethylation of EB with ethanol than that was observed in EB transformation (Table 5). As noticed in the product analysis (Section 3.2 and Table 4), the majority of the EB converted into DEB and only small amount of benzene was produced. The estimated activation for the cracking reaction was very high (78.8 ± 12.8) which is consistent to the very low selectivity of benzene during the ethylation of EB with ethanol. Therefore, in presence of ethanol, the contribution to either DEB or benzene via disproportionation (as shown in Scheme 2) can be considered negligible. The much lower activation energy (Table 5) for the ethylation route is also consistent to the above explanation. The catalyst with $SiO_2/Al_2O_3 = 80$ requires the least amount of

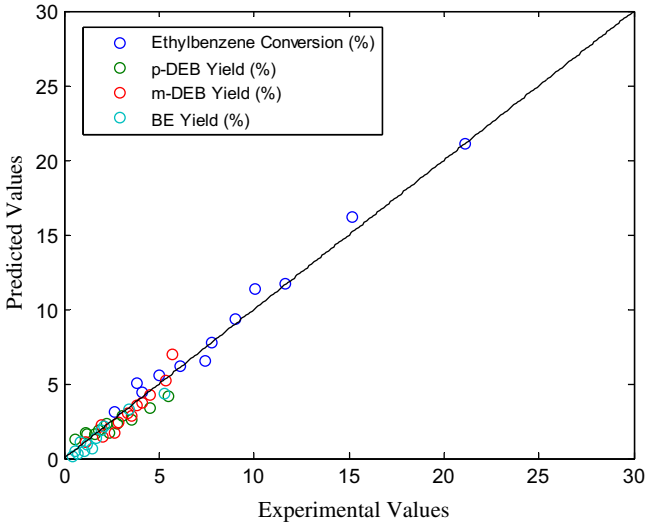


Fig. 12. Reconciliation plot between model predictions and experimental data. Experimental data: data points, model prediction: continuous line.

activation energy forming p-DEB compare to HZ-27 and HZ-150. This finding is also consistent to the product analysis results, which shows that highest p-DEB yield with the $SiO_2/Al_2O_3 = 80$ containing HZSM-5 catalyst.

The estimated kinetic parameters for the fitted parameters substituted into the developed the mole balance equation and equations were numerically solved using fourth-order-Runge–Kutta routine. Figs. 10 and 11, are the reconciliation plots for the EB conversion during disproportionation and ethylation, respectively. The model predicted and experimental EB conversion and products yield are compared in Fig. 12. Both the predicted conversions and yield data fit the experimental data in an excellent manner.

5. Conclusion

The physicochemical characterization of HZSM-5 catalysts with three different SiO_2/Al_2O_3 ratios, reaction and kinetics study of EB disproportionation and EB ethylation with ethanol using these catalysts has been carried out. The following conclusions were drawn from the study:

(1) The physicochemical characterizations results shows that the variation of SiO_2/Al_2O_3 ratios mainly affected the acidity of the catalysts while the specific surface area and the crystal structure and crystal sizes remain almost unchanged.
(2) Low temperature favors the EB ethylation reaction while higher temperature is favorable for both disproportionation and cracking reactions. In both the reactions, the EB conversion increases significantly with the increase of reaction temperature.
(3) In EB ethylation the DEB selectivity is almost the double of DEB selectivity in EB disproportionation while the benzene selectivity just opposite. The formation of benzene in ethylation is much lower.
(4) The amount of benzene in the reaction product increased as the temperature and reaction time were raised, showing that cracking reaction is favored at higher temperature and contact time.
(5) The HZSM-5 catalyst with $SiO_2/Al_2O_3 = 80$ seems to be the most effective giving superior activity and selectivity towards DEB.
(6) P-DEB selectivity is very high using HZ-280 catalyst, because of its low acidity lead to minimize the isomerization of p-DEB to m-DEB; however EB conversion and the products yield for this catalyst is comparable to the other catalysts in this study.
(7) Kinetic analysis of the reactions shows that during the EB disproportionation, the value of the activation energy for EB cracking is comparable to the activation energy of EB disproportionation which is consistent to the high benzene selectivity in this route. On the other hand, during the EB ethylation with ethanol, a small amount of benzene was formed via the cracking of EB, which has been reflected by higher activation energy of the EB cracking reaction. The kinetics analysis also confirms that during EB ethylation the disproportionation of EB is negligible.
(8) In EB ethylation, the HZSM-5 catalyst with $SiO_2/Al_2O_3 = 80$ requires lowest amount of activation energy to form p-DEB which was reflected in higher p-DEB yield.
(9) Although, the DEB yield of the $SiO_2/Al_2O_3 = 80$ catalyst is high, the p-DEB selectivity with such catalyst is comparable to the other catalysts studied in this study.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.02.040.

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